## Silesian University of Technology

Faculty of Mathematics and Physics Institute of Physics





PhD THESIS

# Studies of CuPc ultra-thin layers deposited on Si(111) native substrates

MACIEJ KRZYWIECKI

Supervisor: Professor Jacek Szuber

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In memory of I. K.

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## INTRODUCTION

#### 1.1 Motivation

In last two decades the incredible progress in electronics has been done. We can observe the meaningful increase in application of micro- and nanoelectronic components not only in the so-called "high-tech" devices used mainly in military or advanced science industry but also ones penetrating the civil technology.

Market demands forced scientists and companies to search for more and more efficient and cost-effective materials. Currently the world consumes an average of 13 terawatts (TW) of power. By the year 2050, as the population increases and the standard of living in developing countries improves, this amount is likely to increase to 30 TW [1]. The threat of possible energy crisis renders the power efficiency as one of the most desirable property of materials. For several years now much of the effort has been focused on organic semiconductors due to their very promising attractive properties.

the The extraordinary features of organic semiconductors: suitability/compliance efficient for low-temperature processes, electroluminescence, and reasonable charge carrier mobility have led to expectations of new "plastic" electronics with applications ranging from flexible flat panel displays and smart cards to low-cost and efficient solar cells [2]. Organic light emitting diodes (OLEDs), in particular, have already attained performance suitable for display technologies and are being commercialized. The ultimate penetration of organic electronics into the marketplace depends upon the success in fabrication of additional devices, e.g. organic field effect transistors (OFETs), which can favorably, compete with traditional electronics based today mainly on silicon and gallium arsenide.

Organic semiconductors have been known since the late 1930s. Then, it occurred that organic solids can also have semiconducting properties. One of the first discoveries was anthracene which exhibited photoconducting properties. It was used by Chester Carlson in his early work leading to the first photocopier system. The demand for paper-size semiconductor sheets for applying toner and charge had been an impulse for the interest growth in organic semiconductors as an alternative solution for charging and image duplication. The crystalline semiconductors available at that time appeared to be unsuitable for xerographic applications. Companies from the photography and xerography branches had been concerned in the examination of photoconductivity and photosensitization of organic semiconductor films. In 1986, the attempts made at Kodak laboratories resulted in the application of novel thin film evaporated organic semiconductor for solar cells and light emitters (the predecessors of OLEDs) becoming a small revolution in electronics. The past 20 years have brought a huge development in the discussed area. A successful application of thin organic semiconductor films in OLEDs and OFETs has increased the interest in the new technology [3,4]. The progress is rapid - IDTechEx estimates that organic (so-called printed) electronics market will grow to \$30 billion in 2015 and reach \$250 billion by 2025 [5]. Peter Gammel, chief technology officer at Advance Nanotech claims that they will be able to incorporate intelligent organic circuits into a variety of objects, from clothing to packaging. Indeed, a lot of research is being done on properties of organic semiconductors and their durability in various conditions. Many companies, like Dupont, PlasticLogic, Cambridge Display Technology and e-Ink, are currently exploring the ways/avenue to employ the organics in the flexible devices as they can operate continuously even after a deformation and a longterm exposition into hostile environments. Such flexible devices could be used in nanoelectronics for smart textiles and product tagging. Novel nanoelectronic and energy-efficient applications have even become the center of attention of European Commission which introduced the MONA-LISA project on the properties of organic semiconductors [6]. This program aims to study the transport of energy and charge in organic semiconductors and also addresses the problems of controlling the materials properties by varying the size, susceptibility for contact with other materials or environmental conditions.

One of the most promising organic semiconducting material in last few years have been phthalocyanines (Pcs), especially their modified subgroup – metallophthalocyanines (MePcs). Up to now, phthalocyanines have been commonly used as a dye for high-speed CD-R media. Their huge advantage bases on provision of a versatile chemical system – elements from group IA to VB can all combine with phthalocyanine ring making more than 70 already known MePcs of different properties [7]. This allows for choosing material most appropriate for a given application.

Phthalocyanines are excellent candidates for evaporated thin-film organic devices. They can be easily evaporated since the weak intermolecular attraction between their small organic molecules can be thermally disrupted and a material flux can be formed using a heated crucible. Moreover, a MePc together with dielectric and another semiconductor creates ready electronic structure like OFET or organic solar cell. The finest example of such structure might be MePc/SiO<sub>2</sub>/Si that is an ultra-thin film of phthalocyanine evaporated on oxidized silicon substrate.

Rapid development of devices with high performance in the micro- and nanoelectronic industries requires a careful and comprehensive control of materials of interest. The most important attributes related to the future thinfilm electronic devices are the surface electronic properties. They are strongly dependent on physicochemical properties of a thin film and, especially in the case of ultra-thin films, are also substrate-dependent. These properties are in turn determined by a technology of the thin film formation. Furthermore, the influence of organic substrate/overlayer interfaces on the device performance cannot be overestimated as they determine charge injection and charge flow characteristics in the devices.

Although in recent years one can observe a rapid advancement of organic semiconductors technology, it is only the beginning of exploration of thin films and their applications. It is hoped that the experimental and scientific efforts presented in the present dissertation will bring a useful contribution to the understanding of organic semiconductors and their ultra-thin films.

#### 1.2 Outline of the Thesis

The present Dissertation is divided into six chapters and contains the list of Figures, list of Tables and list of References as well. Six chapters constituting main body of the Thesis are as follows:

- Chapter 1 introduction consists of the motivation of undertaken studies and the outline of the Thesis;
- Chapter 2 presents properties of copper phthalocyanine with brief review of recent studies related to aspects of the present examinations;
- Chapter 3 shortly demonstrates subject of studies and specifies the aim and scope of the Thesis;
- Chapter 4 details the experimental methodology and investigation methods used within this Dissertation together with description of the laboratories in which the examinations were carried out;
- Chapter 5 presents the results of studies. It is subdivided into three parts devoted respectively to: the investigation of substrates, the analysis organic overlayers (this part contains the description of substrate/CuPc interface) and the interaction of CuPc layers with ambient air;
- Chapter 6 gathers the conclusions of conducted experiments and contains summary of this Thesis.

The work presented within this Thesis has so far resulted in three original papers published in journals recognized by the Institute of Scientific Information (ISI) in Philadelphia:

- I. M. Krzywiecki, L. Grządziel, L. Ottaviano, P. Parisse, S. Santucci, J. Szuber, XPS study of air exposed copper phthalocyanine ultra-thin films deposited on Si(111) native substrates, Mat. Sci. Pol. 26 (2008) 287.
- II. M. Krzywiecki, L. Ottaviano, L. Grządziel, P. Parisse, S. Santucci, J. Szuber, Influence of substrate doping on the surface chemistry and morphology of Copper Phthalocyanine ultra thin films on Si(111) substrates, Thin Solid Films 517 (2009) 1630.
- III. M. Krzywiecki, L. Grządziel, H. Peisert, I. Biswas, T. Chasse, J. Szuber, X-ray Photoelectron Spectroscopy of native and RCA-treated Si(111) substrates and their influence on surface chemistry of Copper Phthalocyanine thin films, Thin Solid Films (2009), doi:10.1016/j.tsf.2009.09.013.
- IV. L. Grządziel, M. Krzywiecki, H. Peisert, T. Chasse, J. Szuber, Influence of ambient air exposure on surface chemistry and electronic properties of thinfilm CuPc sensing layers, Thin Solid Films, TSF-D-09-01580, under review process.

Two other papers are in preparation. Besides the main field of interest, the XPS investigations of carbon components were described in the paper: P. Tomkiewicz, A. Winkler, **M. Krzywiecki**, T. Chasse, J. Szuber, *Analysis of mechanism of carbon removal from GaAs(100) surface by atomic hydrogen*, Appl. Surf. Sci. 254 (2008) 8035, which can be treated as a spin-off paper.



### **COPPER PHTHALOCYANINE: STATE OF THE ART**

Phthalocyanines have been known for years as dyes. The name comes from the Greek words naphtha and cyanide rock oil and dark blue. Last years phthalocyanines became a center of attention of organic electronics.

Present chapter is divided into three main parts. The first presents the main properties of the investigated within this Thesis copper phthalocyanines. The significant part is devoted to their semiconducting behavior.

Besides the general physical-chemical attributes description, the application of phthalocyanines in organic transistors and organic solar cells is briefly described in second part of this chapter.

The third part is a state of the art summary of the upto-now investigations of copper phthalocyanine. This section contains review of examinations devoted to surface morphology, surface electronic properties, phthalocyanine /substrate interface and the CuPc-ambience interaction. At the end the planned to be used within this work substrate investigations review is also reported. The (metal-free) phthalocyanine is an organic compound with formula  $H_2C_{32}H_{16}N_8$ . It was firstly synthesized by accident in 1907 [7] as a product of heating an alcoholic solution of the 1,2-cyanobenzamide [8]. It is also widely known as metal-free phthalocyanine. Twenty years later a copper phthalocyanine CuPc (Cu C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>) was obtained during the preparation of 1,2-dicyanobenzene from dibromobenzene and CuCN. In the mid-1930s the complex investigations had started. Linstead and co-workers [9] were the first to systemize all earlier observations. These studies led to conclusion that the vast range of phthalocyanines are based on the same structure, shown in Figure 2. 1a [10]. These observations also showed that through the exchange of the central hydrogen atoms with ions of some metals it is possible to get a whole family of isostructural schemes with a general symbol MePc (where Me means the ion of metal). The family is known as metallophthalocyanines (MePc); their structure is shown in Figure 2. 1b.



Figure 2. 1 Molecular structure of (metal-free) H<sub>2</sub>Pc (a) and MePc (b) [11].

Although these compounds have similar molecular structure, due to the nature of the central metal ion, they have quite different physical and chemical proprieties. The most important metallophthalocyanines are: copper (CuPc), zinc (ZnPc), magnesium (MgPc), lead (PbPc) and platinum (PtPc) phthalocyanines [12].

In the past phthalocyanines were used mainly as dyes due to their deep and very intensive color. However, recently they have been shown to possess a number of special features, which made them useful for electronic and academic purposes. Some of those properties are:

- easiness of crystallization and sublimation
- very high cleanness (10<sup>14</sup>-10<sup>16</sup> traps/cm<sup>3</sup>) after crystallization,
- exceptionally high thermal stability due to high decomposition temperature (500°C in air and 900°C in vacuum) [13],
- high chemical stability even strong acids and alkali do not cause the decomposition of the phthalocyanines,
- interesting optical properties, especially intensive light absorption in the wavelength range from 400 to 700 nm due to integral conjugated  $\pi$ -electron system with 18 electrons,
- intriguing electrical properties, mainly their electrical conductivity which strongly depends on the composition of ambient atmosphere [12].
- they provide a versatile chemical system elements from group IA to VB can all combine with phthalocyanine ring making more than 70 already known different MePcs [7].

#### 2.1 General properties

All recent investigations have shown that phthalocyanines possess highly complicated crystallographic structure [12]. In early 1930's the several X-ray diffraction spectroscopy studies was made by Robertson [14]. He proved that metallophthalocyanines can crystallize in three polymorphic structures, designated by the letters  $\alpha$ ,  $\beta$  and x. These already known structures are shown in Figure 2. 2.



Figure 2. 2 Scheme of main three molecular phases of phthalocyanine; based on Ref. [15].

Generally, a phthalocyanine is a large planar molecule [16] with an extensive delocalized  $\pi$ -electron system. Although most of its metal complexes are planar, those with metals which are too large to fit into the space between the four central nitrogen atoms (e.g. lead) show significant non-planarity [17]. The intermolecular forces between these large polarisable molecules in the solid state are prevailingly attractive dispersion forces which are rather not strongly directional. There are also the short-range repulsion forces. This leads to abovementioned polymorphism and the existence of different molecular packing arrangements with the similar overall lattice energy. The  $\alpha$  and  $\beta$  phases are the common polymorphic forms of metal phthalocyanines. Those structures are both monoclinic (see Figure 2. 2). The main difference between  $\alpha$  and  $\beta$  is the angle between the stacking axis and the normal to the molecular plane which is 25° or 26° for  $\alpha$  structure and 45° for the  $\beta$  one [18]. The comparison between them is shown in Figure 2. 3.



Figure 2. 3 Model of thin film of copper phthalocyanine in  $\alpha$  and  $\beta$  phases; based on Ref. [19].

All recent investigations show that the  $\beta$  phase is the most stable of all. Such crystals can be produced by sublimation in nitrogen beam and in the temperature range from 400° to 500°C. The example of this structure can be the CuPc. The  $\alpha$  phase can be obtained by sublimation of phthalocyanines at low pressure onto substrates maintained at the temperature of 20°C [18]. The  $\alpha$ phase is metastable and can be naturally converted to  $\beta$  one by heating and by solvent treatment. Here, the examples are PtPc and CrPc. In CrPc the angle between the stacking axis and the normal to the ring is approximately 20° [20].

In the case of non-planar structures, the phthalocyanines occur also as two polymorphs. The triclinic one obtained at 320°C, with molecules inclined at about 60° to the stacking axis, and the monoclinic one obtained at 250°C. The monoclinic structure consists of stack of molecules and the molecules within each stack lie out of plane [18]. The example is PbPc, in which all molecules are arranged in this style and the lead atoms are lying directly above each other [17].

The morphologic differences are very important for the application aspects of phthalocyanines. For example, the  $\alpha$  phase is very sensitive to oxygen presence. Due to repeatability issues in the growth of Pc crystals, the thin films of phthalocyanines have recently attracted the interest. Especially phthalocyanines of transition metals have become the object of intensive studies.

More detailed information on the growth of crystals and thin films, conditions of this process and on possible transitions between  $\alpha$  and  $\beta$  phases can be found in Refs. [14,18].

Table 2. 1 shows the periodic table with all possible elements that make complexes of metallophthalocyanines. The properties of each metallophthalocyanine is strongly dependent on a central metal ion, so that some of its properties can be anticipated by the studying the position of the element in the periodic table.

Ia	IIa	IIIa	IVa	Va	Via	VIIa		VIII		$\mathrm{I}_{\mathrm{b}}$	IIb	$\mathrm{III}_{\mathrm{b}}$	IV <sub>b</sub>	$V_{b}$	$VI_{b}$	VII <sub>b</sub>	0
<u>H</u>											<u>He</u>						
Li	Ba								В	С	Ν	0	F	Ne			
<u>Na</u>	<u>Mg</u>											<u>Al</u>	<u>Si</u>	Р	$\mathbf{S}$	Cl	Ar
<u>K</u>	<u>Ca</u>	Sc	<u>Ti</u>	<u>V</u>	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	Se	Br	Kr
Rb	$\mathbf{Sr}$	Y	<u>Zr</u>	Nb	Mo	Тс	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Cd</u>	<u>In</u>	<u>Sn</u>	Sb	Te	Ι	Xe
Cs	Ba	La	<u>Hf</u>	Та	W	Re	<u>Os</u>	Ir	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	<u>T1</u>	<u>Pb</u>	Bi	Ро	At	Rn
Fr	Ra	Ac														1	
Lan	thani	ides	Ce	Pr	Nd	Pm	Sn	Eu	Gd	TB	Dy	Ho	Er	Tm	Yb	Lu	
	If																
A	ctinid	es	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	
	5f																

Table 2. 1 Periodic table with highlighted elements which can create complexes with metal-free phthalocyanine [21].

#### 2.1.1 Phthalocyanines as semiconductors

The observation of semiconducting properties of MePcs has induced many studies on their electrical properties. In MePcs molecule the dominant orbitals are the  $\sigma$ in-plane orbitals and  $\pi$ -conjugated ones. The symmetry of  $\sigma$  orbitals is due to  $\sigma$ coordination of nitrogen lone pairs directed towards the center of the ring with the central metal atom. In succession, the interaction of nitrogen  $p_{\pi}$  orbitals with metal ones gives the perpendicular-to-the-plane overlaps. While the macrocyclic ligand, thanks to the  $\sigma$  orbitals, is a donor of electrons to the metal, the  $\pi$  orbitals of the ligand can be  $\pi$  donor as well as  $\pi$  acceptor [11]. The  $\pi$  orbitals form a conjugated system alongside the pyrrolic nitrogen orbitals. Following the Hund-Mulliken approach the atomic orbitals of the molecules form the molecular orbitals which exhibit strong anisotropy [22]. For instance,  $\pi^*$  orbital excitation in a planar  $\pi$ -conjugated carbon system is allowed for electromagnetic waves with electric field E vertical to the molecular plane (parallel to  $2p_z$  orbitals), whereas the transition into  $\sigma^*$  is allowed for E parallel to the molecular plane as shown in Figure 2. 4.



Figure 2. 4 The angle of electric field favors either the excitation of  $\pi^*$  molecular orbitals (a) or the  $\sigma^*$  ones (b). Based on Ref. [22].

Similarly to the inorganic semiconductors, overlapping wave functions of the molecular orbitals result in the formation of the energy band-like structure. Since the application of the band theory formalism in organic materials has met several difficulties (see e.g. Ref. [11]), there are only semi-classical models describing the band structure of the MePcs. Hence, the valence and conduction bands mentioned throughout this dissertation should be understood rather as the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) levels, respectively. As shown in Figure 2. 5 they are separated by the band gap, either optical (1.7 eV in CuPc) or transport one (2.3 eV in CuPc) dependently on the excitation method, which is discussed in Section 2.3.4.

Table 2. 2 contain the CuPc HOMO and LUMO energy positions reported in the literature with respect to the vacuum level. It is worth stressing that the values are varying depending on the measurements method. For comparison, the pure (metal-free)  $H_2Pc$  HOMO positions were also included.



Figure 2. 5 Simplified illustration of HOMO and LUMO band formation arising from bonding and anti-bonding  $\pi$  orbitals; based on Ref. [11].

Table 2. 2 The literature HOMO and LUMO energy positions with respect to the vacuum level for copper and pure (metal-free) phthalocyanine.

	HOMO [eV]	LUMO [eV]	Method	Reference
	5.2	3.6	Photoelectron emission	[23]
CuPo	5.0		Cyclic voltammetry	[24]
Curc	5.1		UPS	[24]
	5.6		UPS	[25]
HDo	5.9		Photoelectron emission	[26]
112F C	5.9		UPS;XPS	[27]

Charge carriers in MePcs are holes and electrons in  $\pi$  orbitals. Although most of all organic solids are insulators, when their constituent molecules have IIconjugate systems, electrons can move via  $\pi$ -electron cloud overlaps. Charge transport in organic semiconductors is dependent on  $\pi$ -bonding orbitals and quantum mechanical wave-function overlap [28].Conduction of charge carriers is usually described by quantum mechanical tunneling due to limited  $\pi$ -bonding overlap between molecules. Such a description fits particularly well to disordered organic semiconductors. The degree of order (or disorder) determines one of two extreme carrier transport mechanisms - band-like or hopping one. The former is usually observed in highly purified molecular crystals while the latter is reserved rather for more disordered amorphous organic materials. Band mode is observed mainly at room temperatures; the mobility values are then in the range from 1 to 10 cm<sup>2</sup>/Vs [11] and follows the temperature dependence:

$$\mu \propto T^{-n}; n = 1, 2, ...$$
 (2.1)

On the other hand, hopping transport results in lower mobility which is also temperature dependent; the hole mobility (CuPc is p-type semiconductor) changes according to the relationship [11]:

$$\mu_h = \frac{e \cdot a_c^2}{kT} \cdot v_h \cdot \exp\left(-\frac{\Delta E_{ac}}{kT}\right)$$
(2.2)

where:  $a_c$  is the lattice constant;  $\Delta E_{ac}$  the activation energy (eagerly often assigned to the energy difference between occupied valence band an empty conduction band; it can be treated as band gap  $E_g$ );  $v_h$  is the hopping frequency.

In the same manner the conductivity  $\sigma$ , one of the most crucial dark properties of the MePcs thin films also is temperature-dependent and follows the formula [11]:

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{\Delta E}{2kT}\right) \tag{2.3}$$

where:  $\sigma_0$  is the intrinsic conductivity;  $\Delta E$  is the thermal activation energy and can be treated as well as the energy bad gap of the semiconductor.

The hopping of charge carriers from molecule to molecule depends upon the energy gap between HOMO and LUMO levels. Carrier mobility experiences regions of faster and slower hopping because it is reliant upon the abundance of similar energy levels for the electrons or holes to move. Performed studies have shown that in a low external electric field the conductivity of organic semiconductor is proportional to T<sup>1/4</sup> and in a high electric field is proportional to  $e^{-(E/aT)}$ , where *a* is a constant of a material [29].

There is one more charge transport mechanism – tunneling. It can also be a very efficient way of charge movement from site to site with the probability related to shape, height and width of the potential barrier between the involved sites. This probability of tunneling  $P_{tu}$  is described by formula [11]:

$$P_{tu} = a \cdot N_{tu} \cdot \exp\left(-\frac{2}{h} \cdot \sqrt{2m(E_{tu} - E)} \cdot l_{tu}\right)$$
(2.4)

where: *a* is a constant;  $N_{tu}$  is the number of collisions of a carrier with the barrier;  $E_{tu}$  is the height of the barrier and  $l_{tu}$  is the width of the barrier.  $P_{tu}$  is not directly temperature dependent but it can be limited by the lattice vibrations.

In charge transfer molecular complexes unpaired electrons can stay stable for a long time and remain the carriers. This type of semiconductor is also obtained by pairing an electron donor molecule and an electron acceptor molecule. The transport properties are strictly correlated with the structural attributes of the molecules, hence there are sometimes significant differences between electronic parameters of the MePcs in different phase. They are shown for the CuPc in Table 2. 3.

Table 2. 3 Electrical properties of the CuPc thin films in  $\alpha$  and  $\beta$  form.  $\sigma$  - conductivity at 300 K,  $E_{act}$  - thermal activation energy and  $\mu$  - mobility. After Ref. [30].

	σ (Ω <sup>-1</sup> cm <sup>-1</sup> )	Eact (eV)	μ (cm²/Vs)
a - CuPc	$2.10^{-12}$	1.96	3.5
β-CuPc	$7.10^{-16}$	1.98	17

Together with charge carrying properties, which are of importance for organic transistors, phthalocyanines as organic semiconductors have extraordinary photoelectric properties. After the illumination with the light, the excited state of MePc is produced. The excited states may relax to a ground state by the emission of heat, fluorescence or a number of other unproductive (non-emitting) ways, or may cause the production of charge carriers following the dependence:

$$MePc \xrightarrow{h\nu} MePc^* \xrightarrow{\kappa(\varsigma)} free \ carriers;$$
 (2.5)

where:  $\xi$  – *electric field* is the electric field. The formula points that the lifetime of the excited state and the efficiency of the generating charge carriers are correlated and depend on the electric field in the material [11].

The photoconduction of the Pcs was first thought to be correlated only with absorption properties of the molecules. In fact the latter are strongly dependent on the ambience of the active layer, i.e. the photoconductivity associated with  $S_0 \rightarrow S_1$  (based on singlet excited states) absorption band is much bigger when  $O_2$  is present in the MePc (the oxygen increases the photocurrent by a factor of 40 [11]). On the other hand the  $S_0 \rightarrow T_1$  transition (originating from triplet excited states) seems to be less sensitive to  $O_2$  [31] but the generated carriers have longer lifetimes allowing them to migrate over longer distances. This shows the importance of the interaction of the MePcs thin films with ambience, especially gases.

#### 2.1.2 Gas interaction with phthalocyanines

One of the most intriguing features of phthalocyanines is the extraordinary sensitivity of their physical properties to a contact with active gases. Several investigations have showed [18,32] that some phthalocyanines are changing their properties, e.g. electrical conductivity, even by several orders of magnitude during the deposition in, even small, concentration of gases. It is an important fact, mainly due to reported influence [11,32] of some gases like  $O_2$  on the dark and photoelectrical properties, which would have an impact on the future organic device fabrication process. The interaction of the organic materials with ambient gaseous reagents is controlled by three basic mechanisms: molecular, kinetic and the electric one. They are widely explained and described in Ref. [18] and will be briefly discussed here.

#### Molecular mechanism.

The principal consideration in gas sensing problem is how the molecular properties of phthalocyanines favor attractive forces between molecules of phthalocyanines and small gas molecules of various types [18]. The relevant factors are the large delocalized  $\pi$ -electron system, the presence of hetero-atoms presence of central transient (nitrogen) and the metal atom (in metallophthalocyanines). In phthalocyanines, the electron cloud is highly polarisable, due to mentioned  $\pi$ -electron system. It is an extremely desired property since it is responsible for relatively high melting point of phthalocyanines and stronger van der Waals interaction with small gas molecules. The former can be useful during the experiments at increased temperatures and, further, in the development of sensor devices (some sensors operate at elevated temperatures).

Since the ionization energy of phthalocyanines is low, the energy required for the formation of charge-transferred states is also low. The easiness of ionization (properly the energy of ionization) was investigated widely in

experiments including electron impact [33], photoelectron spectroscopies [34] and photoionization in a Millikan-type experiment [35]. Next, the high energy of polarization further reduces the overall energy requirement to form this state by stabilizing the products of such a charge transfer process, which was proved by Lyons [36]. Further investigations [18] showed that due to the presence of nitrogen atoms, the electron distribution within the  $\pi$ -electron system is not uniform. Calculations of energy levels and electron density distributions summarized with net effect estimation suggest that charge-transfer interactions with electron acceptor gases should be strongest when the gas molecules approach either the center of the phthalocyanine molecule or the extreme outside of it. However the interaction strength depends also on good matching of orbital symmetries in the region of overlap [18]. In practice, the phthalocyanine film surface presents a range of different adsorption sites corresponding to different crystal faces edges, corners and structural defect sites. A molecule within a stack presents generally its edges as adsorption sites. The adsorption near the center of the molecule is completely blocked by all neighbors of the molecule being in the stack. Differently, the molecule at the end of stack presents its entire surface towards any approaching gas molecules. The differences in exposed area lead to different adsorption energies.

#### Kinetic mechanism.

Adsorption of reactive gases onto heterogeneous phthalocyanine starts at the most reactive sites. In many cases the surface is already covered by another type of molecule [7], usually weakly bonded (i.e. dioxides). It has to be removed before adsorption of a new molecule, which was first described by Langmuir in 1916 [37]. For a heterogeneous surface, such as that of phthalocyanine film, the weakest adsorption sites are populated first [18]. If the species being adsorbed is a stronger electron acceptor than the background adsorbed species, charge-transfer interaction leads to larger surface dipoles whenever one of the new molecules is adsorbed. Adsorption of acceptor species onto stronger binding sites creates in turn larger surface dipoles and accelerates desorption from stronger sites [18].

#### Electrical mechanism.

One of the best known sensing attributes of phthalocyanines is surface conductivity. The gas layer adsorbed at the surface of phthalocyanine creates a surface bond, which strongly changes the conductivity of Pc. The strongest effect is observed during acceptor gas adsorption like oxygen, nitrogen oxide or nitrogen dioxide. Then the energy of activation is decreasing and the conductivity in heavily increasing. The effect is most pronounced in MePcs.

The electrical conductivity of metallophthalocyanine thin films is determined by electron properties of subsurface area [12]. These properties are the consequence of presence of occupied electron states in the upper part of valence band. The surrounding gas is reacting with the surface and changes the electrical conductivity of surface layer by changing the band bending  $eV_s$ , which is described by Morrison's formula [38]:

$$G \approx G_0 \exp\left(\frac{-eV_s}{kT}\right)$$
 (2.6)

where:  $G_0$  is the surface electrical conductivity when surface potential  $V_s$  is zero, k is the Boltzmann constant and T is the absolute temperature.

It has to be mentioned that gas sensing properties of MePc thin films are highly influenced by various factors such as film heterogeneities, differences of degree of crystallite size, relative orientation of crystallites and grain boundaries [39]. It depends on the temperature of adsorption as well. An increase in the temperature decreases the number of molecules adsorbed at the surface of the molecular material [7]. The sensor mechanism of MePcs is based on gas adsorption and creation of free charges in subsurface charge area, which causes the increase in the electrical conductivity by the translation of holes according to the scheme:

$$gas + MePc < = > g(ads) + MePc < = > [g^{-}MePc^{+}] < = = > [g^{-}MePc] + hole$$

$$(2.7)$$

By using the Nernst's equation and assuming the electrical neutrality, it is possible to define the free charges (holes) concentration with equation [40]:

$$[p] \propto [g]^{1/2} \exp(-\frac{E_{CT} - E_D}{2})$$
(2.8)

where: [g] is the concentration of adsorbed gas;  $E_{CT}$  is the energy of charge exchange and  $E_D$  is the hole creation energy. Continuing, the electrical conductivity can be now expressed with formula [40]:

$$G \propto \mu e[g]^{1/2} \exp(-\frac{E_{CT} - E_D}{2})$$
 (2.9)

where:  $\mu$  is the hole mobility and e is the electron charge.

While the acceptor gases, like oxygen or nitrogen dioxide, strongly increase the Pc conductivity, as one can presume, the donor gases like hydrogen or ammonia, decrease the conductivity in almost all phthalocyanines and cause significant increase in the energy of activation [12]. In 1948, Vartayan [41]conducted interaction experiments aimed to study the influence of acceptor and donor gases on the conductivity and defining the difference in adsorption effect (mass or surface) for Pcs crystals and thin films. The exposure of copper phthalocyanine to oxygen caused the change in the conductivity of both crystal and thin film. However that change was relatively small, about 10<sup>-14</sup>÷10<sup>-12</sup> S/m for the evaporated layer suggesting that this was rather a mass effect than a surface one [12]. All kinds of phthalocyanine crystals responded on deposition in  $NO_2$  with marked increase the conductivity the in by 10.15÷10.7 S/m. Such a large changes suggest that this interaction is more a surface effect than a mass one [42,12]. More sensitive to the deposition in NO<sub>2</sub> are metallophthalocyanines, especially PbPc (more than 1500% change in the conductivity in the NO<sub>2</sub> concentration of 0.5 ppm at the temperature of  $170^{\circ}$ C). The response time for PbPc is also quite short (approximately 20s in room temperature) which makes it suitable for the application in sensor devices. The copper phthalocyanine (CuPc) has a similar property. However, it has a bit less sensitivity on NO<sub>2</sub> but it can be a sensor for different type of gases like NH<sub>3</sub> or CCl<sub>4</sub> as well. Table 2. 4 presents examples of threshold sensitivity of copper phthalocyanine upon chosen gases.

The environmental influence, especially the impact of  $O_2$  on the organic layer functioning should be then revealed in aspect of photovoltaic attributes,

aging and stability. Investigations including ambience interaction with CuPc are described in Section 2.3.4.

Gas	Sensitivity [ppm]			
NO <sub>2</sub>	30000			
CO	250			
$O_2$	30			
$H_2$	30			
Cl <sub>2</sub>	5			

Table 2. 4 The copper phthalocyanine thin film sensitivity on chosen gases [12]

#### 2.2 Phthalocyanine-based devices

The promising photophysical and electronic properties of organic semiconductors such as phthalocyanines called forth new concepts in their application in organic electronics and photovoltaics. As it was mentioned in Chapter I, nowadays the organic thin film transistors (OTFT), organic field effect transistors (OFET) and thin-film organic solar cells are in the center of attention. In the following subchapter the basic concepts of these two most important organic-based electronic devices are briefly discussed.

#### 2.2.1 Organic transistor

An OTFT is analogous to an inorganic thin film transistor (TFT) in basic design and function. It is a three-terminal device, in which a voltage applied to a gate electrode controls current flow between source and drain electrodes under an imposed bias [43]. In an inorganic device, the active semiconductor layer is generally composed of lightly doped Si, or combinations of group III-V elements, In these materials, the such as GaAs. applied gate voltage causes the accumulation of minority carriers at the dielectric interface, e.g. electrons in a p-type material, named the 'inversion layer'. In this very shallow channel, the carriers injected from the source and drain electrodes may pass, resulting in current flow. On the other hand, the active layer in an organic transistor is composed of a thin film of highly conjugated small molecules. In contrast to inorganic materials, the current in organic ones is conducted by majority carriers. This difference is related to the nature of charge transport in each of these semiconductors (see previous subsection). In inorganic ones (which are usually well organized, i.e. single-crystal silicon), the delocalization of electrons over equivalent sites leads to the band-type mode of transport with charge carriers moving through a continuum of energy levels in the solid [43]. In less-ordered organic ones, the most probable mechanism is hopping between discrete, localized states of individual molecules. The presence of impurities or inconsistencies in the structure often results in the existence of so-called 'traps'. These features alter the relative energy levels preventing the undisturbed flow of charge carriers.

The OFETs, which are the basic building blocks of `plastic' integrated circuitry take the advantages of the OTFT structure which is suitable for low conductivity materials [44].In addition, they offer a straightforward method to investigate the charge transport in organic semiconductors. The electric field and temperature dependence of the charge carrier mobility can be investigated for high carrier concentrations [44]. An OFET is also a three-terminal device with voltage applied to the gate electrode. This voltage is used to form a conductive channel (in the semiconducting layer at the interface with the dielectric) which is contacted by the grounded source and drain electrodes. The current is then the flow of majority charge carriers. For a p-type OFET, applying a negative gate-source voltage will cause the accumulation of holes near the semiconductorinsulator interface. The charge carrier density is proportional to the gate voltage. Then applying a negative drain-source voltage will cause a current to flow across the channel, which is dominated by the charges closest to the semiconductordielectric interface [44]. The simplified scheme of architecture of top and bottom contact type of OTFT is shown in Figure 2. 6 together with CuPc-based OFET based on the top contact OTFT structure.



Figure 2. 6 Scheme of different OTFT architectures: (a) bottom contact; (b) top contact; (c) modified top contact scheme for CuPc-based OFET.

Top contact devices have been reported to show superior performance for certain organic semiconductors (such as CuPc) compared with their bottom contact counterparts. It has been suggested that this results from a reduced contact resistance between the electrode and the organic layer because of an increase in the area for charge injection [45]. The complexities of current flow in organic materials have added another look to the development of the organic electronics. In addition to the challenges presented by fabrication, a particular attention must be paid to the design of materials that will meet the performance demands of the OTFT and OFETs in their parent applications [43]. Such structures have been investigated in the aspect of their electronic properties e.g. top-contact type CuPc-based field effect transistors prepared on various high dielectric constant (high-K) gate oxide thin films, such as silicon dioxide, and aluminum oxide prepared by RF magnetron sputtering [46]. It was found that the electronic parameters (like subthreshold slope) were strongly dependent on the gate capacitance and the considerable interfacial capacitance with a thickness of only 3-4 nm [46]. It points to the significant importance of the organic/substrate interface properties.

#### 2.2.2 Organic solar cell

As it was mentioned in subsection 2.1.1, the effective generation of charge carriers is important for solar cells. In order to reach the most efficient generation a mixture of electron donating and accepting materials (e.g. a polymer-fullerene or phthalocyanine-fullerene blend) is used and plays a role of active layer [44]. This layer consists of two ingredients forming disordered, reciprocally penetrating networks of the donor and acceptor phase, forming a bulk heterojunction. The interface in the junction is then not planar but spatially distributed over the entire active layer volume. The light absorption in the active layer generates strongly bounded electron-hole pairs that are excitons. They can pass by diffusion only short distances (about 10-20nm) before they recombine, which seems to be the most important technological limitation (and the exciton-based material-restriction) of organic solar cells. After photoexcitation, the electron is transferred from the donor to the highly electron accepting material [44]. The charge transfer occurs on a time scale of <100 fs

having thus an efficiency close to unity. Then the charges which are not strongly bounded yet, are selectively transported in the respective semiconductor phases: the holes move within the Pcs network while the electrons travel along e.g. fullerene pathways. It should be emphasized that the efficiency of such a bulk heterojunction solar cell depends substantially on the internal structure (morphology) of the absorber layer [44]. Next step is to extract (via drift) the photogenerated charge carriers selectively to the respective electrodes. In this order, an energetically asymmetric structure is essential to obtain an efficient solar cell. A preferred direction for the charge transfer can be assured by the built-in electrical field induced by two electrodes with different electron affinities. One of these electrodes has to be transparent and is called "the window electrode"; it is the layer formed from a strongly doped transparent conductive oxide (TCO) most often the indium tin oxide (ITO). The back-contact is an ohmic contact to the acceptor phase and should be built of a low work function metal (e.g. aluminum). The idea of organic solar cell and its structural scheme is depicted in Figure 2.7



Figure 2. 7 The generic scheme of organic solar cell structure (a) and corresponding band diagram of the organic bulk heterojunction (b). Figure based on Ref. [44].

The preceding considerations prove clearly that the thorough understanding of the mechanisms involved in the junction formation is necessary. Furthermore, the complex investigations of organic / dielectric interfaces and structural properties are also essential to improve the performance of the organic devices. This approach was applied by Komolov and Schaumburg in Ref. [47], where they proposed the organic/n-Si structure for photovoltaic applications and for constructing the efficient OLED device. In those studies the authors monitored the electron injection from Si conduction band into the organic films. These first detailed investigations of such structures have given the clear evidence that the interfaces will be playing the main role in upcoming devices. OLED and photovoltaic applications were also analyzed by Tadayyon et al. [48] who determined the most efficient organic layer thickness for such structures is 12–18 nm. In summary, the matter of charge transfer and the influence of the interfaces and the substrate on the organic overlayers in terms of the performance of organic electronics have become the center of attention.

#### 2.3 CuPc thin films - review

The history of CuPc examinations started relatively early [17, 18] before the World War II. Nevertheless, the modern investigations of thin films in the aspect of new applications began just ten years ago. Up to now the attention in the studies have been paid to the different structures, determined by the expected utilities. For the last decade the main effort was made to examine the CuPc thin films deposited on glass (for sensor, OLED and OFET applications), metals (mainly on gold; generally for organic electronics) and the most recently - on inorganic semiconductors (silicon, indium phosphate and gallium arsenide). Taking into account considerations enclosed in previous subchapters, one of the most interesting is the oxidized silicon – CuPc structure, which is discussed within this Thesis. Nevertheless, for characterization of this structure and for comprehensive understanding of the phenomena taking place on the substrate/organic overlayer interface, the review of examinations on similar objects is necessary. They have already provided crucial information on the CuPc properties and its behavior under different conditions and various treatments. The schematic timeline of studies on the CuPc thin films conducted within chosen workgroups is shown in Figure 2.8. The electronic properties of evaporated layers, their topography and morphology and interaction with the substrate have remained the main fields of interest for many years now. However, recently the increasing concern has been shifted to the formation of substrate/organic overlayer interface and its properties.

year 1997		CuPc on Si (7x7), L'Aquila Ottaviano, Santucci			
		CuPc on SiO₂/Si Osso → structural properties	CuPc on Au Tubingen Peisert, Knunfer, Fink	CuPc on glass Wong → structural properties	
2000		CuPc on SiO₂/Si Komolov, Moller → interfacial properties	Chasse → Interface		
			CuPc on Au	CuPc on glass	
2003		CuPc on SiO₂/Si Mang Ling → topography and electronic	Peisert, Knupter, Xiu, Chasse → interface and doping impact (mainly F)	→ interface properties for OLED application	
г	ļ	proprties for OFET application		CuPc on glass	
2006		CuPc on SiO₂/Si Gao, Xu, Zhu → characterization with thermally grown oxide→ layer thickness investigation	CuPc on Si-H <sub>2</sub> passivated Chemnite Zahn, Gorgoi Surfach electronic properties	Itoh, Higuchi → topography and electronic properties for OFET applicaton	

Figure 2. 8 Scheme of main branches of worldwide CuPc investigations.

#### 2.3.1 Morphological properties

Up to now the MePcs films were investigated with the use of many research methods. The investigations have been focused mainly on the changes in phase composition, structure, morphology and surface chemical composition of asdeposited CuPc thin films due to different heat treatment conditions [49], different substrate and the growth nature [50]. The wide range of research methods have included mainly X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) [49 – 58]. The main body of research were done on thermally evaporated CuPc structures with the thicknesses over 100 nm [49,51,52].

X-ray diffraction methods proved that the initial CuPc powder consists primarily of the stable  $\beta$  –form [49]. Films deposited at room temperature assumed mainly  $\alpha$ -form with a preferential orientation in the (200) direction for films with thickness of 80 nm. The preferential orientation decayed with the increasing thickness, but the crystal form remained unaltered. The same investigations show the temperature and ambience sensitiveness of the CuPc films. All thin films subjected to a heat treatment at 250 °C and exposed to air show the presence of O<sub>2</sub> and strong adsorption of H<sub>2</sub>O at the surface. This water could be partially desorbed by heating and the reaction  $\beta$ -CuPc with oxygen is of a minor nature. The affinity of copper for oxygen is decreasing with increasing annealing temperature, so the authors stated that the incorporation of OH<sup>-</sup> groups into the film prevents the oxidation of the metal atoms.

The *a*-phase of thin CuPc layers deposited in vacuum as well as the grain-type surface morphology was confirmed independently by Zhivkov et al. [51]. The studies on potential gas sensor applications presented in Ref. [51] showed also finest size of the grains (10 nm) and a most homogeneous surface morphology for the layers with thicknesses below 250 nm. An increase of the layer thickness or the deposition angle and deposition rate was found to result in a deterioration of the homogeneity of the layer and enlargement of the grains. The various temperature studies (150-483 K) by Nonaka et al. [53] demonstrated that the morphology of phthalocyanines is indeed temperature-dependent. CuPc grown on Si (001) at low temperatures were investigated with XRD and AFM. At 150 K a very smooth *a*-phase was obtained with root mean square (RMS) roughness of 0.89 nm. The electron-spin resonance measurements showed that the molecular plane was tilted  $21^{\circ}\pm3^{\circ}$  with respect to the surface of the substrate.

Furthermore, the morphology of vacuum deposited copper phthalocyanine (CuPc) thin films have been also studied by Grządziel et al. [52]. Using the contact mode Atomic Force Microscope (AFM) the authors determined the RMS roughness and average grain size of 500-nm-thick layers deposited on Si(111) at various substrate temperatures and after ex-situ post-deposition annealing up to 410 K. Experiments showed the gradual increase in surface roughness, average and maximum grain height of in-situ deposited CuPc thin films with increasing substrate temperature. After the post-deposition UHV annealing of CuPc films, these surface morphological parameters were evidently greater but almost constant regardless of the substrate temperature during the deposition (see Table 2. 5).

Substrate temp. (K	)	RMS (nm)	Av. grain size (nm)	Max. grain size (nm)
During deposition	295	3	12	20
During deposition	330	6	29	56
Post deposition annealing	410	17	64	115

Table 2. 5 Values of RMS, average and maximum grain size reported in Ref. [52].

The same methods (XRD, AFM) were used by Osso et al. [54] to characterize the structure and morphology of the ultra-thin films of hexadecafluorophthalocyanine ( $F_{16}$ CuPc) grown by organic molecular beam deposition (OMBD) under ultra high vacuum (UHV) conditions on oxidized Si(001) substrates. The film thickness in these studies ranged from 12 to 45 nm, while the substrate temperature was varied from 150° to 300 °C. The out-of-plane lattice parameter  $a_c$  was determined to be 14.5 Å. The surface morphology showed needle-like features randomly oriented in the film plane, with a length of up to several hundreds nm and a length-to-width ratio of around 10:1. These authors also reported temperature dependence of the surface morphology of CuPc.

Since it was found that substrate has a significant impact on the CuPc overlayer, the molecular organization of copper phthalocyanine (CuPc) thin films deposited at various substrates and under different conditions was investigated. Films deposited near room temperature (at 30 °C) on quartz and post-annealed gold-coated quartz substrates have been studied by optical absorption, XRD, AFM and field emission scanning electron microscopy (FESEM) [55]. The adsorption of CuPc molecules on Au-750 (Au annealed at 750°C) occurred in a standing (but tilted a little bit) geometry. Relatively big particles of spherical and elliptical shapes were observed with sizes from 100 to 500 nm. On Au-500 substrates the estimated average particle size was much lower, about 40-60 nm. On gold-coated quartz substrate pre-annealed at 750 °C the CuPc demonstrated regular "flower-like" structure with different shape and size ranging from 200 nm to 1 µm. The whole film was covered uniformly by such nanoparticles. The "flowers" was found to consist of some "nanoribbons" of CuPc with a diameter of about 25 nm and few nanometers in length. This structures was assigned to the interaction of CuPc molecules with annealed gold template (i.e. the Au-750 had the same type of surface with spherical and elliptical particles of various sizes). Authors of Ref. [55] claimed that the initial nucleation of CuPc molecules occurred at room temperature on the gold particles and form "flower-like" structure through the process of self-organization.

Also the interaction of the MePc molecule with Si(100) with the 2x1 reconstruction has been discussed [56,57]. The dangling bonds, characteristic for non-passivated surfaces, are known to limit molecular diffusion on the surface. Thus, on hydrogen passivated H–Si(100) 2x1 surfaces two CuPc adsorption modes have been reported. Interaction between a benzene ring and a dangling bond results in the rotation of CuPc molecule while the bonding of the central Cu atom with a surface dangling bond results in a stationary molecule. The adsorption of the CuPc molecule on a hydrogen terminated Si(111) 7x7 was analyzed by Nakamura et al. [50] with the use of scanning tunneling microscopy

(STM). They studied the nature of growth of 20-nm CuPc thin films on substrates maintained at 60°C and found that for low coverages (below 1 monolayer) the molecules adsorb randomly and surface steps have no influence. CuPc molecules migrate and form crystalline islands upon substrate heating up to 140–180 °C while non-ordered molecular lattice was observed at room temperature. For higher coverages (4 to 5 monolayers) the molecules formed ordered domains. This demonstrates that in order to form ordered structures (such as those described in subsection 2.1) of CuPc on H–Si(111) 7x7 (and possibly also on other terminated/passivated surfaces) a thickness of few monolayers is required. The suggested reason of such behavior was due to potential height of migration barriers in comparison with the van-der-Waals potential between a migrating molecule and molecular cluster.

The important thing is that there are only few papers describing the ultrathin films. They were comprehensively investigated only by Tadayyon et al. [48] and thus further investigations, especially of CuPc on oxidized silicon (as a pretender to application in OTFT and organic solar cell) seems to be necessary. It is also worthwhile to mention that the molecular stacking and crystallite orientation may be controlled and changed using the magnetic field during vacuum deposition of CuPc film [58]. The use of this processing parameter may open up a new way to adjust the orientation and quality of the deposited CuPc films.

#### 2.3.2 CuPc surface chemistry

The surface chemistry is believed to be the main determinant of electronic properties of semiconductor surfaces [59]. In this work by the surface chemistry one should recognize the surface chemical bonding information, composition, stoichiometry and depth distribution of the surface-related species.

Surface chemical properties of copper phthalocyanine thin films were mainly investigated by X-ray photoemission spectroscopy (XPS) [60,61]. The analysis of surface bonds is usually limited to investigation of CuPc characteristic peaks involving Cu 2p, C 1s, and N 1s. Sometimes, if the layer is extremely thin, O 1s XPS peak, located at approximately 534 eV, is also visible as a result of substrate contribution to the spectra, or as a result of ambience (or gas) exposure.

The Cu 2p peak contains of two strong spin-orbit-split components, one located at 957.1 eV and another located at 937.2 eV, corresponding to the electron states of Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  orbitals, respectively [60].

The most characteristic for CuPc is the C 1s peak. Due to phthalocyanine particle composition, it has a very specific three-part shape. Two main components are related to C–C and C–N bonds. According to the atomic composition of CuPc molecule there are two kinds of carbon atoms: 8 carbon atoms bound with 2 nitrogen atoms and 24 carbon atoms of an aromatic hydrocarbon character [62]. The number ratio of the carbon atoms of an aromatic hydrocarbon character to the carbon atoms bonding with nitrogen atoms is 3:1. The binding energy of carbon atoms in C–N bonds was observed at 287.9 eV [63]. It is known that the exact binding energy of the electron at orbitals is related to the carbon atom is affected by the electronegativity of the atom bonded with it.

Generally, it can be said that the larger the electronegativity of the related atom, the smaller the electron density around the carbon atom, so the binding energy of the carbon atom increases as the electronegativity of the related atom increases. The electronegativity of carbon and hydrogen is less than that of nitrogen, so the binding energy of the carbon atoms of an aromatic carbon character is less than that of the carbon atoms bonding with nitrogen atoms. A third component of C 1s XPS peak is a satellite peak observed at 289.1 eV, whose binding energy is slightly greater than that of carbon - nitrogen bonds [61].

The studies show that main N 1s peak is located at 401.3 eV [62], while a shoulder peak is at 400.2 eV. Similarly to C 1s, the nitrogen atoms are also in two chemical environments: four N atoms bound with two C atoms to form C-N=C bonds, and the other four N atoms bound not only with C atoms but also with Cu atom through coordination bond. From the discussion in Ref. [62] the peak located at 400.2 eV corresponds to the binding energy of the nitrogen atoms in C-N=C bonds [64], while the peak recorded at 401.3 eV could be related to the N atoms bound with carbon and copper.

#### 2.3.3 CuPc surface electronic properties

At the beginning it is worth to explain what should be understood under the term surface electronic properties within presented work. Figure 2. 9 presents a schematic energy band diagram of the near-to-the-surface region of the n-type semiconductor. Following this scheme, by revealing the surface electronic properties of the semiconductor subsurface area one should understand the determination of the parameters like:  $\varphi$ - the work function,  $\Phi$ - ionization energy,  $X_{\rm s}$ - surface electron affinity and eV<sub>s</sub> – the surface band bending.



Figure 2. 9 A schematic diagram of the energetic scheme of near surface region of an ntype semiconductor, including surface states, where:  $\varphi$ - the work function,  $\Phi$ ionization energy,  $X_{s-}$  surface electron affinity,  $E_{C}$  and  $E_{V}$  are the bottom of the conduction band and top of the valence band respectively.  $E_{F}$  corresponds to the Fermi level [65].

The electronic properties of copper phthalocyanine have been investigated by means of photoemission studies by Vilesov's group [66]. They determined ionization energy to be equal to  $\Phi=5.0\pm0.1$  eV. The energetic parameters of subsurface area of CuPc films, including surface band bending and surface electron affinity, were defined later by Szuber [67]. The input data used in these studies were: the work function  $\varphi=4.17\pm0.05$  eV, the energy of ionization  $\Phi$ =5.0±0.1 eV [68] and the band gap E<sub>g</sub>=1.98 eV [69] known from the electric investigations. Also the surface Fermi level position was known with the value of  $E_{\rm F}$ - $E_{\rm V}$ =1.0 eV [70]. These data allowed to calculate the band bending and the electron affinity which were  $eV_s$ =-0.17±0.15 eV and  $X_s$ =3.02±0.15 eV, respectively [67]. The estimations carried out by Szuber that the energetic bands in CuPc layer are bent upwards were confirmed by Grządziel [12] who used the determined in her work values of work function  $\varphi$ , energy of ionization  $\Phi$ , band gap  $E_g$ , Fermi level position  $E_F$ - $E_V$ , obtained the band bending  $eV_s$ =-0.50±0.20 eV and the electron affinity  $X_{s}=3.22\pm0.20$  eV. The band gap of 1.98 eV is attributed only to very thick layers. In case of ultra-thin layers, when there is indeed no bulk material it is rather incorrect hence the optical and transport band gap differing by about 0.6 eV should be taken accordingly to investigated phenomena. It has to be emphasized that these investigations concerned the layers with the thickness of 500÷1500 nm and cannot be adopted directly for the electronic properties of ultra-thin films considered within this Thesis what is shown in following Table 2. 6 summarizing the surface electronic properties of CuPc. One can see significant differences, especially for work function values for thin and ultra-thin layers.

CuPc	Φ (eV)	φ (eV)	$X_{s}$ (eV)	eV <sub>s</sub> (eV)
1500 nm on Si	$5,0\pm0,1$	$4,17\pm0,05$	$3,02\pm0,15$	$-0,17\pm0,15$
$20~{ m nm}$ on ${ m SiO}_2/{ m Si}$		$4.5 \pm 0.1$	3.2	
20 nm on H-Si	$4.82 \pm 0.07$	$3.88 \pm 0.07$	$2.5\pm0.2$	

Table 2. 6 Comparison of electronic properties of thin and ultra-thin layers of CuPc. For references – see text.

#### 2.3.4 CuPc/substrate interface properties

The importance of interfacial charge phenomena at the semiconductor/gate insulator interface was raised by Itoh and Miyairi [71]. Since organic/inorganic interfaces play an important role in thin-film based devices a number of investigations of CuPc deposited on inorganic semiconductors like InP, GaAs, H-Si, Si, and Si/SiO<sub>2</sub> have been done.

However, the inorganic/organic semiconductor interface is a very complex matter. Hence, before the interface between CuPc and inorganic oxidized semiconductor substrate will be discussed, first the easier to analyze systems of copper phthalocyanine on metals should be described. As an example the Au substrate can be proposed and the investigations into energy level alignment done by Knupfer and Peisert [22,72]. They claimed that possible shifts of the cutoff of the photoemission spectrum and thus of the vacuum level suggest the formation of an interfacial dipole layer  $\Delta$  or band bending near the interface [73]. The situation is shown in Figure 2. 10b.

The contact of two materials allows the achievement of a thermodynamic equilibrium via charge flow across the interface to equalize the chemical potentials on both sides [22]. Discussed herein electronic energy level alignment is determined by fundamental properties of the two materials: their work function and charge carrier densities. Since the absence of chemical interaction and surface reconstruction on both side of the inorganic/organic semiconductor interface have been reported, observations described widely in literature and hereafter (for Ref. – see text) were often interpreted as the formation of a local interface dipole. A number of possible factors that provoked dipole formation were proposed such as chemical reactions, ion formation, mirror forces or surface electronic rearrangement as well as the presence of permanent dipoles at the interface [74]. It was shown that interfaces between gold and differently fluorinated copper phthalocyanines (CuPc, CuPcF<sub>4</sub>, CuPcF<sub>16</sub>) are free from chemical interactions [75,76] becoming an ideal model system to investigations of fundamental properties of organic/metal interfaces. The absence of any unexpected special features in photoemission spectra at the earliest stages of deposition of CuPc on Au(100) was interpreted as lack of interaction at these interfaces regardless of the orientation of the CuPc molecules. On the other hand, the strong energetic shifts of all core level features towards higher binding energies with increasing layer thickness especially for coverages up to 2 nm was observed. Rapid changes occurred within the first 1–2 nm, whereas the variations at thicknesses larger than 2 nm were small. Results obtained at a nominal thickness of about 1.5 nm clearly pointed to different reasons for the observed shifts and led to the assignment of the shifts at low coverages to the formation of interface dipoles [75]. It was shown that these changes were caused by screening effects. The contribution of final state (FS) screening effects to the observed shifts was estimated (in the case of discussed interface systems) via the extra-atomic relaxation energy, which was roughly proportional to the ability for screening by the environment and the distance from the metal surface, r [22]. Screening by the environment is determined in macroscopic dielectric models by the polarization charge  $(1 - 1/\epsilon)e$ , where  $\epsilon$  is the dielectric constant of the environment. In interface systems, the charge screening ability of the substrate is said to be inversely proportional to the distance from the substrate surface via  $e^{2}/4r$ . For metal substrates, as it was written in [22],  $\varepsilon$  becomes infinite (also known as image charge screening), and the FS screening is proportional to  $e^{2}/4r$ , whereas for semiconducting substrates the dielectric constant is similar to the organic and therefore no layer dependent changes in the FS effects are expected. Screening, although explaining the binding energy shift near the interfaces was believed to be negligible at distances larger than 2 nm from the interface [75,77]. The changes of surface electronic properties apart from interface have been attributed to band bending in the conventional sense (i.e. changes of the electrostatic potential as a consequence of the equilibration of the chemical potentials of the two materials in contact). These changes were reported to be very small, of the order of 0.1–0.2 eV, which coincides with the small number of charge carriers in the undoped (intrinsic) organic semiconductors.



Figure 2. 10 a) Variations of the valence and conduction levels in the area of the metal/organic interface; b) schematic determination of the energy level alignment at CuPc/Au interface with the use of photoemission spectroscopy [22].

The screening abilities of the metal was found to introduce an unconventional band bending (Figure 2. 10a) near interfaces between organic semiconductors and metals [78,77]. The image charge screening is substantially larger in organic semiconductors as compared to inorganic (traditional) ones which results in the reduction of the transport energy gap near the metal. This reduction is believed to be up to several tenth of an eV. Authors of Ref. [22] explained this phenomena as a direct consequence of the considerably smaller static dielectric constant ( $\epsilon$ ) of organic materials ( $\epsilon$  in the range of 3–4 in comparison to more than 10 for Si, Ge or GaAs) and due to the more enclosed wave function of the molecular electronic states of organic semiconductors in comparison to the band-like states in Si-like semiconductors.

The transport gap  $E_g$ , was determined for the unfluorinated CuPc using a combination of photoemission and inverse photoemission spectroscopy [79]. It was about 2.3 eV, which is 0.6 eV larger than the onset of the optical absorption. The work function calculated from the measured ionization potentials gave 3.9 eV for CuPc and 4.55 eV for CuPcF<sub>4</sub>. The change in  $\varphi_m - \varphi_{org}$  (difference in work functions of metal and organic overlayer – often denoted as built-in potential  $V_{bi}$  [22]) is generally compensated by the formation of an interface dipole  $\Delta$ . Interestingly, the interface dipole followed linearly the work function difference  $\varphi_m - \varphi_{org}$  also for other undoped organic semiconductors showing that linear dependence is universal for undoped organic semiconductors on metals.

In Ref. [22] it was proven that mainly image charge screening as well as surface rearrangement contributed to the interface dipoles. However that statement did not reveal the phenomena completely. Thus further mechanisms need to be considered. It was demonstrated that an exponential energy distribution of the transport energy levels (defined in Ref. [22]) can change the influence of the band bending on the distribution of electronic states. From transport studies it is well known that the electronic levels in many organic semiconductors are exponentially or Gaussian-like distributed in energy [22].

Observed in Ref. [22] "band bending" was caused within the first 2 nm of the organic film. Simultaneously, the authors of Ref. [22] noted that the term "band bending" in that context should not be taken literally as it actually describes the energy variations of the exponentially or Gaussian-like distributed transport levels. The attribution of the interface dipoles to band bending, in case described in Ref. [22] corresponded well to the Schottky–Mott rule [80] for the energy level alignment at semiconductor interfaces. Following Ref. [22], the phenomena that determine the energy position of the electronic states as a function of the distance from the interface can be assigned to:

- → a shift of the electronic states as a consequence of image charge screening by a nearby metal for distances smaller that 1.5 nm;
- → a reduction of the metal work function at the interface by 0.2–0.4 eV as compared to its value for bare metal;
- → a strong "short-range" interface dipole at 2 nm from the interface (which might be related to the ill-defined energy levels in organic molecular semiconductors and thus could be described in terms of "band bending" of the distributed transport levels).

Second main branch of investigations concerned CuPc deposited on nonorganic semiconductors. In 1998, the group of T. Chasse, C.-I. Wu and A. Kahn performed a number of experiments involving CuPc deposited on p-type InP(110) substrates [81]. Authors analyzed the CuPc 10 nm ultra-thin films in the aspect of energy level alignment at CuPc/substrate interface. Main findings were that CuPc has a reduced sticking coefficient on InP which resulted in presence of InPrelated features in the photoemission spectra even for 10-nm-thick CuPc layers. Such features could be caused by inhomogeneous growth of the film. The main electronic parameters were also determined. In particular they obtained the CuPc ionization energy  $\Phi$ =4.95±0.15 eV upon the assumption of optical band gap  $E_g=1.7$  eV, which corresponded well to their previous studies [82]. The interface formation was described by downward substrate band bending for the thicknesses up to 0.5 nm. Simultaneously, no band bending was observed for CuPc (the absence of molecular level shifts) which was explained with the formation of interface dipole barrier of 0.65±0.15 eV. This suggests that at such an interface the negative charge is transferred from CuPc to InP substrate. These results were one of the first that demonstrated the break of traditional rule of vacuum level alignment and in succession suggested a displacement of negative charge from an organic layer to an inorganic substrate in the direction consistent with the relative electron affinities and ionization energies of the solids [81].

Furthermore, the detailed investigations conducted in the group of Zahn involved CuPc evaporated on semiconductor substrates like sulfide-passivated GaAs and hydrogen-passivated Si. The former incorporated photoelectron spectroscopy studies of phthalocyanines growth on S-GaAs(001) surfaces [83]. The authors reported formation of a chemically inert interface between GaAs and CuPc but the organic molecules affected the surface electronic states of the substrate. The CuPc generated the states above GaAs valence band, which changed the Fermi level position, and caused the broadening of the core level emission peaks. Following that slight interface dipole was inferred for the S-GaAs/CuPc junction. The latter concerned the ultra-thin (up to 20 nm) CuPc and  $F_{16}$ CuPc layers on H-Si(111) and included inversed photoemission spectroscopy (IPES) to determine the thickness-dependence of LUMO level position [84]. In that approach the LUMO was attributed to arise exclusively from  $\pi$  orbitals without the interference from the central metal ion. Together with increasing thickness the movement of the LUMO was observed towards the Fermi level position. As in the case of previous investigations of Chasse et al. the saturation of the shift occurred at the thickness of 10 nm. However, at these studies between 3 and 10 nm of layer thickness only one measurement at 5.7 nm was done. Nevertheless, the LUMO position after the saturation (final thickness) was determined to be  $1.60\pm0.25$  eV for CuPc and  $2.20\pm0.25$  eV for F<sub>16</sub>CuPc. The LUMO position shift during the interface formation was 0.4 eV and 1.2 eV respectively but in the opposite directions. While for CuPc the movement was towards the Fermi level, for the F<sub>16</sub>CuPc was in away from E<sub>F</sub> position what was reported to be due to change in molecular orientation and different growth mode as described earlier by Yamane et al. [85] and Peisert et al. [86].

Detailed studies of the electronic properties of CuPc on H-Si conducted by Gorgoi et al. [87] led to determination of work function, ionization energy and electron affinity for the layers up to 20 nm. The combination of ultraviolet photoemission spectroscopy (UPS) and IPES allowed the determination of the band gap width as 2.2±0.25 eV (corresponding to transport gap of the CuPc) and the peak-to-peak (understood as the distance between max. energy positions of corresponding peaks) energy distance between LUMO and HOMO was as  $2.9\pm0.2$  eV. This value of the transport gap is in good agreement with that reported by Hill et al., i.e. 2.3±0.4 eV [79]. The electronic parameters of 20-nmthick CuPc layer were: the ionization energy  $\Phi = 4.82 \pm 0.07$  eV, the work function  $\varphi$ =3.88±0.07 eV and the electron affinity X=2.5±0.2 eV. The investigations detected also the interface dipole formation of the value 0.34±0.07 eV. For the first layers the changes of the parameters occurred similarly to the previous investigations by group of Chasse and group of Zahn; the  $\Phi$  decreased from 5 eV at the beginning to almost 4.5 eV for 2- nm-thick layer and then saturated for the thicknesses over 5 nm. The work function was continuously decreasing from starting point of 4.25 eV to the mentioned earlier final value of 3.88±0.07 eV with the saturation at about 18 nm of CuPc. Electron affinity remained stable. Once more the formation of the interface and the changes of the electronic parameters were assigned to the molecular reorientation taking place with increasing CuPc layer thickness [85,86]. This, in turn, affects the HOMO and LUMO positions as the features originating from  $\pi$  molecular orbitals [88,89].

The interface formation of CuPc films up to 10 nm on GaAs surfaces was also analyzed by Komolov and Moller [90]. The starting point in that case was that the electron charge transfer is common for interfaces between metal and semiconductor surfaces [91,92]. The electronic parameters determined for various thicknesses were the surface work function and structure of unoccupied electron states (DOUS - Density Of Unoccupied States). The electron charge transfer layer at the interface described in Refs [91,92] was found to be more than 5 nm apart from GaAs surface. The work function  $\varphi$  was changing together with CuPc layer formation from 4.9±0.1 eV for bare GaAs substrate through 4.4±0.1 eV for 2-2.5nm CuPc to 4.5±0.1 eV for the final 10-nm layer. It has to be noted that the thickness of about 2-3 nm seems to be crucial for interface formation which was also observed for organic/metal structures and corresponds to formation of the complete monolayer [22]. The charging observed with total current spectroscopy (TCS) for CuPc structure at early stages of deposition was proposed to be correlated with the polarization of the CuPc molecule [90]. The polarization becomes weaker for thicker layers according to the model of extended interface dipole proposed by Komolov and Moller for CuPc/n-Si and CuPc/SiO<sub>2</sub>/Si structures [93].

Since the investigation showed that the electron affinity rule for energy level alignment often was braking down at such type (inorganic/organic semiconductor) of interfaces [81,94], Komolov and Moller tried to apply once more the electron spectroscopy techniques to investigate the energy level alignment upon interface formation [93,95]. The investigations involving 20-nm CuPc layer evaporated in a stepwise manner on n-type Si (100), SiO<sub>2</sub>/n-Si and SiO<sub>2</sub>/p-Si. The substrates were specially prepared (HF, H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> etching and thermal UHV growth of oxide) with the oxide thickness being 4 nm in thickness. Conducted TCS investigations showed that DOUS structure was corresponding well to calculated molecular orbitals [96] for the electronic sates lying up to 10 eV above Fermi level and proved that the entire spectra was predominantly formed by the organic part of the molecule (the central metal atom played secondary role in that case). For n-Si substrates the authors suggested the decomposition of the CuPc molecule during the evaporation which was manifested by the lack of TCS signal for CuPc thicknesses up to 3 nm. This was quite remarkable since the Pcs were known to be stable upon deposition on solid substrates [97]. The decomposition diminishes for thicker films (the substrate effects on CuPc molecules are weaker) and the reported stable layer had the thickness of 10 nm. A conclusion drawn was that single-crystal silicon is more reactive and causes reconfiguration of the  $\pi$ -electron system of the CuPc molecules. The work function was determined as 4.8±0.1 eV for the very first layers and was descending to 4.5±0.1 eV for the saturated 12 nm layers. The surface potential was found to be gradually changed (upwards) by 0.8±0.1 eV with increasing layer thickness (0-12 nm). Using the electron affinity value (3.2 eV) and ionization energy (4.95 eV) [97], the Fermi level position was estimated to be in the lower part of the band gap. Contrary to clean n-Si substrate, the destruction of CuPc molecules was not observed on the oxidized silicon. Similarly the complete film was created when the thickness was 10 nm. For the SiO<sub>2</sub>/n-Si the surface potential change was reported and assigned to polarization of the CuPc film as well as to subsurface depletion and to band bending in the substrate. Unlike on the monocrystalline substrate, the work function was increasing from  $4.0\pm0.1 \text{ eV}$  to  $4.5\pm0.1 \text{ eV}$  for the final thickness. For SiO<sub>2</sub>/p-Si no charge transfer or  $\pi$ -complex formation at the interface was detected. The work function was determined as  $4.5\pm0.1$  eV for the saturated 10nm CuPc layers regardless doping of oxide-covered substrate. On the other hand, the ultraviolet photoemission spectroscopy measurements done by Tadayyon [48] showed that the structure of the occupied CuPc molecular orbitals does not change for thicknesses up to 16 nm.

The direction of the charge transfer at the forming organic/inorganic interface was investigated widely in [81,74]. Formation of a polarization bond that corresponds to formation [95] of an interface dipole within one molecular layer is one of the mechanisms explicating the charge transfer phenomena. Proposed by Komolov and Moller [93,95] and mentioned earlier extended dipole model suggests that interaction of the CuPc molecules with the substrate can conduct to deformation of the  $\pi$ -electron core of the phthalocyanine molecules or to their polarization. Negative charge of the first molecular layer is then transferred over the interface while its positive charge is partially compensated by the negative charge coming from the next molecular layer (what was said to take place within the polarization layer). The proposed model assumes that total positive charge left in the polarization layer is equal to the negative charge transferred over the interface [95].

The effect of the orientation of molecules on the molecular electronic structure was studied on the CuPc/graphite system. Yamane et al. studied film thickness dependences by means of metastable-atom electron spectroscopy and ultraviolet photoelectron spectroscopy [98]. Although this system is not exactly the same as that investigated in this Dissertation, its analysis gives an idea on origin of the interfacial dipole formation. They observed a decrease in the vacuum-level position and a corresponding band-bending-like shift in the highest occupied state only for thick films where the molecular tilt angle increased gradually with the film thickness. Those shifts were explained by electric dipoles produced in the film by a gradient of the intermolecular electronic interaction along the surface normal due to the continuous increase in the molecular tilt angle. The result indicates that the change in the molecular orientation is an important origin of the band-bending-like shift in the molecular electronic states even if the molecule had no permanent electric dipole. However, the detailed mechanism of the dipole formation still remained unrevealed.

#### 2.3.5 Ambience influence on CuPc

In the light of considerations enclosed in Section 2.1.2 and 2.2, the mechanisms of interaction of CuPc layer with ambience are of great importance to future organic devices fabrication and functioning. Phthalocyanines (especially CuPc) were intensively investigated in last two decades in the aspect of their susceptibility to ambience atmosphere and how deposition in molecular oxygen influences the electronic properties of subsurface area of CuPc thin (500÷1500 nm) films. It was confirmed that adsorption of oxygen causes the increase in the work function  $\varphi$  by about 0.15 eV and energy of ionization  $\Phi$  by about 0.1 eV.

The increase (around 30 times) in the electrical conductivity was observed by Laurs and Heiland [99] after exposure of the CuPc thin films to about  $10^8 \text{ L O}_2$  [1 L (Langmuir) =  $1.33 \cdot 10^{-4}$  Pa s]. This well known effect was interpreted as an increase in the concentration of hole traps within the CuPc thin films after O<sub>2</sub> adsorption [100].

More evident effects were observed for the freshly evaporated CuPc thin films exposed to the air atmosphere, and then to the molecular hydrogen  $H_2$ exposure of 10<sup>8</sup> L, as shown in the spectra of effective density of states N(E) (Figure 2. 11) recorded on freshly evaporated CuPc thin films deposited on Si(111) substrate kept at 330 K (curve a), then exposed to the air (curve b) and subsequently exposed to hydrogen (curve c).


Figure 2. 11 The spectra of photoemission yield Y(E) of the freshly evaporated CuPc thin films deposited on Si (111) substrate kept at 330 K (curve a), then exposed to air (curve b) and subsequently, exposed to molecular hydrogen (curve c). Reprinted with permission of Authors of Ref. [52].

A influence of the molecular hydrogen interaction with CuPc thin films on its electronic properties is in good consistency with the small changes of electrical conductivity observed by Uwira et al. [101]. Only for Pd-doped CuPc films the molecular hydrogen exposure causes about 50% decrease in their electrical conductivity [101]. After air exposure the spectrum of effective density of electronic states N(E) of the freshly evaporated CuPc evidently changes, particularly in the region close to the top of valence band where a rather sharp band of electronic states has appears [52].

Moreover, the work function  $\varphi$  of freshly evaporated CuPc thin films after air exposure increases by about 0.12 eV and reaches the value similar to the one obtained recently on *ex situ* studied CuPc thin films [102], whereas the value of ionization energy  $\varphi$  remains constant. The determined surface Fermi level position in the band gap was equal to  $E_{F}-E_{V}=0.60\pm0.13$  eV.

Table 2. 7 summarizes the information about  $O_2$  influence on electronic parameters of CuPc subsurface area.

Substrate temperature, K		Exposition in O2, L	Fermi level shift $\Delta \mathrm{E}_\mathrm{F},\mathrm{eV}$	Ionization Energy Φ, eV
Post-deposition annealing at 410 [103]		$10^{5}$	$0,03\pm0,03$	$5,20\pm0,20$
		$10^{6}$	$0,09\pm0,03$	$5,20\pm0,20$
During deposition [52,104]	295	$10^{6}$	$0,02\pm0,03$	$5,10\pm0,10$
		$10^{7}$	$0,02\pm0,03$	$5,10\pm0,10$
		$10^{8}$	$0,04\pm0,03$	$5,10\pm0,10$
	330	$10^{6}$	$0,05\pm0,03$	$5,12\pm0,10$
		$10^{7}$	$0,07\pm0,03$	$5,12\pm0,10$
		$10^{8}$	$0,10\pm0,03$	$5,12\pm0,10$

Table 2. 7 The influence of oxygen exposure on Fermi level shift  $\Delta E_F$  and ionization energy  $\Phi$  for the ex-situ and in-situ prepared CuPc thin films at different temperatures of substrate.

## 2.3.6 Substrate

Due to described earlier phthalocyanine-based devices the most natural for presented within this Thesis substrate is oxidized silicon hence the Si and SiO<sub>2</sub>/Si structure are briefly discussed herein. Table 2. 8 contains basic electronic properties of silicon in comparison to its main competitor – the gallium arsenide. Since the silicon on its own is well known as the substrate for electronics and surface science, only those its surface features which are relevant to this Dissertation will be discussed hereafter.

Properties	GaAs	$\mathbf{Si}$	Unit
Band gap	1.42	1.10 - 1.12	eV
Dielectric constant	13.1	11.8	1
Intrinsic carrier concentration	$2.25 \mathrm{x} 10^{6}$	$6.8 \mathrm{x10^{10}}$	cm <sup>-3</sup>
Electron mobility (undoped)	8500	1400	cm²/Vs
Hole mobility (undoped)	250	450	cm²/Vs
Effective electron mass	$0.067 \ m_e$	$1.08 \ m_e$	-
Effective hole mass	$0.45~m_{e}$	$0.56 \ m_e$	-
Electron bulk lifetime (SRH)	10-7	$10^{-5}$	$\mathbf{S}$
Hole bulk lifetime (SRH)	10-7	$10^{-5}$	$\mathbf{S}$
Threshold field	3.3	1.7	kV/cm
Peak drift velocity	$2.1 x 10^{7}$	$10^{7}$	cm/s
Band to band transition	Direct	Indirect	-

Table 2. 8 Comparison of chosen bulk electronic properties of Si and GaAs [105].

Si and SiO<sub>2</sub>/Si interface were thoroughly described in Ref. [106]. The surface properties (especially surface chemistry investigated by photoemission spectroscopy) were comprehensively described in review article by Iwata and Ishizaka [107]. Figure 2. 12 presents the three different possible oxidation states of silicon and the most probable scheme of their mutual location at oxidized silicon wafer (substrate).



Figure 2. 12 The different possible oxidation states of silicon (a) and their most probable distribution at  $SiO_2/Si$  structure (b). Figure inspired by [107]

Up to now the studies of oxidized silicon were focused mainly on artificially  $SiO_2$ , the dielectric material with a carrier mobility of grown oxide. 9.09×10<sup>-5</sup> (cm<sup>2</sup>/Vs) [108] covering naturally all delivered substrate wafers, most often was thermally grown on silicon substrates with different crystallographic orientation. For instance, thin SiO<sub>2</sub> (8-12 nm) and the SiO<sub>2</sub>/Si interface, formed on RF hydrogen plasma-cleaned Si(100) and Si(111) by 850°C dry oxidation in the initial growth regime were studied by Szekeres and Paneva [109]. The authors made a comparison of different substrate preparation methods including hydrogen passivation, plasma etching and RCA treatment (RCA standard cleaning procedure is described in Section 4.5 as one of the preparation methods used within this Thesis). They found that the oxidation of a hydrogen-enriched Si surface layer results in larger oxide thickness in comparison to oxides on standard RCA-cleaned Si and has an opposite influence on the thickness of the interface for the two orientations, i.e. increase for Si(100) and decrease for Si(111), and yields an interface composition closer to stoichiometric  $SiO_2$ . It was suggested that the result of hydrogen plasma exposure of Si is a less dense hydrogen-rich surface region, where the diffusion of atomic oxygen is accelerated. Table 2. 9 summarize the parameters of the oxides obtained on two mentioned substrates for different methods.

	Treatment	Oxide thickness (nm)	Interface thickness (nm)	Composition
Si (100)	RCA	8.9	0.67	${ m SiO}_{0.8}$
	RCA+ H <sub>2</sub> Plasma at 100°C	9.7	1.15	${ m SiO}_{1.4}$
Si (111)	RCA	8.0	1.00	${ m SiO}_{0.8}$
	RCA+ H <sub>2</sub> Plasma at 100°C	9.3	0.77	${ m SiO}_{1.4}$

Table 2. 9 The oxide and SiO2/Si interface thicknesses and its composition as a function of the pre-oxidation treatment. After Ref. [109].

It was believed that due to the denser packing of a Si(111) surface, the oxide should be thicker than for Si(100), however it has not been reported. Analyzing the geometric structure of oxide layer it was found [110] that the angle of Si–O–Si bond for the given structural unit is 127°, which is typical for a Si–O<sub>2</sub>–Si<sub>2</sub> molecular cluster. Thus, it was concluded that, in comparison with oxides grown on hydrogenated Si, standard oxide possesses an additional amount of underoxidized silicon, which is most probably located in the interfacial region.

The Si/SiO<sub>2</sub> interface formation was also observed. It was found that the formation of thicker  $Si/SiO_2$  interface could be a consequence of the enhanced oxidation rate and possible formation of interface roughness.

The hydrogenated substrates exhibited more perfect oxidation of silicon atoms resulting in an interface composition closer to the stoichiometric  $SiO_2$ . That statement was supported by the observed higher oxide thicknesses and the results of oxidation kinetics studies [111,112]. A multiple-angle spectral ellipsometric studies revealed that 850°C oxidation of hydrogen-enriched silicon via RF hydrogen plasma yielded thicker oxides in the thin film regime with a compressive stress level of  $6.1 \cdot 10^8 \text{ N/m}^2$  (same for both types of substrates). The same investigations [111,112] showed that the process-induced stress on the oxidation kinetics was found to be negligible. The refractive index of the oxide was determined to be 1.466 [109].

On the other hand, a few years later the same group of Szekeres et al. found from the analysis of the pseudo-dielectric function of Si in presence of the oxide, the oxidation-induced stress depended on the plasma treatment temperature and is on the order of  $10^8 \text{ N/m}^2$ , but it was smaller than that in oxides on standard RCA-cleaned Si. The stress levels were further investigated with IR methods and showed that the structure of SiO<sub>2</sub> grown on hydrogenated silicon possesses a relatively larger contribution of six-fold SiO<sub>4</sub> rings indicating a more ordered and less-stressed SiO<sub>2</sub> lattice [113]. The oxides grown on hydrogenated Si had lower stress levels in the oxides and better substoichiometric composition of the interface.

Since the effect of surface roughness may affect the device performance and reliability, considerable effort has been made to obtain perfectly clean and smooth Si surfaces prior to oxidation [113]. Further comparisons between cleaning and preparation methods were done by Donose and Taran [114]. The lateral force microscopy was used to determine the microstructural changes in the silica surfaces subjected to three commonly applied cleaning methods: the RCA ammonium and hydrogen peroxide wet cleaning, the mild water plasma cleaning, and the UV/ozone cleaning. Measurements shown that all procedures produce clean surfaces with identical hydrophilicity, RMS roughness, and surface charge. The friction force on the wafers treated by the RCA has been found to be several times higher than for wafers treated by the plasma and UV/ozone procedures (Table 2. 10).

]	Cleaning procedure	Roughness – RMS (nm)	Surface potential (mV)	Friction coefficient
A	cetone/water	$0.10\pm0.09$	-	-
	RCA	$0.08 \pm 0.01$	65	$0.100 \pm 0.010$
	Plasma	$0.07 \pm 0.02$	75	$0.022 \pm 0.005$
	UV/ozone	$0.09 \pm 0.01$	70	$0.025 \pm 0.004$

Table 2. 10 Chosen properties of differently treated Si substrates [114].

The results were explained with the changes of the surface properties during the RCA cleaning in which a chemical oxide layer is continually generated and removed. Observed increase in the friction force of the newly-formed oxide layer was supposed to be generated by small variations in the roughness [114]. Third-order roughness termed also micro-roughness was determined by AFM measurements [115] and was on the atomic scale. Initial micro-roughness of "as delivered" Si(100) and (111) wafers was in the range of 0.38–0.43 nm. It should be noted that these studies are one of the rare examinations of the native oxidized wafers.

The defect centers, related to oxide charge and interface traps, induced in thin  $SiO_2$  layer by technological procedures were also studied [116]. Characterization of defects was performed by analyzing the frequency dispersion of the capacitance–voltage characteristics. The results showed that pre-oxidation hydrogen RF plasma cleaning of Si wafers could yield lower interface defect densities, lower oxide stress, surface roughness level, and improved crystallographic structure in comparison to standard RCA Si clean.

The analysis of the absorption from ellipsometric spectra [113] of the pseudo-dielectric functions  $\langle \varepsilon_2 \rangle$  of Si and of the transmittance from the infrared spectra of ultra-thin SiO<sub>2</sub> layer thermally grown on Si at 850°C showed that oxidation of hydrogenated silicon yielded more uniform oxides with lower intrinsic stress and better interface structure but simultaneously was technically much more advanced and expensive in the aspect of device fabrication.

Although there is an ample literature study on  $SiO_2$  and the  $Si/SiO_2$  interface, they mainly concerns thermally or generally artificially grown oxides. Thus, the Si substrates covered with native oxide grown unintentionally during the contact with the atmosphere need to be investigated before the growth of CuPc films.



# AIM AND SCOPE

In the light of considerations presented in previous chapter it is clearly visible that the fabrication technology of organic devices demands ready-to-use, well defined structures based on entirely investigated materials of precisely determined properties. It can be foreseen that one of the most promising substrates in next few years will be the oxidized inorganic semiconductor like oxidized silicon. This Thesis tries to reveal the possibility of native substrate usage for organic electronics applications. Present Chapter reveals the main objectives undertaken within this Dissertation and precisely defines scope of conducted experiments. This Dissertation bases on three novel and original approaches: the new, native substrate, the application of ultra-thin CuPc layers and the exclusive combination of morphological, photoemission and diffraction methods giving a comprehensive image of such a fine structure.

## 3.1 Object

The object of studies presented in this Thesis is the  $Si/SiO_2/CuPc$  structure. It was clearly written that such structure has a great opportunity for becoming crucial part of newly constructed organic electronic devices in the next few years. Although similar structures have been investigated by various groups, some deficiencies are significant:

- ➤ lack of investigations devoted to layers evaporated on silicon covered with native oxide → up to now the studied structures were based on artificially prepared (i.e. thermally grown) oxides or passivated (i.e. hydrogenated) silicon;
- ➤ only modest information about ultra-thin (below 20 nm) CuPc films → the up-to-now obtained layers were rather thicker than 100 nm which excluded them from applications like exciton solar cells and ultra-thin organic transistors;
- shortage of comprehensive and correlated studies of CuPc/SiO<sub>2</sub>/Si structures involving morphology as well as electronic properties and surface chemistry;
- ➤ lack of Si/SiO<sub>2</sub>/CuPc dual-interface structure investigations → at present the exact energy level alignment and the mechanisms of charge transfer remain unknown;
- almost no information on the influence of the type of substrate conductivity on properties of ultra-thin CuPc films and organic layer/substrate interface.

The approach presented here includes comprehensive (mostly in-situ) examinations of copper phthalocyanines ultra-thin films deposited on n- and p-type Si(111) substrates covered with native oxide with the use of variety of research methods including a wide set of photoemission methods (especially unique Photoemission Yield Spectroscopy) and surface imaging methods like Atomic Force Microscopy and Scanning Electron Microscopy augmented by other auxiliary methods.

Second original feature includes the application of the reference samples, which are the ultra-thin layers (16 nm) of CuPc deposited on RCA-treated substrates of n- and p-type of conductivity. Regarding the fact that there is not ample of literature on RCA-treated samples, this technology was chosen as the well established and repeatable one. Although RCA samples are used as the reference, the variety of used methods allows for comprehensive description of such objects. Hence, the range of performed studies testifies the novelty of this work. The CuPc thickness (16 nm) used within these studies were chosen for two reasons. First due to thin film application in modern devices (regime of thickness <20 nm) and second: 16 nm is approximately the value of three monolayers of

CuPc which should ensure obtaining of stable, uniform layer totally covering the substrate.

## 3.2 Scope of the studies

The investigations presented within this Thesis are focused on the following objectives:

- determination of surface chemistry, morphology and surface electronic properties of Si substrates covered with native oxide and after the RCAtreatment;
- > comparison of above parameters for two: n- and p-type of substrates;
- determination of surface chemistry, morphology and surface electronic properties of 16-nm ultra-thin CuPc films deposited on native and RCAtreated Si substrates with the different type of conductivity;
- investigation of substrate/CuPc interface formation including energy level alignment with consideration of the type of substrate conductivity and substrate preparation technology;
- determination of aging effects and ambience influence on surface chemistry, morphology and surface electronic properties of ultra-thin CuPc films with consideration of the type of substrate conductivity.

The specified goals have forced an application of variety of research methods which can all be divided into imaging, photoemission, diffraction and thermal ones. Depending on the information needed, the following methods have been used:

- Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) for surface morphology and topography determination;
- X-ray Photoemission Spectroscopy (XPS) for investigation of surface chemistry and electronic parameters;
- Ultraviolet Photoemission Spectroscopy (UPS) and Photoemission Yield Spectroscopy (PYS) for determination of electronic parameters of subsurface area;
- > X-Ray Diffraction for surface morphology (CuPc phase) determination;

All the experiments, including the substrate preparation and CuPc film growth have been performed at three scientific centers: Institute of Physics (Silesian University of Technology, Gliwice, Poland), Department of Physics (University of L'Aquila, Italy) and Institute of Physical and Theoretical Chemistry (University of Tübingen, Germany).



## **EXPERIMENTAL METHODS**

Present chapter is devoted to brief description of experimental methods used within this Dissertation. First, the basis of imaging methods like AFM and SEM are described. The brief note about equipment of these methods is also enclosed. Second, the chapter is focused on photoemission methods including XPS, UPS and PYS. The fundamental physical phenomena employed in the basis of the methods are described together with the applied equipment. Next, the auxiliary XRD method is described.

The chapter contains also the specification of experimental setups used to presented herein experiments. The description has been parceled into three subsections devoted to laboratories in Gliwice, Tuebingen and L'Aquila.

At the end of the chapter the sample preparation techniques as well as the data processing methods are shortly discussed.

## 4.1 Imaging methods

For comprehensive description of surface morphology and topology the atomic force microscopy and scanning electron microscopy were employed. Hereafter, the short descriptions as well as the main physical assumptions of these two methods are presented.

## 4.1.1 AFM – Atomic Force Microscopy

The atomic force microscope (AFM) (also known as scanning force microscope – SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution of the order of a nanometer. An atomic force microscope is capable of imaging features as small in diameter as a carbon atom (0.25 nm) and as large as the cross section of a human hair (80  $\mu$ m), what gives enormous possibilities for investigating samples surface topography and morphology.

The direct precursor to the AFM was the scanning tunneling microscope (STM), developed by Gerd Binnig and Heinrich Rohrer in the early 1980s. This achievement earned them the Nobel Prize in Physics in 1986. But the STM has one major disadvantage: it was possible to use it only with conducting specimens. In the fall of 1985 Gerd Binnig and Christoph Gerber used the cantilever to examine insulating surfaces. The first AFM was made by meticulously gluing a tiny shard of diamond onto one end of a tiny strip of gold foil [117]. A small hook at the end of the cantilever was pressed against the surface while the sample was scanned beneath the tip.



Figure 4. 1 Scheme of AFM device showing an idea of the measurement. Piezoelectric transducers are responsible for XYZ movement of the sample during the scan.

The force between tip and sample was measured by tracking the deflection of the cantilever and by monitoring the tunneling current to a second tip positioned above the cantilever.

The first AFMs delineated lateral features as small as 300 Å. However, the considerable development in the AFM method application began after introduction of microcantilevers, new modified nano tips and new optical beam deflection methods in order to measure the tip movement and twist [118,119]. The beam-bounce method is now widely used as a result of the excellent work by Alexander and colleagues [120]. The new tips (the top of the tip can be built of the order of tens to hundreds atoms) and microcantilevers, are usually made from silicon or silicon nitride [121]. The scheme of the AFM device idea is shown in Figure 4. 1

#### Principles of the method

Principally, the AFM operates by allowing an extremely fine sharp tip to either come in contact or in very close proximity to the examined sample. The tip is usually a couple of microns long and often less than 100Å in diameter, and is placed at the free end of a cantilever that is 100 to  $200\mu m$  long. It extorts that sample is scanned beneath the tip.

The tip with the cantilever are fixed to the device and have only the possibility of movement towards Z axis or can be twisted (Friction force mode – will be described further). The X-Y movement is realized by moving the imaged sample with the piezoelectric stand on which the specimen lies. Different forces either attract or repeal the tip. These deflections are recorded and processed using imaging software. The image is then a topographical representation of the sample that was just investigated and strictly corresponds to tip size what is illustrated in Figure 4. 2. The magnified photo of tip is depicted together with the cantilever in Figure 4. 3.



Figure 4. 2 Two exemplary image profiles obtained by narrow tip (blue line) and wider tip (red line).

Feedback from the photodiode difference signal, through the control software, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electric transducer monitors real time height deviation [117]. In the constant height mode the deflection force on the sample is recorded but it requires insertion of calibration parameters of the scanning tip in the sensitivity of the AFM head during force calibration of the microscope. As one can see, the revolutionary advantage in comparison to other microcopies is that AFM imaging results in a 3D image. The force F between the tip and the sample is related to the cantilever's deflection through Hooke's law:

$$F = k \cdot \alpha \cdot V \tag{4.1}$$

where k is the cantilever's spring constant, V is the measured cantilever's deflection in volts, and  $\alpha$  is called the deflection sensitivity that converts

cantilever's deflection from volts to nanometers [122]. V,  $\alpha$ , and k are the main quantities that the AFM determines in force spectroscopy.



Figure 4.3 The magnified image of a cantilever with a tip (a) and tip itself (b) [123].

The deflection V is measured directly with a position-sensitive split photodiode detector (PSPD). The deflection sensitivity  $\alpha$  is determined from a force vs. distance relation [122]. The cantilever's bending stiffness or spring constant k is usually estimated by its manufacturer, but this estimate can be quite gross; 300 per cent deviation from the stated estimate is not unusual. For this reason, several methods have been developed to arrive at a more accurate estimate. The spring constant k is given by [124]:

$$k = 2\pi^3 l^3 w \sqrt{\frac{\rho^3}{E}} f_0^3 \alpha V \tag{4.2}$$

where: l - cantilever's length; w- width;  $f_0$ - fundamental resonance frequency; E -Young's modulus of elasticity;  $\rho$  - mass density of the cantilever material [122]. As with all AFM techniques, force sensing and force resolution in force spectroscopy are bounded by the overall noise in the system, which includes the AFM, the sample, and the environment in which they are. The sources of noise from the AFM include the thermal noise of the cantilever, mechanical vibrations of the components of the AFM, and electrical and optical contributions of the corresponding components in the system [122]. Resolution and sensitivity are two important characteristics determining the quality of performance of an AFM, and they are both adversely affected by noise. If the AFM is noisy, a sensitive cantilever or detector, a precisely calibrated piezoelectric scanner, and a whole host of other high performance elements of the AFM may as well be replaced by lower-performance, cheaper substitutes because their value is lost in the noise of the AFM [122]. One of the sources of the noise could be also the vibrations related to the laboratory building structure. In order to obtain good AFM results, the vibration isolation platform is needed. The vibration isolation consists of a large mass attached to bungee cords firmly anchored to the building. (Notice that the resonance frequency only depends on the stretch of the bungee cord). Damping of the oscillation is believed to be a result of rubbing of the rubber fibers inside of the bungee cord against the outside lining material. Between the low resonance frequency of the bungee cord system and the high resonance frequency of the microscope hardware itself (>10 kHz), the AFM effectively comprises a band pass filter [117].

From the time-of-scan point of view one can distinguish two different types of AFM apparatus: a conventional AFM and a high-speed one developed by Humphris et al. [125]. In a conventional AFM an electronic feedback loop is used to follow the topography of the sample by adjusting the position of the sample relative to the tip to maintain a constant deflection of the cantilever and thus interaction force. In the high-speed (HSAFM) AFM, as one can read in [125], a passive feedback system is used. A constant external force is applied directly to the tip in order to accelerate the tip toward the sample surface, and the mechanical properties of the microcantilever beam are fixed to control the path of the tip over the surface of the sample. The direct force applied to the tip is independent of the deflection of the microcantilever and is of sufficient magnitude to hold the tip in contact with the surface. Thus the beam of the microcantilever controls the position of the tip in the X-Y plane and the trajectory of the tip in the direction perpendicular to the surface of the sample (e.g. the z axis), but does not provide a significant bending-dependent force to the surface [125].

#### **Operating** modes

Due to the type of operation one can distinguish four main work modes of the AFM: contact mode, non-contact mode, tapping mode and friction force mode.

#### **Contact mode:**

This mode occurs when the tip of the AFM device is investigating the topography of the examined surface in close contact. The tip exerts on the surface pressure of the order  $10^{.7} - 10^{.11}$  N what means that the distance between the specimen and the tip is extremely small. In this mode, the short-range interatomic interaction forces are used. In contact mode AFM the deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value the feedback amplifier applies a voltage to the piezoelectric device to raise or lower the sample relative to the cantilever to restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface and is displayed as a function of the lateral position of the sample.

#### Non-contact mode:

In this mode the tip hoovers 50–150 Å above the sample surface. Attractive Van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Unfortunately the attractive forces from the sample are substantially weaker than the forces used in contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces

between the tip and the sample. This is done by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Van der Waals forces which may extend only a nanometer from the sample surface.

#### Tapping mode:

Tapping mode imaging is implemented by oscillating the cantilever assembly at or near the cantilever's resonant frequency using a piezoelectric crystal. An electronic servo uses the piezoelectric actuator to control the height of the cantilever oscillating with a high amplitude (typically greater than 20 nm) while the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50 to 500 kHz. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features. During tapping mode operation, the cantilever oscillation amplitude is maintained constant by a feedback loop. Selection of the optimal oscillation frequency is software-assisted and the force on the sample is automatically set and maintained at the lowest possible level. When the tip passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases (approaching the maximum free air amplitude). Tapping Mode inherently prevents the tip from sticking to the surface and causing damage during scanning. Unlike contact and non-contact modes, when the tip contacts the surface, it has sufficient oscillation amplitude to overcome the tip-sample adhesion forces. Also, the surface material is not pulled sideways by shear forces since the applied force is always vertical. Another advantage of the Tapping Mode technique is its large, linear operating range. This makes the vertical feedback system highly stable, allowing routine reproducible sample measurements.

#### Friction mode (Lateral Force Measurement)

The lateral twisting of the cantilever can be measured simultaneously with topography and often features that are not necessarily topographically distinct can show contrast in the lateral force signal due to different friction characteristics [126,127]. This suggests that friction imaging can have some degree of material or chemical sensitivity and will be discussed further below. Lateral force images often display atomic-scale stick-slip behavior with the periodicity of the atomic lattice of the sample. Typically, the average value of the frictional force while sliding at a given applied load is measured [128]. This is done by taking half of the difference between the average lateral force measured while sliding in each scanning direction, and so-called "friction loop". The applied load is changed and then the friction measured again, and so on. This produces a so-called friction *vs*. load curve [129]. Usually the tip is scanned repeatedly over a

limited area to restrict the measurement to one part of the sample at a time. If the sample is heterogeneous, a friction load measurement should be obtained on each distinct region [128].

## 4.1.2 SEM – Scanning Electron Microscopy

Scanning Electron Microscope (SEM) employs beam of electrons directed at the specimen to obtain an image [130]. SEM provides the information abut the surface or subsurface structure of the bulk specimen.

In 1935 Max Knoll obtained the first SEM image of silicon steel showing electron channeling contrast [131]. Further investigations on the physical principles of the SEM and interactions between beam and specimen were performed by Manfred von Ardenne (1937) [132,133]. He made a British patent [134] although he never manufactured a working device. The SEM technique was then developed by Professor Sir Charles Oatley (with assistance of his postgraduate student Gary Stewart) and in 1965 was produced under the commercial name "Stereoscan" by the Cambridge Instrument Company.

Construction of the SEM device extorts the existence of certain features, such as electron gun, condenser lenses and vacuum system with multiple detector devices. The diagram of the SEM device is schematically shown in Figure 4. 4 Electrons from a thermionic, Schottky or field emission cathode are accelerated through a voltage difference up to 50 keV. [135]. The smallest beam cross-section at the gun – the crossover – for the thermionic emission is with a diameter of  $10 - 50 \mu m$  and for Schottky guns it is of the order of 10 - 100 nm. Then the beam is demagnified by two or three stage electron lens system as shown in Figure 4. 4. The diameter of electron probe formed at the specimen surface is of order 1-10 nm. An electron probe current is then of the order of  $10^{-9} - 10^{-12}$  A. If the electron probe current increases to  $10^{-8}$  A then probe diameter also increases to  $0.1 \mu m$  [135].

When the working distance (between specimen and the final probe-forming lens) is relatively long (order of centimeters), various electrons and quanta which are emitted can be recorded by detectors inside the sample chamber (the magnetic field at the specimen is very low [135]). However, this mode of probe-forming lens operation increases the spherical and chromatic aberration and, hence, the smallest obtainable size of electron-probe.

Alternatively, the specimen may be placed within the lens, excitation can be increased and the aberrations are then smaller. In this case the backscattered and secondary electrons move along spiral trajectories and have to be detected outside the lens field [135]. Unlike the long –distance mode (which allows examining large samples), in-lens mode allow only small specimen examination which is a serious disadvantage. The electron-probe aperture (the semi-apex angle of the convergent cone of electron trajectories) is small. For hi-resolution measurements apertures of the order of ten miliradians are used. That size of aperture allows the depth of focus much larger than in light microscopy which is an important feature in nano and micro imaging. Hence, specimens with large



variations in depth can be sharply imaged, even at the lowest magnification rate of 20-50 times [135].

Figure 4. 4 Diagrammatic demonstration of scanning electron microscope main components. Based on Ref. [130].

In analogue version of SEM device a deflection coil system is placed in front of the final lens field. It scans the electron probe in a raster across the specimen in synchronism with the electron beam of a separate cathode-ray tube (CRT) [135]. The intensity of the CRT is modulated by one of the signals recorded to form an image. In modern instruments the same effect is achieved by digital control of the beam position on the sample and the resultant image is displayed on a computer screen [130]. The multiple signals (besides the secondary electrons and backscattered ones we have also X-rays and Auger electrons) outgoing from the specimen may be used to tune the contrast of the acquired image and a variety of electron-specimen interactions can be used to form an image and to furnish qualitative and quantitative information. The magnification is controlled simply by increasing or decreasing the scan-coil current. Beam deflection modes involve the constant mode described above and swinging the electron beam when the electron probe is at rest and the angle of incidence is raster-scanned (it is used for crystal analysis by forming an electron channeling pattern).

#### **Electron-specimen** interactions

One can say that elastic and inelastic scattering are the elementary atomic interaction processes in the SEM technique. The final signal used for formation of the image is mainly a result of the complete electron diffusion caused, quoting after [135], by the gradual loss of the electron energy and by lateral spreading resulting from multiple elastic large-angle scattering. The consequence of the gradual diminution of electron energy is the finite range of the electrons R (of the order of 10 nm - 10 µm). This range depends in succession on electron energy and target density, while the space (area in the sample's volume) of the corresponding interaction determines the information depth and the lateral extension of the information volume that contribute to each of the possible signals.



Figure 4. 5 Some of signals used In the SEM: secondary electrons (blue), backscattered electrons (red), Auger electrons and X-rays. The interaction volume is divided on areas corresponding to secondary electrons, backscattered electrons and X-rays detection. A mechanism of secondary electron creation is also depicted. Figure inspired by [130].

Figure 4. 5 shows the most important interaction processes and their information volumes. The energy spectrum of electrons emitted from the sample consists of secondary electrons (SE), backscattered electrons (BSE) and Auger electrons (AE). Besides that the energy spectrum emitted from the sample contains also the X radiation what is discussed further.

The region into which the electrons penetrate the specimen is known as the interaction volume. Various radiations are generated as a result of inelastic scattering, although as the primary electrons lose, the amount and type of the secondary radiations will alter [130]. The radiation generated within this volume can be detected only when it escapes from the specimen.

The secondary electrons are rather low energy ones with the most probable energy of 2-5 eV. These electrons are generated by inelastic collisions to such high energy levels that the excited electrons can overcome the work function before being decelerated to the Fermi level [135].

The broad spectrum of BSE between 50 eV and the primary electron energy E=eU is caused by deceleration of electrons that have suffered multiple energy losses and undergone multiple scattering through large angles. However, electrons will not be backscattered out of the specimen if they have penetrated more than a fraction of a micrometer. So the BSE signal originates from very shallow area of the samples' surface.

Creation of the Auger electron is an alternative to X-ray emission after ionization of an inner shell. The de-excitation energy released when an electron from an upper shell fills the vacancy in the ionized shell or is transferred to another atomic electron, which leaves the specimen as an Auger electron. A kinetic energy of an electron is determined by  $E_2$ - $E_1$  (electron energy on upper and lower shell respectively) decreased by the energy necessary to overcome the ionization energy and the work function. Otherwise, the de-excitation energy can be converted to an X-ray quantum energy  $hv=E_2$ - $E_1$ .

Similarly to the backscattered ones, secondary and Auger electrons are highly susceptible to elastic and inelastic scattering and can leave the specimen only from a very thin surface layer that is a few nanometers thick [135]. They are generated by the narrow beam of primary electrons entering this thin surface layer and simultaneously by backscattered electrons on their way back to the surface.

It has to be noted that although secondary electrons are generated both by the primary electrons entering the specimen and by the escaping backscattered electrons, the former are more numerous, and therefore the detected secondary electron signal originates mainly from a region which is little larger than the diameter of the incident beam [130]. SE having the smallest sampling volume are capable of giving a better spatial resolution than others discussed herein.

The numbers of secondary and backscattered electrons emitted from the specimen for each incident electron are known as the secondary electron coefficient ( $\delta$ ) and the backscattered electron coefficient ( $\eta$ ) respectively.

While  $\eta$  is strongly dependent on the atomic number of the specimen, the  $\delta$  coefficient depends mainly on accelerating voltage (maximum of yield is in the range of 1-5 keV). Coefficient  $\eta$  seems to be almost independent from voltage.

Secondary electrons, the most used in SEM technique, are detected by a scintillator-photomultiplier system (Everhart-Thornley detector). The backscattered electrons can be also detected by the same detector as the SE ones but it yields with worsening the quality of the obtained image. Hence, modern SEM devices are equipped with separate BSE detectors which can be one of three types: scintillator (e.g. Robinson detector), solid-state and through-the-lens detector. Specific construction of mentioned devices will not be discussed here for brevity and is thoroughly described in [130].

## 4.2 Photoemission methods

Photoemission spectroscopy (PES) methods are a wide group of methods exploiting the photoelectric effect discovered first by Hertz in 1887, later observed by Lenard [136] in 1900, and then theoretically revealed by Einstein in 1905. The idea of this effect is that photons can induce emission of the electron from a solid body when the energy is greater than the work function of the irritated material (is grater than the binding energy – BE – of the highest occupied energy level). The PES methods are based on illumination of examined sample with monochromatic photon beam with precisely defined energy and on spectrum registration of emitted photoelectrons. The first photoelectron spectrum was registered in 1954 by Siegbahn [137]. This event has set the beginning of the photoelectron spectroscopy method. One of the most important values in photoelectron spectroscopy is the energy of incident photons. It determines the depth of penetration in subsurface area, the atom ionization mechanism and mechanism of photoemission from investigated material.

Going further, in the range 3-50 eV and with simultaneous weak absorption of the radiation, it is possible to obtain photoionization of occupied electron states in the band gap, connected with photoemission from the subsurface area of the sample. This is the basis of Ultraviolet Photoemission Spectroscopy (UPS).

If the energy of incident light is in the range from 500-1500 eV, then the photoionization of deep (core) energetic levels occurs, which is also combined with photoelectron emission from the sample's subsurface area. It is caused by very strong absorption of radiation energy enclosed in the mentioned range. This gives the basis to Synchrotron Radiation Photoelectron Spectroscopy (SRPS) and X-Ray Photoelectron Spectroscopy (XPS). A separate technique is the Photoemission Yield Spectroscopy (PYS), where the examined sample is illuminated with monochromatic photon beam at very precisely defined energy, which does not exceed the value of 6.2 eV.

The disadvantage of these methods is that they require UHV (Ultra High Vacuum, that means the pressure is less than 10<sup>-7</sup>Pa) conditions. UHV is needed due to detected particle - an electron, and is required in order to avoid that contaminants from the residual gases in the vacuum chamber adsorb on the sample and affect the surface during the measurements.

However, the usage of electron has also many advantages, such as:

- Simplicity of detection
- Easiness of focusing the electron bundle
- Cleanness (after detection electron vanishes).

#### Theoretical background – the three step model of photoemission

With reference to Spicer's Model [138], electron's photoemission from the solid state is consequence of three following steps (shown schematically in Figure 4. 6), one after another:

- the optical excitation of the electron,

- transport of the excited electron through the sample to the sample's surface,



- emission of the excited electron to the vacuum.

Figure 4. 6 Schematic diagram of three stages of an electron photoemission process from a subsurface level of solid body. Figure based on Ref. [139].

The total probability of photoemission (P) is a product of probabilities of the three above-mentioned stages [140]. It can be described with the following formula:

 $P'(hv, E, x) \propto P_i(hv, E, x) \cdot P_t(E, x) \cdot B(E)$  (4.3) where:  $P_i(hv, E, x)$  – probability of photoionization (optical excitation) of the electron in subsurface area of the solid body;  $P_t(E, x)$  – probability of reaching the

electron in subsurface area of the solid body;  $P_t(E, x)$  – probability of reaching the surface by electronfrom the depth x, without the significant loss of energy; B(E)-probability of electron's escape to the vacuum.

#### **Step One - Optical excitation**

The ionization of an atom takes place when the photons beam is penetrating its subsurface area. During this process the absorption of photons proceeds. The probability of optical excitation of an electron at depth x from the surface of the sample, by the photon which has the energy hv, to a higher energy state in an interval from E to E + dE, may be described by formula:

$$P'(h\nu, E, x) \propto P(h\nu, E) \cdot P(h\nu, x)$$
(4.4)

where: P(hv, E) - probability of optical excitation of the electron by the photon with energy hv to a higher energy state in an interval from E to E + dE; P(hv, x) - probability, that photon with energy hv, reaches the depth x.

It has to be mentioned that the optical excitation depends additionally on matrix element M [141]. M defines the type of specified electron's transition from the base energy state to higher energy state in interval E to E+dE. It is known that both transitions are possible: the direct transition (when the momentum vector is maintained) and indirect transition (with change of momentum vector).

The probability of excitation also depends on the initial and final state's density in solid body, respectively  $n_i(E-h\nu)$  and  $n_f(E)$ . For the indirect transition the probability can be described as:

$$P(h\nu, E) \propto M^2 \cdot n_i (E - h\nu) \cdot n_f (E)$$
(4.5)

In case of semiconductor [12], the initial states are states occupied in valance band while the final states are unoccupied energy levels above the vacuum energy level  $E_{\text{vac}}$ . Assuming, that the density of final states  $n_f(E)$  is constant and do not depend on energy E of an optical excited electron, the equation (4. 5) is simplified to the formula (4. 6)

$$P(h\nu, E) \propto M^2 \cdot n_{\nu}(E - h\nu) \tag{4.6}$$

where:  $n_v(E-h\nu)$  – density of the occupied energy states in a valence band of a semiconductor.

The probability, that the incident photon reaches the depth x in the penetrated solid state body [142] can be approximated by formula:

$$P(h\nu, x) \propto e^{-\alpha(h\nu)x} = e^{\frac{-x}{l_{\alpha}(h\nu)}}$$
(4.7)

where:  $\alpha(h\nu)$ - a total coefficient of a light adsorption in a solid body defined as a relative rate of loss of light intensity along its track in a solid state body;  $l_{\alpha}(h\nu) -$ depth of penetration of the body by the incident light beam. For most of semiconductors it does not exceed the length of 15nm. The total photon absorption coefficient at the depth x is defined as:

$$\alpha(h\nu) = \alpha_{p}(h\nu) + \alpha_{c}(h\nu) \tag{4.8}$$

where:  $\alpha_p(h\nu)$  – an adsorption coefficient of an optical electron excitation to the energy E > Evac;  $\alpha_c(h\nu)$  – an adsorption coefficient of an optical electron excitation to the energy E < Evac.

Taking into account above mentioned considerations, the total probability of optical excitation can be described as:

$$P(h\nu, E, x) \propto M^2 \cdot n_{\nu} (E - h\nu) \cdot e^{-\alpha(h\nu)x}$$
(4.9)

Seeing that, the energy of incident photon beam determines the depth of out coming information.

#### **Step Two - Transport to the surface**

Due to scattering, an optically excited in subsurface layer electron, is losing energy during its way to surface. The scattering factors are:

- phonons
- valence band electrons
- subsurface crystal structure defects.

The most essential are the electron-electron and electron-phonon scattering. There are two kinds of energy intervals, and for each of them the different type of scattering is prevailing. For the energy of electrons E < 6eV the dominant type of scattering is electron-phonon one. The electron-phonon collisions cause either [10] a little loss of energy in spite of a big number of dissipations on photons, or a little number of dissipations on photons, what means that most of optical excited electrons are not dispersed. The probability of scattering is practically the distance between two subsequent collisions [143] and depends on number of phonons N:

$$l_{e-p} \propto (N-1) + N = 2N+1 \tag{4.10}$$

N - a number of phonons submitted to Bose-Einstein statistics described as:

$$N = \frac{1}{\exp(E_p / kT) - 1}$$
 (4. 11)

where:  $E_p \approx k \cdot \Theta$  is the phonon energy, and  $\Theta$  is the Debye temperature.

The average loss of energy caused by electron-phonon scattering may be expressed as:

$$\Delta E_p = E_p \cdot \frac{1}{2N+1} \tag{4.12}$$

In the room temperature the loss is weak and does not depend on electron's energy. In this case the distance between two sequence collisions is in the range  $3\div30 \text{ nm}$  [139].

For the electron's energy E >> 6eV the dominant type of scattering is electron-valance band electron scattering. Then there is a possibility of simultaneous emission of primary electrons and secondary, once or multiple scattered electrons. It gives an additional input to the photoemission spectrum and cause change of electron's energetic distribution N(E) as shown in Figure 4. 7.



Figure 4. 7 A general scheme of the electronic states in semiconductor, the density of states including core levels and valance band states, and corresponding photoelectron spectrum on the strong background of scattered electrons. Figure based on [144].

The total probability that photon excited in a solid at the depth of x having an energy E reaches the semiconductor's surface without a significant loss of its energy may be approximated by formula:

$$P_t(E,x) \propto e^{-\frac{x}{L(E)}}$$
(4.13)

where: L(E) is the effective escape depth of photoelectrons, which is dependent, by energy E of optically excited electron, on energy hv of incident photon beam. The conclusion is, that L(E) depends on depth of solid penetration in relation to mean free path  $\lambda_e(E)$  of an electron. The dependence of attenuation (and indirectly the dependence of mean free path) on electron's energy was primarily proposed by Seah and Dench (shown at Figure 4. 8).



Figure 4. 8 The energy dependence of attenuation length  $\lambda_a$  of electrons in solids [145].

In semiconductors  $\lambda_e(E)$  is about 1nm what means that only electrons from depth 3  $\lambda_e(E)$  may reach the semiconductor's surface without a significant loss of energy. Statistically, it can be assumed that 99% of electrons outgoing from the sample without significant energy loss comes from mentioned area of depth  $3\lambda_e$ . That is why 3  $\lambda_e(E)$  is called the information depth.

#### **Step Three - Electron's escape**

If the optically excited electron reaches the sample's surface, without a significant loss of its initial energy, it can escape from the solid body. The probability of passing through the potential barrier (the vacuum level) may be described by formula:

$$B(E) = \begin{cases} 1 & dla \ E > \varphi \\ 0 & dla \ E < \varphi \end{cases}$$
(4. 14)

where:  $\varphi$  is work function of the electron in solid state body.

#### Photoemission intensity

The fundamentals of quantitative analysis in photoelectron spectroscopy is the expression complying the considerations from formulas (4. 9),(4. 13) and (4. 14). describing the number of photo-emitted, optically excited to higher energy state electrons  $dN_e(hv, E, x)$  doming from the layer with thickness dx on the depth x and the incident photon beam with energy hv and intensity  $N_0(hv)$  [12]:

$$dN_{e}(h\nu, E, x) \propto [1 - R(h\nu)] \cdot N_{0}(h\nu) \cdot M^{2} \cdot n_{\nu}(E - h\nu) \cdot e^{-[\alpha(h\nu) + \frac{1}{L(E)}]x} dEdx$$
(4.15)

where: R(hv) is the coefficient of reflection of light from a solid's surface [146].

The more general model of three-step photoemission from the semiconductor, involving the band model was proposed by Berglund and Spicer[147]. Later it was developed by Kane [148] and Ballantyne [149]. This model also takes into account the angular effects during the light incidence and photoelectron emission [139].

#### 4.2.1 XPS – X-Ray Photoemission Spectroscopy

X-Ray Photoemission Spectroscopy is one of the major techniques for studying solids, surfaces and thin films. Because the method provides information about sample's atomic composition and the chemical states of the observed atoms it is also known as ESCA (Electron Spectroscopy for Chemical Analysis). In this technique, photon with energy hv after penetration of surface is absorbed by an electron occupying the core level with a binding energy  $E_1$  (see Figure 4. 9). Then, this electron gains enough energy to be emitted into the vacuum with energy:  $E_{kin} = hv - E_B - (E_{vac} - E_{Fermi})$ . So the electron energy distribution of emitted photoelectrons should correspond to the energy distribution of electron states in the examined solid surface [150]. The emitted photoelectrons are collected by the energy electron analyzer generating the XPS spectrum. Of course the whole process is being complicated by the probability that photons might be absorbed by electron states. Additionally, processes like plasmon excitation, electron excitation and so on also complicate the spectra and will be described further in this subsection.



Figure 4. 9 Scheme of the X-Ray photoelectron creation as the base for the XPS method (based on [150]).

The binding energies in described method are measured with respect to Fermi level of the electron spectrometer (detector) [150]. This level should be placed at the point where photoelectron emission decays to zero. In that point Xray photoelectron spectrum can be directly recorded as the function of binding energy and stays fixed independently of the measured sample.

Each element has a characteristic binding energy of the peaks. One can determine the composition of the material surface using the areas of the peaks taken with appropriate sensitivity factors. The chemical state of the emitting atom can slightly alter the shape of each peak and binding energy. For this reason, chemical bonding information can be obtained with XPS as well. Using XPS all elements can be detected with the exception of hydrogen and helium, to which the method is insensitive. Normally, in the outmost 10nm of thin films surface XPS can identify all elements (present at concentration >0.1 atomic %) except H and He [151].

#### X-Ray satellites and "ghosts"

When one uses the non-monochromatized Al or Mg lamp some satellite peaks may appear. They are placed on the low binding energy side of the photoemission peaks, however there is one dominant peak  $K\alpha_{3,4}$  which appears at approximately 10 eV lower binding energy and has an intensity of about 8% of the corresponding peak.

Another artifact is the existence of the "ghost lines" which sometimes appear in the photoemission spectra while using the twin anode sources. It may happen that using the Al anode the electrons emitted from the filament can hit the Mg anode causing the emission and then a low intensity radiation from Mg anode can appear in the higher intense Al X-Rays. It sometimes causes that some dominant peaks appear with very low intensity shifted by the difference in photon energy between Al and Mg radiation [150].

#### **Plasmon excitation**

Photoelectron emitted from the solid can excite also the collective oscillation in the conduction electron gas as a coherent superposition of the electron-hole pairs. Two kinds of plasmon excitations can be distinguished, the bulk and the surface ones. The energy of the surface plasmons is about 0.7 lower (by factor) than the bulk plasmons. The photoelectrons causing this phenomenon are loosing some energy (a multiple of plasmon energy) and appear on the high energy side of the corresponding main peak. For the free electron gas, the bulk and surface plasmon energies are given correspondingly by [150]:

$$\omega_p(bulk) = \sqrt{\frac{ne^2}{\varepsilon_0 m}} \quad ; \quad \omega_p(surface) = \sqrt{\frac{ne^2}{2\varepsilon_0 m}}$$
 (4.16)

#### Satellites in core level spectra

Other features observed at the high energy side (in a binding energy scale) of the main peak are satellite peaks. They can be divided into shake-up satellites (the excitation is into a bound state) and shake-off ones (excitation into the continuum). The former occur when outgoing photoelectron interacts with a valence electron exciting it to the higher energy level. Then the core electron is observed as having reduced energy and so giving satellite structure [152].

The shake-offs occurs when the valence electron is completely emitted from the sample, but such features are rarely observed. They manifest themselves rather as a broadening of the main peak or as the contribution to the inelastic background.

In order to obtain the desired information from the XPS spectra it is necessary to convert the peak intensities to atomic concentrations. It seems to be quite simple if one considers a homogenous sample but it may occur rather complicated while the examined material is a thin film which is essentially thinner than the information depth of the technique [152]. There is a significant number of sample and spectrometer related factors which have to be considered while quantifying the XPS spectra. The most common sample factors are:

- ➤ the cross-section for emission (related with the probability of the electron emission due to incident radiation (see beginning of Section 4.2) which is in succession dependent on [152]:
  - o investigated element,
  - o ejected electrons' orbital,
  - o energy of incident radiation,
- the escape depth of an electron (depends mostly upon electrons' kinetic energy and the sample's nature – for details see beginning of Section 4.2 above).

The most significant spectrometer related factors are:

Ι

- the transmission function of the spectrometer (can be treated as a proportion between the number of transmitted through spectrometer electrons to their kinetic energy),
- ➤ the efficiency of the detector,
- > roaming magnetic field affecting the low energy electron transmission [152].

## Quantification:

For the simplest description the intensity of XPS peak can be given by formula:

$$= J\rho\sigma K\lambda \tag{4.17}$$

where: J- photon flux,  $\rho$ - concentration of atom or ion in examined solid,  $\sigma$ - the cross section for photoelectron production, K- element covering all instrumental factors,  $\lambda$ - electron attenuation length.

Mostly, the intensity is taken as the integrated area under the corresponding peak after the background subtraction. For the background determination the s-shaped Shirley function or Tougaard function are used most often. For direct quantification, the so called sensitivity factor F is determined. F factor is in fact the combined factor consisting of previously mentioned in formula (4. 17) factors  $\sigma$ , K and  $\lambda$  with some additional features like characteristic loss features [152]. Taking this into account and with assumption that X-Ray flux remains stable and constant one can determine the atomic percentage of the concerned elements with formula:

$$[A] atomic \% = \{ (I_A / F_A) / \sum (I / F) \} \cdot 100\%$$
(4.18)

where  $I_A$  is the intensity of XPS line corrected for the background. Of course, the above statement remains true if the specimen is homogenous within the volume sampled by XPS. The corresponding molar ratio between two elements in homogenous solids is then given by relation [59]:

$$\frac{X_A}{X_B} = F_{AB} \frac{I_A / ASF_A}{I_B / ASF_B}$$
(4.19)

where  $F_{AB} = \sqrt{(\frac{\overline{a_B}}{a_A})^3}$  is the matrix factor;  $a_i$  (i=A or B dependently on specimen) is

the atom size and  $\ensuremath{\mathrm{ASF}}_i$  is the corresponding to the specimen atomic sensitivity factor, determined as:

$$[ASF] = \sigma(E_{kin}) \cdot T(E_{kin}) \cdot \lambda(E_{kin})$$
(4. 20)

while  $\lambda(E_{kin})$  is the inelastic mean free path,  $T(E_{kin})$  is the spectrometer transmission function and  $\sigma(E_{kin})$  is the photoionization cross-section. The atomic sensitivity factors are usually given as the ready-to-use values ascertained for a given class of spectrometers [59,153].

#### Analytical possibilities

As one can see, XPS is a powerful method for surface investigation. Due to fact that photoemitted electrons carry the combined chemical and electronic information, the wide application of XPS include the following:

- analysis and identification of surface elemental composition on the basis of binding energy  $E_B$  of recorded peaks with use of reference spectra [153],
- identification of the chemical state of surface atoms due to core level chemical shift (CLCS), which is recognized as the difference in binding energy of free atom and that one in chemical bonding [59],
- . identification of surface bindings on the basis of spectral line shape and chemical shift of binding energy  $\Delta E_{B,}$
- depth profiling by the angle-resolved measurements (ARXPS Angle Resolved XPS, basing on changes of the electron take-off angle,



Figure 4. 10 Ideological band diagram of the semiconductor subsurface area. Letter "b" in brackets corresponds to bulk values while the letter "s" is for surface ones.  $L_D$  is the Debay's length of attenuation and  $E_B$  is the binding energy.

The XPS method allows also on determination of the electronic properties of the examined solid surface. Because of relatively low sensitivity of the method in the range of energies corresponding to valence band, XPS is focused on investigations of  $E_B$  changes of chosen spectral lines. This allows on the determination of the relative change of Fermi level of the examined surface. The theoretical background of the procedure was proposed by Grant [154,155] and is illustrated on the band diagram in Figure 4. 10.

The determination of electronic parameters bases on measured energies of core levels. Of course it is not so easy since one knows the exact  $E_V$  position for examined material. Because  $E_{CL}$ - $E_V$  on the surface is equal to the same difference in bulk, making use of diagram in Figure 4. 10 one can determine the interface Fermi level (the relative surface Fermi level position  $E_F(s) - E_V(s)$ ) and band bending  $(qV_{BB})$  as:

$$E_F(s) - E_V(s) = E_{CL}(s) - (E_{CL} - E_V)$$
(4. 21)

$$qV_{BB} = (E_{CL} - E_V) + (E_F(b) - E_V(b)) - E_{CL}(s)$$
(4.22)

where:  $E_F(b) - E_V(b)$  can be treated analogous to  $E_F(s) - E_V(s)$  as a relative Fermi level position in the bulk.

#### **XPS** Equipment

XPS equipment consists of two crucial elements: the source of radiation and the electron energy analyzer. The system requires the ultra-high vacuum conditions as a working environment. For XPS, Al Ka (1486.6eV) or Mg Ka (1253.6eV) are often the photon energies of choice (usually working in twin-anode device). Other X-ray lines can also be chosen such as Ti Ka (2040eV). The monochromatized systems are used for the best energy resolution.

For the photoelectron detection the so called hemispherical analyzers (HSA) are used most often. The typical HSA construction is based on three fundamental components: the multi-mode lens system, electron energy separator and the electron detector. The idea of XPS setup is shown in Figure 4. 11. Electrons emitted from the sample are focused by the multi-mode lens system, then separated in the hemispherical separator and detected by the channeltron electron multiplier.

The multi-element two-stage transfer lenses are designed to yield ultimate transmission and well-defined optical properties. The lens system may be operated in several different modes for angular and spatially resolved studies to adapt the analyzer to different tasks. The most commonly used modes are: Large Area (for survey spectra) and High Magnification (for exact analysis of small surface). All lens modes can be set electronically. Due to lens aberrations rays entering the lens far away of the lens axis at larger angles could find a path to the analyzer entrance. Hence the lens columns are often equipped with Iris aperture. With an Iris aperture these rays can be eliminated. The Iris can be used as well to continuously adjust the angular acceptance of the analyzer. Using this Iris the angular resolution can be continuously adjusted between  $\pm 1^{\circ}$  and  $\pm 9^{\circ}$  while keeping the acceptance area on the sample constant.

The separator leads the photoelectrons focused by the lens system to the detector using the electrostatic potentials applied to the separators' hemispheres. Then the electrons move on the circular trajectories. Only the electrons with the kinetic energy determined with current electric potential will reach the detector; the rest will be filtered by hitting the hemispheres.



Figure 4. 11 Ideological scheme of XPS instrumentation configuration.

The resolution of a HSA with radius R and slit s is given as:

$$\Delta E \approx \frac{s}{2R} \cdot E_{kin} \tag{4.23}$$

However, for the maintaining of the resolution for different kinetic energy of photoelectrons, collected electrons are electrostatically retarded in a lens column to a fixed energy called pass energy  $E_{pass}$ . Usually for survey scans the  $E_{pass}$  is abut 80 eV while for spectral windows 10-20 eV.

## 4.2.2 UPS – Ultraviolet Photoemission Spectroscopy

The Ultraviolet Photoemission Spectroscopy (UPS) is traditionally the complimentary method to the XPS. While XPS provides the information about core levels (due to its high-energy radiation source) the UPS with its range of irritating energy from 20 to 50 eV gives the information about the energy distribution of the electrons from the valance band and from the states below the Fermi level.

In UPS, the source of photons is a differentially pumped inert gas discharge lamp (usually Helium lamp – see Figure 4. 12); for detection of photoelectron the same analyzer as in case of XPS is used). It produces discrete low energy resonance lines (e.g. He I 21.2 eV and He II 40.8 eV) [156] with an inherent width of a few electronovolts. This technique is widely used in study of electron band structure of metals, alloys and semiconductors and of absorption phenomena [157]. The electron energy distribution is well described by equations at the beginning of Subsection 4.2".



Figure 4. 12 SPECS Helium lamp model 10/35.

In photoemission measurements the Fermi level of two conductors in contact must line up with each other, hence the Fermi level of the sample and that of the metal of the sample holder become the same. The exact position of the Fermi edge is crucial for UPS. For accurate determination of  $E_F$  one should replace the sample by a metal to obtain a spectrum of photoelectrons versus  $V_S$  with a sharp step at the Fermi level of the metal, which must be the same as that on the sample to be measured. Thus the natural origin of energies in photoelectron spectroscopy is the common Fermi level.

The energies can also be referred to the vacuum level (a point outside the sample but close to it). For  $\hbar \omega_L$  equal to the photoemission threshold energy *I* the photoelectrons exit with zero energy with respect to the vacuum level. If the photoelectrons arise from the bulk valence band (i.e. if no occupied surface states exist) *I* represent the energy of the vacuum level with respect to the top (the highest energy state) of the valance band  $E_V$ . The vacuum level can also be referred to the Fermi level which is then named work function and is represented by  $\varphi$ . The electron affinity  $\chi$  is defined as the energy of the vacuum level referred to the bottom of the conduction band  $E_C$ .



Figure 4. 13 EDC diagram with assigned most important parameters:  $V_{S0}$ -the energy cut-off;  $V_{SV}$ -the energy onset;  $V_{SF}$ -Fermi Level position.

Figure 4. 13 shows a schematic photoemission spectrum of semiconductor versus the potential  $V_{s}$ . The potential  $V_{s0}$  at which photoemission disappears corresponds to the energy of the vacuum level since no electrons can be emitted

having an energy in the vacuum lower than the vacuum level. The top of the valance band corresponds to  $V_{\rm SV}$  while the Fermi level corresponds to  $V_{\rm SF}$ .

#### Analytical possibilities

As it was mentioned above, the low photon energy in UPS means that deep core electron levels cannot be excited and only photoelectrons emitted from the valence band or shallow core levels are accessible.

The UPS method enables determination of the electronic parameters of the subsurface area by means of detailed analysis of recorded electron energy distribution curves (EDC). Having the Fermi energy position  $E_F$  (obtained as the center of Fermi edge slopes) acquired from the reference metal sample (within this Thesis Ag) it is possible to determine the electronic parameters of the subsurface area in the examined sample such as ionization energy ( $\Phi$ ), work function ( $\varphi$ ) and electron affinity ( $\chi$ ). These electronic parameters are interrelated by the following formulas [158]:

$$\Phi = \hbar \omega_L - e(V_{SV} - V_{S0}) \tag{4.24}$$

$$\varphi = \hbar \omega_L - e(V_{SF} - V_{S0}) \tag{4.25}$$

$$\chi = \Phi - E_g \tag{4.26}$$

where: Eg is the energy gap of the material,  $\hbar\omega_L$ -the energy of incident photons, eV<sub>S0</sub>-the energy cut-off, eV<sub>SV</sub>-the energy onset (corresponding to the top of the valence band or for organic materials the onset of the HOMO peak) and eV<sub>SF</sub>- the Fermi Level position. The low kinetic energy cut-off (eV<sub>S0</sub>) is determined by the energy-axis intersection with a straight line fitted to the slope of the spectra (between 30% and 70% of its height). The energy onset is determined by fitting the straight line (till background level) to the slope of the HOMO peak [159]. Additionally, the variation of energy cut-off allows to determine  $\Delta\varphi$  and the change in valence band onset (that is to say the HOMO onset) indicates  $e\Delta V_s$ directly from the UPS spectra as suggested by Gopel [160]. Then,  $\Delta \chi$  is a difference between  $e\Delta V_s$  and  $\Delta \varphi$ .

UPS can also be used to identify molecular species on surfaces by identifying characteristic electron energies associated with the bonds of the molecules. In UPS method, the same analyzer as in XPS can be used.

Another variation of the UPS method, the Angle Resolved UPS (ARUPS) can be used to determine the band structure of the material under investigation.

#### 4.2.3 PYS – Photoemission Yield Spectroscopy

The Photoemission Yield Spectroscopy (PYS) was primarily developed by Sebenne's group in Paris [161]. In contrast to classic photoemission methods like XPS, UPS or SRPS (Synchrotron Radiation Photoemission Spectroscopy), this method is based on measuring the total number of photoelectrons per incident photon at a given light energy hv, so to examine the sample one needs only the source of monochromatic light (with the range 200-300 nm – usually Deuterium or Xenon discharge lamp) and the detector of emitted electrons (electron

multiplier setup with emitter follower). The bases of the method are shown on Figure 4. 14. Together with increasing photon energy hv, the photoelectrons are excited from the deeper parts of the band gap below the Fermi level and from the upper part of the valance band [141].



Figure 4. 14 Simplified band model of PYS. Figure based on [162].

#### Physics of the method

According to theoretical considerations at the beginning of Section 4.2 the photoemission yield Y(hv) can be described by the following formula:

$$Y(h\nu) = \frac{N_e(h\nu)}{N_f(h\nu)} \propto \int_{E_{\nu}}^{h\nu} M^2 \cdot n_{\nu} (E - h\nu) \frac{L(E)}{1 + \alpha(h\nu)L(E)} dE$$
(4.27)

where: M- the transition matrix element;  $N_e(hv)$ - number of photoelectrons;  $N_f(hv)$ -number of incident photons. The above expression does not take into account the presence of occupied surface states on the semiconductor's surface and combined with it band bending  $eV_s$  near the sample's surface.

Under the assumption, that the matrix elements are constant and L(E) does not depend on primary electron's energy then the formula (4. 27) may be simplified to [163]:

$$Y(h\nu) \propto L(E) \int_{E_{\nu}}^{h\nu} n_{\nu} (E - E_{\nu}) dE$$
 (4.28)

where:  $n_v(E-E_v)$ - the effective density of occupied energetic states in valance band, without complying the existence of occupied surface states and band bending;  $E_v$ - the threshold energy of photoemission, corresponding to the highest occupied energetic level in semiconductor (with above assumptions it is the top of the valance band or the HOMO level in organics). If there is a real surface of semiconductor considered, it is necessary to consider the occupied surface states localized in band gap of semiconductor just below the Fermi level  $E_F$  and in upper part of the valance band [12]. The Photoemission Yield Spectroscopy from the occupied bulk energetic states of a valance band with taking into account the band bending near the sample's surface can be described as:

$$Y_{vs} \propto \int_{E_{vs}}^{hv} \int_{0}^{\infty} n_{vs} [E - E_{v}] \cdot e^{-[\alpha(hv) + \frac{1}{L(E)}]x} dx dE$$
(4. 29)

where:  $E_{vs}$ - the threshold energy of photoemission (in another words the energy of ionization  $\Phi$ );  $n_{vs}(E-E_v)$  – the effective density of occupied space energetic states in valance band of semiconductor, which is dependent on the distance between the top of the valance band  $E_v$  and the vacuum level  $E_{vac}$  [141].

When the potential barrier  $V_x$  in the subsurface space charge area has the character of Schottky's barrier, it can be expressed as:

$$V_x = V_s \left[ 1 - \left(\frac{1}{L_D}\right)^2 \right],$$
(4.30)

where  $L_D$  is Debey's length of screening, (in another words the thickness of subsurface bulk charge layer, then the expression (4. 29) can be assumed as:

$$Y_{vs}(hv) \propto \int_{E_{vs}}^{hv} \int_{0}^{\infty} n_{vs} \{E - E_{vs} - eV_s [1 - (\frac{x}{L_D})^2]\}^n dx dE.$$
 (4.31)

The n parameter describes the type of scattering and model of assumed optical transition. Under the assumption, that the effective depth of escape L(E) of optically excited electron is much smaller than the Debey's length, i.e.  $L(E)/L_D <<1$ , the formula (4. 31) may be simplified to the following:

$$Y_{vs}(hv) \propto \int_{E_{vs}}^{nv} n_{vs} (E - E_{vs})^n dE.$$
 (4.32)

It is important to remember, that the above assumption is true only for nondegenerated semiconductors.

In 1967 E.O. Kane [164] developed a simplified model of photoemission. This model takes into account possible transitions: direct and indirect, with possibility of elastic scattering in the space charge area and on the surface of the examined body. Kane also gave an dependencies describing Photoemission Yield Spectroscopy in the upper part of valance band for various mechanisms of optical excitation and emission of an electron from the body. Together with subsurface effects the dependence can be introduced [148] as:

$$Y(h\nu) = A (h\nu - E_{\nu})^{\frac{m}{2}},$$
(4.33)

where: A - a constant; m – an integer number, in range from 2 to 7 (dependent on photoemission mechanism, shown in Table 4. 1).

The development of Kane's model was made by Ballantyne [149]. He took into account the loss of optically excited electron's energy caused by electronphonon dissipations. The corrected dependence of the photoemission yield spectroscopy, for all types of transitions, can be approximated with formula:

$$Y(h\nu) \propto \frac{\alpha(h\nu)(h\nu - E_{\nu})^3}{(h\nu)^2 E_s(h\nu)}$$
(4.34)

where:  $E_s(hv)$  is the energy connected to dissipations on phonons.

<b>Electron states</b>	Transition / Scattering	Y(hv)
	Indirect transition:	
	- without scattering	$(h\nu - E_{\nu})^{5/2}$
Space states	- with scattering	$(h\nu - E_{\nu})^{5/2}$
	Direct transitions:	
	- without scattering	$(hv - E_v)^1$
	- with scattering	$(h\nu - E_{\nu})^2$
	<u>Surface scattering:</u>	
Surface states	- "rough surface"	$(hv - E_v)^{5/2}$
	- perfect surface	$\left(h\nu-E_{\nu}\right)^{3/2}$

 Table 4. 1 Dependence describing the Kane's model parameters[12].

The disadvantage of both of mentioned models is the lack of influence of band bending on excitation and transport of the electron to the surface. The photoemission yield from the occupied, localized in band gap below the Fermi level  $E_F$ , electron states can be described as:

$$Y_{ss}(h\nu) \propto \int_{E_F}^{n\nu} n_{ss} (E - E_F) dE$$
(4.35)

where:  $n_{ss}(E-E_F)$  is the effective density of filled surface states.

It is important, that the effective density of occupied surface states [12] does not depend on the level and type of semiconductor's doping, and it can be easily described with Fermi-Dirac statistics. However, the above considerations can be applied only in case of the high density of surface states in the semiconductor's band gap, which causes the pinning of Fermi level  $E_F$  near the center of band gap at the semiconductor's surface.

#### Analytical possibilities

The conclusion coming from the foregoing analysis is that the Total Photoemission Yield Spectroscopy contains the contribution [141] of all occupied (bulk and surface), localized below the Fermi level, states in the range of  $E_F$  to hv- $E_F$ . Together with an increase of photons energy from hv to hv+d(hv), the photoemission yield increases about dY(hv). The reason is that all occupied states localized in range of energy hv to hv+d(hv) below the  $E_{vac}$  level take also part in the photoemission.

It is possible to separate in every one photoemission yield spectrum the low-energy and high-energy part. For the low- energy one are responsible the photoelectrons which are emitted from occupied surface states in the band gap below the Fermi level  $E_F$ . For the high-energy branch are responsible the photoelectrons emitted also from filled surface states and from the upper part of semiconductor's valance band [163].

The Photoemission Yield Spectroscopy allows for determination of a number of energetic parameters of semiconductor's surface like work function, ionization



energy, electron affinity or surface band bending. Some of them are presented already in Figure 2. 9 in Chapter 2 and in Figure 4. 15.

Figure 4.15 Scheme of energetic band model of semiconductor with its suitable shape of photoemission yield spectrum for three chosen cases [165]: a) strongly doped semiconductor p-type – surface potential barrier  $V_s>0$ ; b) weakly doped semiconductor p-type- the flat bands; c) strongly doped semiconductor n-type- surface potential barrier  $V_s<0$ 

By fitting the low-energy part of Y(hv) spectrum to Fermi-Dirac's function it is possible to determine the work function value  $\varphi$  as the energetic distance between Fermi level  $E_F$  and vacuum level  $E_{vac}$ . In the other cases the value of work function can be assumed as threshold of low-energy part from experimental photoemission spectrum. By fitting the high-energy part of spectrum to Kane's or Ballantyne's [149] function, one can determine the ionization energy  $\Phi$  as a difference between the top of the valance band  $E_v$  and the vacuum level  $E_{vac}$ .

The separation of contribution from the occupied surface and bulk electron states may be done due to specific properties of subsurface space charge area [12]. For different type and doping level, the relative position of occupied surface and bulk energetic states varies [163] as it is shown in Figure 4. 15. One can there observe suitable shapes of the photoemission yield spectrum Y(hv) for different band structures

The next feature of PYS is the of band bending determination. If the band gap  $E_g$  and the difference between Fermi level and the top of the valance band in the bulk (*E<sub>F</sub>*-*E<sub>v</sub>*)<sub>b</sub> is known, the band bending  $eV_s$  is then:

$$eV_s = (\Phi - \varphi) - (E_F - E_y)_b$$
 (4.36)

and the surface electron affinity  $X_s$  of the semiconductor:

$$X_s = \Phi - E_g \tag{4.37}$$

Apart from earlier considerations it has to be mentioned that the photoemission yield derivative with respect to the photon energy dY(hv)/d(hv) corresponds to the effective density of all occupied energetic states in the semiconductor [12]. The effective density N(E) is a sum of the value proportional to the density of the occupied bulk electron states  $N_{vs}(E, l_e)$  and the value proportional to filled surface electron states  $N_{ss}(E)$  localized in the band gap below the Fermi level  $E_F$ . The value  $N_{vs}(E, l_e)$  is defined by the sort of optical transition and the effective depth of escape of optically excited electron from the solid body:

$$\frac{dY(h\nu)}{d(h\nu)} \approx N(E) \propto N_{vs}(E, l_e) + N_{ss}(E)$$
(4.38)

The  $N_{ss}(E)$  value depends only on the type of electron transition. The measured exemplary PYS data with plotted effective density line of all occupied states is shown in Figure 4. 16.



Figure 4. 16 The experimental curves illustrating a way of finding the effective density of all occupied energetic states in semiconductor [166]

Summing up, it is worth to emphasize that PYS method offers resolution of 0.03 eV (which is of the order of kT), which is not available for other methods. It has, however some drawbacks, too. The main disadvantage of this method is that information comes from the depth of approximately three monolayers of examined material.
## 4.3 Auxiliary method - X-Ray Diffraction

The history of the technique starts at the beginning of the 20<sup>th</sup> century. In 1912 two researchers, Friedrich and Knipping, under the supervision of Max von Laue, first observed the diffraction of the X-rays at the University of Munich. Later, in 1918 Paul Ewald built a theory allowing for quantitative explanation of the basic physical interactions affiliated with X-ray diffraction techniques.

X-Ray Diffraction (XRD) is a versatile, non-destructive method for measuring characteristic X-ray diffraction angles and intensities from crystallites irritated by a monochromatic X-ray beam. Electrons in the components atoms of crystallites are coerced to vibrate by the incident radiation resulting in sharp, coherent scatters of the X-ray. The diffraction pattern from a crystalline specimen is specific for the crystal form of the particular crystalline body. Therefore the XRD method can be applied for qualitative and quantitative evaluation of crystal forms [167].

For the non-crystalline materials the interference scatters of X-rays are rather poor and result in broad, diffuse maxima in the patterns. Thus, for such substances the utility of this method seems to be limited.

In crystalline materials the molecular and atomic species are ordered in a three-dimensional array [167] (lattice – the 2-D visualization is provided in Figure 4. 17). The smallest lattice is designated as the unit cell in crystallography. Three arbitrary lattice points define a plane in the crystal. Planes separated by a certain interplanar spacing from each other form a family of planes which is called a crystalline plane and is usually indexed by using Miller indices (hkl). A detailed theoretical basis for crystallography can be found in [168] and will not be discussed here for brevity. Essential is, that the occurrence of X-ray diffraction and the direction of the beam diffracted by a crystallographic plane obey the Bragg's law. According to this, X-ray diffraction occurs only when the scattered beams follow the dependence:

$$2d_{kl}\sin\Theta = n\lambda \tag{4.39}$$

where:  $d_{hkl}$  denotes the interplanar spacing;  $\Theta$  is the angle of diffraction; n is integral multiple, the order of the reflection;  $\lambda$  is the wavelength of the incident radiation (see Figure 4. 17).



Figure 4. 17 Schematic visualization of some of the possible crystalline (lattice) planes (marked in blue, green and red colour) and Bragg's diffraction of the incident radiation (with wavelength  $\lambda$ ). d – the interplanar spacing.

The angle of diffraction  $(2\Theta)$  due to a plane (hkl) is determined by the intrinsic interplanar spacing, hence by the lattice constants and the wavelength of the incident X-beam.

The intensity of X-ray diffraction, among others, depends on [167]:

- structure factors (depend upon the position of atoms in the unit cell),
- degree of crystallinity (dependent on experimental temperature and physical properties),
- density of the specimen,
- temperature reactor,
- volume of the specimen,
- absorption characteristics (factor depending on component atoms of the sample),
- > intensity and wavelength of the irritating radiation,
- polarization factor (depending on monochromatizing method) ,
- > Lorenz factor (depends on geometrical reactor of the apparatus).

The intensity ratio is defined by the ratio of the peak intensity of a particular diffraction angle to the intensity of the standard peak, which is usually selected as the strongest maximum in the diffraction pattern.

The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. Identification of the phase is important because the material properties are highly dependent on structure.



Figure 4. 18 The ideological scheme of the X-Ray Diffraction technique in reflection mode.

The XRD technique applied in this Thesis aimed the copper phthalocyanine ultra-thin film phase identification. It has to be denoted that the thin film diffraction refers not to a specific technique but rather a collection of XRD techniques used to characterize thin film samples grown on substrates. There are some special considerations for using XRD to characterize thin films [169]. Primarily, the reflection geometry (shown in Figure 4. 18) is used for these measurements as the substrates are generally too thick for transmission technique. Secondarily, high angular resolution is required because the peaks from semiconductor materials are sharp due to very low defect densities in the material. Consequently, multiple bounce crystal monochromators are used to provide a highly collimated x-ray beam for these measurements [169]. The scanning angle for XRD measurements taken from organic materials usually ranges from  $5^{\circ}$  to  $40^{\circ}$  [167].

Thin film diffraction is also used for characterization of the crystallographic structure and preferred orientation of substrate-anchored thin films. Basic XRD measurements made on thin film samples include [169]:

- **Precise lattice constants** measurements derived from  $2\Theta \Theta$  scans, which provide information about lattice mismatch between the film and the substrate and therefore is indicative of strain and stress;
- Rocking curve measurements made by scanning a  $\Theta$  scan at a fixed 2  $\Theta$  angle, the width of which is inversely proportional to the dislocation density in the film and is therefore used as a gauge of the quality of the film;
- **Superlattice** measurements in multilayered heteroepitaxial structures, which manifest as satellite peaks surrounding the main diffraction peak from the film. Film thickness and quality can be deduced from the data;
- Glancing incidence x-ray reflectivity measurements, which can determine the thickness, roughness, and density of the film. This technique does not require crystalline film and works even with amorphous materials;
- **Texture** measurements.

### 4.4 Experimental setup

The work presented within this Thesis has been done in three different laboratories in Europe: Institute of Physics, Silesian University of Technology, Gliwice, Poland; Institute of Physical and Theoretical Chemistry, Tubingen University, Germany; and in Department of Physics, University of L'Aquila, Italy. Herein, the technological details of the exploited experimental setups are described.

### 4.4.1 Gliwice

The experimental vacuum system at the Institute of Physics, Silesian University of Technology, Gliwice, Poland is constructed as multipurpose, technological and analytical multi-chamber setup. Main constituents are the sample preparation chamber, technological chamber for evaporating organic materials and two analytical chambers. All chambers are connected with vacuum transport system allowing for in-situ investigations (Figure 4. 19).



Figure 4. 19 Scheme of the multi-chamber UHV experimental setup in the Institute of Physics, Silesian University of Technology.

The first one is equipped with highly efficient annealing system for sample bakeout and the TPD method based on Stanford Mass Spectrometer SRS RGA100. The technological chamber allows obtaining ultra-thin layers of organic materials. It is furnished with home made source (based on Knudsen cell – Figure 4. 20) evaporating organic materials from resistively heated quartz crucible. The source has temperature feedback with the power supply for better process control.



Figure 4. 20 Evaporation source for organic materials assembled in the Institute of Physics, Silesian University of Technology.

For monitoring the evaporation process one uses the quartz crystal microbalance with standard gold 6 MHz sensor and the Inficon XTC-3M controller. The device allows for determination of the deposited layer thickness with resolution of order of 0.1 Å. Working pressure during evaporation is of order of  $10^{-6}$  Pa while the base pressure is of order of  $10^{-7}$  Pa.

For surface chemical and electronic analysis setup is equipped with photoemission methods (XPS, PYS, SPV-Surface Photovoltage. XPS method uses SPECS PHOIBOS 100 hemispherical analyzer equipped with HSA 3500 power supply unit and SPECS XR-50 twin-anode X-ray source. Base pressure is of order of 10<sup>-7</sup> Pa. The second analytical chamber is furnished with PYS and SPV methods. Base pressure is of the same order as in case of XPS. The general scheme of PYS spectrometer is shown in Figure 4. 21.



Figure 4. 21 Scheme of photoemission yield spectrometer attached to analytical chamber.

The UV-range light used to illuminate the sample is emitted from deuterium source  $D_2E$  (power 40 W). The light has to be monochromatic, therefore the computer-controlled monochromator of SPM-2 type is used. Next, the monochromatic light is focused by optical system. The main element of the PYS analyzer is the channel electron multiplier (KPE-/5/-371) working in "three-leg" mode. A channeltron works as arrangement of joint dynodes; the electron falls through the head, hits the inner side of the multiplier causing "avalanche" of electrons which results in amplification of the signal. The amplification strongly depends on the applied voltage. In implemented configuration voltage is in the range from 1 kV up to 2,5 kV.

The base pressure in the whole setup is sustained by the ion-sorption pumping systems and additionally, for technological needs (sample loading and evaporation) by the turbomolecular-screw pump setup.

Atomic Force Microscopy measurements in Gliwice are performed with use of Park Systems XE-70 AFM. Scanning is performed by means of a flexure-based closed-loop XY-scanner; resonance frequency of the scanner is 1.7 kHz.

### 4.4.2 Tubingen

The experimental system in the Institute of Physical and Theoretical Chemistry, Tubingen University, Germany, is constructed as the UHV multi-chamber system operating at a base pressure of 10<sup>-8</sup> Pa. Photography of the setup is shown Figure 4. 22.



Figure 4. 22 The UHV system in the Institute of Physical and Theoretical Chemistry, Tubingen University, Germany.

Main components of the system are as follows: sample preparation chamber, technological chamber (for evaporation of the organic materials) and analytical chamber. Vacuum in all chambers is continuously sustained by the turbomolecular- oil rotary pump two stage pumping system. Rotary pumps have oil traps attached to prevent the system from oil vapors contamination.

Technological chamber is furnished with home-made evaporation source. The evaporated material is resistively heated (by tungsten coil) in ceramic. The source is fitted with a shutter preventing from unwanted evaporation and type K thermocouple. The growth of the evaporated layer is carried out with quartz crystal microbalance Inficon XTC 2 equipped with standard 6 MHz water cooled sensor. Inficon controller allows for determination of the thickness with the resolution of order of 0.1 Å.

The analytical chamber is furnished with XPS and UPS methods. Both of mentioned methods use common HSA analyzer setup SPECS PHOIBOS 150 with multi-channel detector and HAS 3500 power supply. In case of XPS the sample is irritated with a monochromatized X-ray source SPECS XR-50 with SPECS FOCUS-500 mirror monochromator. For UPS measurements the sample is irritated with SPECS UV Source - UVS 10/35 a differentially pumped, high performance helium lamp powered with PS-UVS20-A power supply. The manipulator in the chamber is precisely controlled in three dimensions XYZ and has an adjustable  $\Theta$  angle allowing on ARXPS and ARUPS measurements.

### 4.4.3 L'Aquila

The investigations performed on the experimental system in the Dept of Physics in L'Aquila involved the XPS, XRD, SEM and AFM measurements. The XPS experiments on the CuPc films have been performed in a separate ultra high vacuum chamber (8·10<sup>-8</sup> Pa) equipped with a monochromatized Al  $K_{\alpha}$  X-ray source, and an PHI hemispherical analyzer Omicron 125. XRD (X-Ray Diffraction) measurements were carried out, with a Siemens D5000 diffractometer operated in Bragg-Brentano mode. General view of UHV setup in Department of Physics, University of L'Aquila, Italy is presented in Figure 4. 23.

For the morphology investigations the laboratory is equipped with a SEM Zeiss-LEO 1530 working at 5 keV beam energy. The SEM pictures taken within this work were done in SE mode.



Figure 4. 23 Photo of UHV experimental system in the Department of Physics, University of L'Aquila, Italy.

The laboratory is also furnished with an ex-situ AFM imaging system equipped with a Digital Instruments (Nanoscope IV controller) using commercial silicon tips (frequency range 310-370 kHz); scanning is performed by means of a Veeco Nanoman closed loop XY head.

### 4.5 Procedure of sample preparation and investigation

Two types of Si (111) (covered with native oxide) substrates (BOSCH GmbH) were used in this experiment: the n-type (Phosphorus-doped with a carrier concentration  $7 \cdot 10^{13}$  cm<sup>-3</sup>) and p-type (Boron-doped with carrier concentration  $1 \cdot 10^{15}$  cm<sup>-3</sup>). Two independent types of substrates sets – the "native" and the "RCA" ones (each set contained n- and p-type of substrate) – were used in the experiments.. The "native" substrates were prepared by degreasing with acetone in ultrasonic bath, then rinsing with deionized (DI) water and then drying with pure air (Microcare BigBlast<sup>TM</sup> Canned Air). They were investigated by means of XPS, ARXPS, UPS, PYS and AFM methods.

To obtain the RCA substrates the Si native substrates were treated according to the RCA wet cleaning procedure [170,171,172]. The original procedure was developed by Kern and Puotinen at Radio Corporation of America (RCA) in 1965 [173,174]. It is based on sequential oxidative desorption and complexing with the  $H_2O_2$ -NH<sub>4</sub>OH-H<sub>2</sub>O and the  $H_2O_2$ -HCl-H<sub>2</sub>O solutions. The process takes place at 70±5° C. After that, the samples need to be rinsed with DI water and then dried with pure air. The grown oxide remains stable for approximately 5 min. so the prepared substrate should be placed in vacuum conditions within this time.

The  $SiO_2$  grown on the course of RCA was investigated in the same manner (except PYS) and in the same vacuum system as the starting p- and n-Si native substrates, hence, taking into account the recognized repeatability of the RCA treatment Si/RCA-SiO<sub>2</sub> substrates can be regarded as the reference samples.

The CuPc ultra-thin films were evaporated thermally from the home-made source based on RADAC-II effusion cell. The source was equipped with resistively heated quartz (Gliwice) or ceramic (Tuebingen) crucible and with thermocouple giving the temperature feedback to the power supply. Before the evaporation the CuPc powder (99.9% of CuPc delivered by Sensient Imaging Technologies GmbH, Syntec Division) was kept for 24 h in the 10<sup>-9</sup> mbar vacuum and then purified by baking for two hours in 130°C and afterwards for another two hours in 230°C. This procedure ensured no water vapors presence in the phthalocyanine as well as the devoid of most of the phthalocyanine's contaminants.

The stepwise-manner evaporation took place at the temperature of 390-410°C. The CuPc deposition speed was less than 0.1 Å/s. The film thickness was controlled with a quartz crystal microbalance device and verified with XPS by monitoring the attenuation of the intensity of the substrate Si2p peaks due to the organic overlayer after each step of evaporation [175,176].

The CuPc ultra-thin films were examined with XPS and UPS in three time steps.: i) "in situ" soon after the film growth (with no exposure to air); ii) after 12 hour exposure to air; iii) –only XPS– after a long term (interesting for technological applications) one-year exposure to air. The air exposure was performed by keeping the samples in a dry box in a clean room at room temperature.

Due to the technological and organization reasons there is lack of longterm UPS measurements as well as some other data which will be enumerated further.

### **Photoemission investigations**

Three XPS systems were used within the presented work. Regardless of the setup used the spectra were recorded in the fixed analyzer transmission (FAT) operating mode. The pass energy for survey spectra was set to 80 eV while for the spectral windows the energy was set to 10 eV. The binding energy of recorded spectra was calibrated to Ag3d 5/2 (368.2 eV) and Au4f 7/2 (84.0 eV) [177]. The Au or Ag foil was kept on the same sample holder close to the examined sample. The full width at half maximum (FWHM) of the Au 4f 7/2 peak was 0.74 eV and this is a measure of the instrument energy resolution. (for Ag 3d 5/2 peak the FWHM was 0.78 eV). In order to check the uniformity of the samples several areas were investigated and the most representative are shown.

For the quantitative and qualitative analysis of XPS data the peaks recorded in spectral windows were decomposed by means of sum of convoluted Gaussian and Lorentzian functions. The Gaussian component arises from instrumental broadening (and statistical variations of the surface properties) while the Lorentzian originates from the limited lifetime of the core-level hole [59]. For the analysis the CASA XPS software was used. The software allows to control of all fitting parameters including Gaussian-to-Lorentzian ratio, peak-topeak area ratio, FWHM and position.

The fitting was performed with the minimum number of peaks due to expected components regime. Nevertheless, the number of introduced components had to assure the acceptable fit of experimental data which was controlled by the residual curve. The Full Width at Half Maximum parameters were allowed to vary in a narrow margin ( $\pm 10\%$ ) to account possible changes in the examined surface. Fitting was made with constant chemical shift preferably than with fixed binding energy position of peaks. The spin-orbit splitting (if needed i.e. for peaks like Si2p) was fixed according to bibliographical data.

The semi-quantitative analysis of the surface was based on integrated areas of the components calculated after the Shirley-function type background subtraction. The relative concentrations of the components were calculated using formulas given in section 4.2.1 and taking into account atomic and relative sensitivity factors enclosed in Table 4. 2.

The UPS measurements were taken by means of the differentially pumped He I UV source at work pressure  $2 \cdot 10^{-5}$  mbar. The spectra were taken by the same hemispherical electron energy analyzer PHOIBOS 150 as in the case of XPS measurements. To ensure that electrons with the lowest kinetic energies can be analyzed, an additional bias voltage of 3 to 10 V was usually applied to the sample. Energy step for UPS examination was set to 0.05 eV. For UPS data analysis the He I satellite peaks (at 1.87 eV and 2.52 eV of binding energy and intensities 1.8% and 0.5% of the main spectra intensity respectively) were numerically subtracted from the spectra. The HOMO peaks were decomposed by means of CASA XPS software. The background subtraction of the HOMO region was done with use of Tougaard function. The fitting was made with the minimum number of peaks regime assuring the acceptable fitting.

Element	Spectra line	ASF	RSF
С	1s	0.205	1.00
Si	2p	0.170	0.86
0	1s	0.630	2.76
Ν	1s	0.380	1.74
Cu	2p	4.300	22.81
Ag	$3d_{5/2}$	2.25	17.71
Au	$4\mathbf{f}_{7/2}$	1.900	19.44
Mo	$3d_{5/2}$	1.2	9.68

Table 4.	2 The	Atomic	sensitivity	factors	(ASF)	and	Relative	Sensitivity	Factors	for
selected	elemen	its used f	for qualitat	ive analy	ysis of	expe	rimental	data within	this wor	k.

PYS measurements were taken with the excitation wavelength range 200-300 nm with 1-nm resolution. Dwelling time for one wavelength was set to 100 s. Geometry of the setup ensured that almost no electrons but coming from the sample were detected. To avoid unwanted excitation by other light sources all viewports (except one necessary to introduce the monochromated light) of the vacuum chamber were kept covered with alumina covers and the whole laboratory was darkened. The vacuum ion pump and ionization vacuum gauge were turned off during taking the spectra to avoid undesirable ionization. The vacuum was sustained by the adjoining preparation chamber at a level of 10<sup>-8</sup> mbar.

The taken PYS spectra were smoothed after the numerical background subtraction by means of PYS-OPTIMIZER software. The computer program used in the analysis enabled also Kane's function fitting of the high-energy part of the PYS spectra. Due to technical reasons all PYS data for CuPc samples were recorded ex-situ.

#### **Imaging investigations**

The AFM, SEM and XRD investigations were taken ex-situ due to technological limitations of the available experimental setups. The working parameters were described in previous Section 4.4.

The AFM quantitative analysis was made by means of WSxM and Gwyddion free-of-charge software. For all taken images the polynomial flattening was applied. The programs used in the analysis enabled determination of surface topography parameters including roughness (represented by RMS value), grain size analysis or the surface cross-sections. The SEM and XRD measurements were done only for native samples due to problems with accessibility of laboratory in L'Aquila.

### Uncertainties

The variety of used investigation methods leads to significant number of uncertainty parameters which should be taken under consideration while describing the results. For better clarity, all uncertainty values (if they are not indicated in text), are given here. Table 4. 3 below presents the values of uncertainties assumed within this Thesis for different experimental methods and for different parameters determined in Chapter 5.

Parameter	Method	Uncertainty value
FWHM, (eV)	UPS	0.05
Work function $\varphi$ , (eV)	UPS	0.05
Ionization energy $\Phi$ , (eV)	UPS	0.07
$E_{F}$ - $E_{V}$ ( $E_{F}$ - $E_{HOMO}$ ), (eV)	UPS	0.07
Oxide thickness, (nm)	XPS / linear regression	0.15
Work function $\varphi$ , (eV)	PYS	0.03
Ionization energy $\Phi$ , (eV)	PYS	0.03

Table 4. 3 The uncertainties assumed within this Thesis



# **RESULTS AND DISCUSSION**

This chapter presents the main results of experiments conducted within this Dissertation. It starts with the detailed substrate description including the careful determination of surface morphology, surface chemistry and electronic properties of its subsurface region. All these investigations are aimed to precisely define the "starting point" for the evaporated 16-nm ultra-thin CuPc layers.

The second part is devoted to CuPc layers which are the main concern of this Thesis. The performed experiments are focused on the characterization of the surface morphology, surface chemistry, electronic properties of CuPc layers and their interface with the substrate, and the initial stages of formation of this interface.

The third part is concentrated on the interaction of grown thin CuPc layers with ambient air and the stability issues upon long-time air exposure.

For clarity, the results are presented along with the discussion.

## 5.1 Si (111) substrate

In order to investigate the CuPc ultra-thin layers, first the properties of the Si substrates (two sets: native and RCA-treated, both n- and p-type) should be carefully revealed and determined. Although there is an ample literature on this topic, some data of interest in this Dissertation is missing. Moreover, in order to facilitate reproducibility, there is a necessity of using the same experimental systems for studying Si as those used for CuPc investigations. Hence, this Section describes such studies on surface morphology and chemistry as well as the electronic properties of Si substrates.

### 5.1.1 Surface morphology

Determination of substrate topology and morphology has been done by means of imaging AFM method. The studies mainly aimed to determine the surface roughness in order to check if the surface structure could have an impact on the final CuPc layer morphology.

The roughness of the native n- and p-Si substrates prior the CuPc deposition was determined with AFM method. In both cases the two substrates were almost atomically flat with RMS (Root Mean Square), roughness equal to 0.15 nm (determined with the uncertainty of 0.01 nm). Figure 5. 1 depicts the AFM image over  $1x1 \ \mu\text{m}^2$  area taken for n-type native Si(111) substrate with corresponding topography histogram. As one can see, the substrate surface exhibits uniform and slight periodic-like structure.



Figure 5. 1 Native p-type Si(111) 1x1 µm AFM image with corresponding topography histogram. The images for n-type Si are identical with the same roughness.

Although, the RCA-cleaned substrates were not investigated this time, this treatment has been shown to give extremely flat Si(111) surfaces with RMS roughness of 0.08 nm [115]. This was already discussed in Section 2.3.6 Altogether, both substrate pairs can be treated as almost atomically flat and not varying significantly from each other.

### 5.1.2 Surface chemistry

In order to determine the substrate chemistry, both pairs of Si(111) substrates were examined with XPS and ARXPS methods. Survey spectra of all substrates (Figure 5. 2) exhibit identical spectral features including silicon (Si2p, Si2s), O1s and (weak) C1s XPS peaks of similar relative intensities. The signals originate from the substrate (Si), the native oxide layer (Si, O), and carbonaceous contaminants (C). The peak protruding at about 980 eV B.E. is the oxygen (O KLL – identified by CASA<sup>TM</sup> XPS library) Auger line and is not taken under consideration within this Thesis.



Figure 5. 2 The comparison of survey XPS spectra recorded from : native SiO<sub>2</sub>/silicon (left panel) and RCA-treated SiO<sub>2</sub>/silicon substrates.

To determine the surface bonding configuration between silicon and oxygen, the shape of the Si2p peak region was carefully analyzed. Two components were resolved (with spin-orbit splitting of 0.60 eV) and according to their energy position they were assigned to elemental silicon (Si<sup>0</sup>) and silicon dioxide (Si<sup>4+</sup>). The widths at half maximum (FWHM) were 0.65 eV (0.76 eV for RCA) for Si<sup>0</sup> and 1.09 eV (1.27 eV for RCA) for Si<sup>4+</sup>. The oxide layer is composed only of SiO<sub>2</sub>; other silicon suboxides are not visible. The chemistry of native oxide on all substrates was basically identical regardless of their treatment and doping. The only effect detected in fittings was a slight broadening of Si components after the RCA procedure.

Figure 5. 3 depicts the Si2p XPS peak for the native and RCA-treated substrates of n- and p-type. The spectra clearly show the contribution from the Si substrate (the doublet at lower binding energy) and from the oxide layer (shifted by about 4 eV on the higher binding energy side). The slight broadening mentioned above is also visible.

The oxide thickness was determined using ARXPS technique. This method is based on acquiring spectra at various sample-analyzer relative angles. Under the assumption (reasonable in present case) that an overlayer is uniform, its thickness can be calculated with the formula derived from the Beer-Lambert equation [178]:

$$d = \lambda_A \cos\theta \ln \left[ 1 + \frac{R}{R^{\infty}} \right]$$
 (5. 1)

where:  $\lambda_A$  is the attenuation length of electrons emitted from a substrate in an overlayer;  $\theta$  is the electron take-off angle; R is the intensity ratio between overlayer and substrate peaks;  $R^{\infty}$  is the intensity ratio between peaks emitted from a thick overlayer (>3  $\lambda_A$ ) and a thick substrate.



Figure 5. 3 Si2p XPS peak for n-type Si samples: native (upper part) and RCA-treated (lower part). According to energy shift of the high binding energy component, the oxide layer is purely  $SiO_2$  (other silicon suboxides are not visible).

According to this formula, the slope of the linear plot of  $\ln(1 + R/R^{\infty})$  versus  $1/\cos\theta$  is the overlayer thickness divided by the attenuation length. The data is shown in Figure 5. 4. Assuming in (5. 1) that  $\lambda_{SiO_2}(E_{Si}) = 3.5 nm$  [179,180], the SiO<sub>2</sub> thickness is 0.8 nm for native Si substrates and 1.3 nm for RCA-treated ones, irrespective of doping type.

It is thus the oxide thickness not its chemical composition that is considerably modified after the RCA clean. This treatment is known to result in the stable and contamination-free  $SiO_2$  layer with thickness similar to obtained in the present studies.

The thickness of carbon contamination layer ( $d_c$ ) may be estimated from the intensity ratio between C1s peak and Si<sup>0</sup> component of Si2p peak [180].



Figure 5. 4 Graphs summarizing the depth profiling analysis for the native p-Si (left panel) and the RCA treated n-Si (right panel) substrates via angle dependent core level XPS.

The intensities need to be corrected for the energy response function of an instrument and atomic sensitivity factors [181]. For a thin oxide layer between silicon and outermost carbonaceous layer, the ratio is:

$$\frac{I_C}{I_{Si}} = \frac{I_C^{\infty}}{I_{Si}^{\infty}} \frac{1 - \exp\left[-d_C / \lambda_C(E_C) \cos\theta\right]}{\exp\left[-d_{SiO_2} / \lambda_{SiO_2}(E_{Si}) \cos\theta\right] \exp\left[-d_C / \lambda_C(E_{Si}) \cos\theta\right]}$$
(5.2)

Assuming that  $\lambda_{\rm C}(E_{\rm C}) \approx \lambda_{\rm C}(E_{\rm Si})$ , that is the attenuation lengths in carbonaceous layer for photoelectrons with kinetic energy  $E_{\rm C}=1200$  eV and  $E_{\rm Si}=1386$  eV are nearly the identical, the formula (5. 2) can be transformed to:

$$d_{C} = \lambda_{C}(E_{C})\cos\theta \ln \left[ \frac{I_{C}}{I_{Si}} \exp\left(\frac{-d_{oxide}}{\lambda_{SiO_{2}}(E_{Si})\cos\theta}\right) \right]$$
(5.3)

which is the total thickness of carbon contamination. The attenuation lengths are  $\lambda_{sio_2}(E_{si}) = 3.5 \text{ nm}$  and  $\lambda_c(E_c) = 3.3 \text{ nm}$ , while the ratio  $\frac{I_c^{\infty}}{I_{si}^{\infty}}$  equals 1.082 as theoretically calculated by Seah and Spencer [180]. The results of the calculations are given in Table 5. 1.

Comparing the results, it can be observed that the thickness of carbon layer on the RCA-treated substrates is lower than on the native ones. The small difference detected on n- and p-type samples after the RCA clean is in fact within the regression uncertainty of about 0.1 nm.

The analysis of surface contamination species was focused on the decomposition of carbon C1s peaks. Figure 5. 5 depicts such decomposition for the p-Si substrate covered with the native oxide (upper panel) and the one after RCA treatment (lower panel).

The carbon contamination components (C-H, C-OH and COOH) were resolved according to Beamson and Briggs. [182]. The major component is due to C-H species. The existence of the COOH component might be doubtful and an alternative explanation might relate it to carbonate ( $CO_3$ ).

	The total thickness of carbon contamination (nm)			
Sample type	n	р		
native	0.47	0.47		
RCA	0.33	0.37		

Table 5. 1 The thickness (in nm) of carbon contamination layer on Si substrates.



Figure 5. 5 C1s XPS peak for p-type Si samples: native (upper part) and RCA-treated (lower part).

However, auxiliary temperature programmed desorption measurements confirmed the existence of low-concentration species with such a mass/charge ratio. Similar organic carbon species have been reported earlier by Matsuo et al. on n-, n<sup>+</sup>-, p- and p<sup>+</sup>-Si (100) [183,184]. Apart from a slight energy shift of 0.1 eV, being actually within the accuracy of the measurement method, there are no considerable variations between the native and RCA-treated p-Si substrates. The same conclusion holds in the case of n-Si ones. The contributions of individual carbon species to total C1s signal are summarized in Table 5. 2.

There are hardly any differences between the data sets. It can be suspected that RCA clean applied on n-type Si substrate removes eagerly the C-H and C-OH species from the silicon surface while the minute quantities of COOH are barely affected (however the differences are within an experimental uncertainty). For the p-type Si samples, only the C-H contribution changes by 3 % while the C-OH and COOH do not change after the RCA treatment. It is highly probable that the carbonaceous layer is reduced as a whole, however the composition is scarcely affected. Hence the relative concentrations of surface species might clarify the situation.

Table 5. 2 The percentage contribution of main components of carbon contamination in C1s XPS peak for Si substrates. The calculations were made for normal take-off angle (values given as % of contribution to the total C1s peak area).

	С-Н		C-OH		СООН	
Sample type	n	р	n	р	n	р
native	78%	77%	15%	15%	6%	7%
RCA	77%	74%	13%	15%	7%	7%

The C/Si, C/O and O/Si relative concentrations calculated from the total areas under C1s, Si2p and O1s peaks/core levels for all substrates are summarized in Table 5. 3.

Table 5. 3 The O/Si, C/O and C/Si relative concentrations for native and RCA-treated nand p-type substrates. The relative concentrations were reduced with atomic sensitivity factors. The calculations were made for normal take-off angle.

	[0/	[O/Si] [C/O]		/0] [C/Si]		'Si]
Sample type	n	р	n	р	n	р
native	0.39	0.36	0.44	0.48	0.17	0.17
RCA	0.39	0.35	0.37	0.46	0.14	0.16

One can see that the reduction in carbon species (by about 20% in case of C/O) occurs more likely on n-type. Since the attenuation lengths of C1s and Si2p electrons in SiO<sub>2</sub> are similar, being calculated as 3.4 nm and 3.5 nm, respectively, from TPP-2M formula [185], it is expected that the relative ratios do not depend on the oxide thickness. Furthermore, the carbon surface concentration, i.e. the number of carbon atoms per square meter, can be calculated using the C/Si ratio according to formula [180]:

$$Dc (in \ C \ atoms \ per \ m^2) = 6.9 \times 1019 Ic / Isi$$
 (5.4)

The results are summarized in Table 5. 4. The concentration is lower for RCAtreated substrates in comparison to the native ones but the removal of adventitious carbon is more pronounced on n-Si.

Moreover, auxiliary ARXPS measurements of C/Si ratio (data shown in Figure 5. 6) indicated that carbon, in case of RCA samples, is placed rather on the surface while on the native ones its distribution is more uniform throughout the whole oxide overlayer. Although the effect is relatively small for p-type RCA, it can be well observed for n-type RCA substrate.

	The total surface concentration of carbon species D <sub>C</sub> (atoms of C/m <sup>2</sup> ) x10 <sup>19</sup>			
Sample type	n	р		
native	1.72	1.72		
RCA	1.37	1.58		

Table 5. 4 Surface concentration of carbon species,  $d_c$ , for native and RCA-treated Si substrates.

For the normal take-off angle the C/Si ratio seems to be almost uniform for all types of examined substrates. However, once the take-off angle is changed, the differences appear. It is strongly visible especially in case of n-Si sample after RCA treatment, which exhibits strong surface sensitivity of C/Si ratio. Contrary to the RCA samples, for native ones the C/Si ratio is increasing slower. Both types exhibit a slight plateau in the take-off angle range between 80 to 70 deg. This could point that the distribution of the carbonaceous contaminants in the oxide layer is more or less of the same gradient, but in the case of RCA treatment is moved towards the sample surface.



Figure 5. 6 C/Si ratios as a function of take-off angle (ARXPS) for n- and p-type native and RCA-treated silicon substrates. The semi-transparent lines (red for RCA and green for native samples) are only for eye-catching of the changes.

Summarizing the substrates surface chemistry investigations, after the RCA treatment there is no significant change in carbon content on p-type Si substrates, while the solid decrease is observed on the n-type Si ones. Nevertheless, regardless of doping, the procedure results in the uniform and stoichiometric (like in case of native substrates but thicker) oxide layer on Si.

There are not many reports describing comparisons relevant to the present work so that the data cannot be referred readily to the previous investigations. There are some papers on differences induced by the RCA clean [186], mainly in aspect of Si surface topology. The authors claim that the RCA clean introduces the atomic scale topological modifications which change the Si surface properties.

The oxide layer thickness of 1.3 nm reported in the RCA-related papers is confirmed in the present Thesis. It is considerably more than the 0.8-nm layer on the native Si substrates. The relative concentrations of the surface contaminants indicate that the RCA technology drives carbon species from the Si to the surface of the oxide layer. In addition, besides smaller thickness of carbonaceous layer, the RCA-treated Si substrates exhibit lower concentration of carbon species. It is worth emphasizing that, if necessary, the RCA treatment can be followed by annealing in ultra high vacuum conditions or by etching e.g. in  $NH_4F$  in order to extract carbon contamination. Interestingly, despite the expectations, the stronger difference in surface chemistry is observed between n- and p-Si substrates rather than between native and RCA-treated ones.

The chemistry of oxide layer is  $SiO_2$  and it is not altered upon the RCA clean. On the other hand, slight modifications of carbon content were detected (RCA treatment partially removes the minor carbon contamination (like C-OH) from n-type substrates). They can be ascribed to greater susceptibility of p-Si to carbon species with OH groups or greater reactivity of p-Si. This seems to be in agreement with former studies described in [II], where it was found that the main divergence between n- and p-type native samples was the slight difference in carbon contamination. One can only suspect that despite the dielectric oxide layer the small interaction between p-type substrate and negative OH groups can occur in case of dissociation of above mentioned carbon components. Alike observations on organic carbon contamination were reported earlier [183,184] and were assigned to the formation of weak electric dipole involving oxygen atom.

### 5.1.3 Electronic properties

In previous section it was shown that the AFM and XPS indicate that the two (nand p-type) native Si substrates are identical as far as their surface morphology, oxide and carbon layer thickness and composition are concerned. After the RCA treatment a slight divergence in surface chemistry between n- and p-type substrate appeared. In this section, the electronic properties of Si substrates are investigated. It has to be remembered that within used experimental methods the Si/SiO<sub>2</sub> structure is examined. So the photoemission signal comes as well from both: the Si and SiO<sub>2</sub> as from the silicon/oxide interface.

The electronic properties investigations made by means of XPS were focused mainly on determination of the energy position of the substrate peaks. Main effort was done to check if there were any differences between the investigated substrates for most characteristic Si2p peak. In fact, the only difference between the native substrates with respect to XPS method is the rigid energy shift of p-Si spectra by about 0.25-0.30 eV towards lower binding energies. The shift is related to opposite doping type which then results in different position of bulk Fermi level. The shift in the case of RCA substrates is below the accuracy of the method. The lack of distinct shift in case of RCA samples may be related with thicker oxide layer on the RCA-treated Si substrates. Figure 5. 7 shows the Si2p XPS peak for both types of native substrates with well visible energy shift.

More appropriate determination of the electronic properties of the used Si substrates was carried out with the UPS technique. Both sets of samples were investigated: the native and RCA-treated ones.



Figure 5. 7 The Si2p peaks of n- and p-type native substrates. One can observe the evident energy shift caused by doping.

As it was mentioned in Section 4.2.2, for semiconductors, the work function  $(\phi)$  and ionization energy  $(\Phi)$  are described by the following formulas [187]:

$$\varphi = \hbar \omega - (E_F - E_0)$$
  

$$\Phi = \hbar \omega - (E_V - E_0)$$
(5.5)

where:  $\hbar\omega$  is the energy of incident photons (here of He I radiation – 21.22 eV), E<sub>0</sub> is the energy cut-off of the UPS spectra. For inorganic semiconductors, E<sub>V</sub> is the linear extrapolation of the low binding energy edge of the valence band spectrum corresponding to the top of the valence band. For organic ones, it is the energy onset of the HOMO (highest occupied molecular orbital) peak (then denoted as E<sub>HOMO</sub> what will be discussed further). The E<sub>F</sub> is the surface Fermi level position obtained as the center of Fermi edge slope of the reference Ag sample. UPS spectra taken for bare (not covered by CuPc) both sets of substrates used within this work are depicted in Figure 5. 8. The significant difference in the intensities of high-energy cutoff area between native and RCA samples is correlated with apparatus parameters (e.g. different sensitivity if the applied detector). However the difference does not impact the accuracy and quality of determination of the electronic parameters of examined samples.

After determination of  $E_F$  and  $E_0$ , the formulas (5. 5) allowed to determine of the absolute values of the work function  $\varphi$  as equal 3.70 eV for n-Si/native SiO<sub>2</sub> substrates and 3.75 eV for p-Si/native SiO<sub>2</sub> one.

According to Seah and Dench diagram [188] the value of mean free path for photons of the energy of He I (21.22 eV) is close to the oxide layer thickness present on substrates. Hence the measured with UPS work function may be interpreted as value of  $\varphi$  of the silicon on the interface between Si(111) and native SiO<sub>2</sub>. For the same reason there is a considerable problem with precise detection of the position of the top of the valence band  $E_V$  of the silicon. On the UPS valence band spectrum only the position of  $E_V$  in SiO<sub>2</sub> was clearly determined and reached value 5.15 eV for native oxide on n-Si and 4.80 eV for p-Si with respect to  $E_F$ . Moreover, employing value of SiO<sub>2</sub> band gap width  $E_g$ = 8.00 eV [189] it is possible to find the position of the bottom of the conduction band Ec with respect to Fermi level  $E_F$  as 2.85 eV for n-Si and 3.20 eV for p-Si.



Figure 5. 8 UPS spectra taken for bare substrates. (a) - native substrates; (b) - RCA-treated substrates.

The same procedure was applied in the case of the reference RCA-treated substrates. The absolute values of the work function  $\varphi$  are equal 4.00 eV for n-Si/RCA-SiO<sub>2</sub> substrates and 4.05 eV for p-Si/RCA-SiO<sub>2</sub> one. Consequently, the position of E<sub>V</sub> in SiO<sub>2</sub> is 5.54 eV for RCA oxide on n-Si and 5.30 eV on p-Si with respect to E<sub>F</sub>. Once again, employing known value of SiO<sub>2</sub> band gap, the position of the bottom of the conduction band E<sub>C</sub> is 2.46 eV for n-Si and 2.70 eV for p-Si.

Since it was not possible to determine electronic parameters of Si(111) subsurface layer from UPS data, the PYS technique was used. Because of the large dynamic range of acquired signal (the Yield spectrum Y(E) can vary within eight orders of magnitude) and high energy resolution, this method is excellent for determination of energetic parameters of the semiconductor space charge layer such like work function and ionization energy, as it was shown in Section 4.2.3. Figure 5. 9 depicts photoemission yield spectra taken for space charge layer of n- and p-Si native substrates (a and b respectively). The low energy threshold of the spectra indicates absolute value of work function equal to 4.44 eV for n-type silicon and 4.82 eV for p-type one. Here, the uncertainty of work function determination is within 0.03 eV.

Additionally, fitting the high energy part of PYS spectrum with Kane's function allows to find the absolute value of Si(111) ionization energy [190]. In the case of n-Si, the photoemission yield curve fits perfectly to power 3/2 law, giving value of  $\Phi$  equal 5.20 eV. For p-Si the best fitting was for power 5/2 law and it pointed ionization energy equal to 5.06 eV. Indices of Kane's law correspond in both cases to indirect electron transition with scattering taking place in case of "real" semiconductor surfaces (e.g. among others when surface defects exists) [190]. Since PYS method is probing only the energies up to 6.2 eV below  $E_{vac}$  it is not possible to detect the high-energy part of spectra corresponding to the ionization energy of the SiO<sub>2</sub> which could confirm UPS data.

The PYS method allows also determining the effective density of the occupied electronic states in the upper part of the valance band and in the band gap below the Fermi level. The diagram showing the distribution of the effective density of states for n- and p-type native substrates is presented in Figure 5. 10. One can see the considerable difference in the N(E) PYS spectra between n- and p-type substrate for the energies below 5.4 eV. In contrary for the energies above

5.4 eV the density of states distribution seems to be more or less the same. It points that the effective density of states is the most differentiated (due to the type of substrate conductivity) is in the band gap region. The PYS data were recorded only for the native samples due to technical difficulties with RCA technology in Gliwice. Further, for the RCA samples the bibliographic data have to be used.



Figure 5. 9 PYS spectra recorded from n-type native Si (111) substrate (a) and p-type one (b).

In order to determine Si(111) bulk position of  $E_V$  and  $E_C$  with respect to  $E_F$ , that is the differences  $\Phi$ - $\phi$  and  $E_g$ - $(\Phi$ - $\phi)$ , the calculation were implemented, applying well known formulas [191]:

$$E_F - E_C = kT \ln\left(\frac{n}{N_C}\right)$$
; for n-type semiconductor (5.6)

$$E_V - E_F = kT \ln\left(\frac{p}{N_V}\right)$$
; for p-type semiconductor (5.7)

where: k is the Boltzmann's constant; T is absolute temperature; n and p are the electron and hole concentrations respectively;  $N_C$  and  $N_V$  are effective densities of states in conduction band and valence band equal to  $2.8 \cdot 10^{25}$  m<sup>-3</sup> and  $1.0 \cdot 10^{25}$  m<sup>-3</sup> respectively [191].

For electron concentration of n-type (n=7·10<sup>13</sup> cm<sup>-3</sup>) silicon,  $E_F$ - $E_C$ =0.33 eV, therefore taking into calculation silicon band gap width  $E_g$  as equal to 1.10 eV [189] the top of the valance band is  $E_V$ - $E_F$ =0.77 eV. It corresponds well with PYS experimental data which point to the value 0.76 eV. In the case of p-type (p=1·10<sup>15</sup> cm<sup>-3</sup>) silicon  $E_V$ - $E_F$  equals 0.24 eV, which is the same value as the value from PYS experiments, and consequently,  $E_F$ - $E_C$  reaches 0.86 eV. As one can see, the above calculated data of electronic properties of bulk Si(111) perfectly coincide with values obtained by PYS methods concerning work function and ionization energy of the silicon.

In order to find the  $E_V$  position of Si(111) at the silicon/silicon dioxide interface with respect to Fermi level ( $E_V$ - $E_F$ ) one should take the literature value of difference between silicon and silicon dioxide valence band onsets  $\Delta E_V = E_V(Si)$ - $E_V(SiO_2)$  obtained by Keister at al. [192]. On the course of soft X-ray photoemission spectroscopy (SXPS) measurements, they reported  $\Delta E_V = 4.54$  eV for 10-Å-thick SiO<sub>2</sub> film grown on Si(111) substrate.



Figure 5. 10 Density of states acquired form photoemission field spectra for n- and p-type native Si(111) substrates.

Taking into consideration obtained within this work  $E_V(SiO_2)$  values, in case of n-type native Si,  $E_V(Si)$ - $E_F$  reached the value of 0.61 eV indicating (in comparison with the bulk value of 0.76 eV) depletion region on the silicon/oxide interface. For p-type native Si substrate,  $E_V(Si)$ - $E_F$  is equal to 0.26 eV and in comparison to the bulk value 0.24 eV suggests only very weak depletion. These tendencies were theoretically predicted by Mizsei [193] and explained by the fact that in the case of the ultra-thin insulator (native SiO<sub>2</sub>) covered semiconductor surfaces (Si) the surface charge tends to shift the surface nearer to the intrinsic condition. The fundamental reason of this behavior is the possibility of charge carrier tunneling in interface Si/SiO<sub>2</sub>. Mizsei concluded also that there is an asymmetry between n- and p-type silicon semiconductors due to very low hole tunneling probability across the oxide layer [193].

Identical considerations made for RCA substrates revealed the change of  $E_V(Si)$  value from 0.76 eV to 1.00 eV in the case of n-type Si/RCA-SiO<sub>2</sub> substrate, indicating accumulation region on the silicon/oxide interface. For p-type Si/RCA-SiO<sub>2</sub> substrate,  $E_V(Si)$  equals 0.76 eV with respect to  $E_F$  and in comparison to the bulk value of 0.24 eV it suggests considerable depletion. It also seems to be coherent with Mizsei's calculations but (contrary to native samples) for thick oxide layers. The RCA samples correspond well to that thick-oxide behavior although the difference in SiO<sub>2</sub> thickness is only approximately 0.5 nm in comparison to native samples. According to Mizsei's model and contrary to native samples, there is no tunnel current in the case of thick-oxide-covered Si surfaces and the changes are said to be caused by the static positive charge at the surface/oxide interface [193].

All the electronic parameters of n- and p-type Si/native SiO<sub>2</sub> and Si/RCA- $SiO_2$  interface are summarized in band diagrams demonstrated in Figure 5. 11.



Figure 5. 11 Summarizing band diagrams of the electronic structure of the  $Si(111)/native-SiO_2$  and  $Si(111)/RCA-SiO_2$  interface: (upper) n-type substrates, (lower) p-type ones. The values in green are taken as the literature values (for reference - see text).

## 5.2 Organic CuPc overlayer

In this section, the results of imaging and photoemission experiments performed on the CuPc ultra-thin layers deposited on n- and p-type Si(111) native substrates are reported. Also, where possible, they are compared to those deposited on RCA-treated ones. The surface morphology, chemistry and electronic properties are analyzed. Furthermore, this section contains the proposed description of the CuPc layer growth on the oxidized silicon. Finally, the substrate / organic layer interface is revealed by photoemission studies and energy level alignment is projected.

### 5.2.1 Surface morphology

Surface morphology of obtained CuPc layers was examined with use of AFM and SEM techniques. The phase of the final 16-nm layers was determined with ancillary ex-situ X-Ray Diffraction (XRD) investigations. XRD data, presented in Figure 5. 12, show that the CuPc thin films are in the  $\alpha$ -phase for both types of native substrates. The same phase and orientation had already been reported in the literature for CuPc film with larger thickness (100-300 nm) [194,195,196]. The XRD data for CuPc on the RCA-treated substrates are not available, but taking into account the literature data and that the evaporation conditions were identical, it is claimed that their phase is the same.



Figure 5. 12 XRD spectra taken for p-type (left) and n-type (right) native-Si samples. Data confirm the a-phase of the obtained CuPc overlayer. The spectra were recorded ex-situ for 16-nm-thick CuPc layers.

Figure 5. 13 presents SEM images of the 16-nm CuPc films deposited onto the n-type (a) and p-type (b) native Si substrates. In order to enhance the clarity of the pictures, the contrast and brightness were adjusted and heightened. As already reported for copper Phthalocyanine thin films [49], on both images one can see a film of randomly oriented in plane crystallites with a length of up to 100 nm and an aspect ratio (length : width) around 10:1. These results correspond well to those previously reported in Ref. [54] for pure and fluorinated copper phthalocyanine. However, notably the crystallites on the n-type substrate are significantly larger than those observed on the p-type one. The crystallite size distributions are ranging between 75-150 nm and 50-100 nm for the n-type and p-type native Si substrate, respectively.



Figure 5. 13 SEM images of CuPc ultra-thin films (16 nm) on : (a) n-type and, (b) p-type native Si(111).



## Figure 5. 14 SEM image needle like crystallite protruding from the surface of CuPc deposited on n-type substrate.

Moreover, as shown in Figure 5. 14, on the n-type sample one can observe occasionally appearing bright dots, which corresponds to occasional needle-like crystallites protruding from the surface. Such features were not detected on the p-type sample. SEM is thus indicating that CuPc film on the n-type substrate has a more open structure than the one observed on p-type  $Si/native-SiO_2$ .

The AFM results are consistent with those obtained with SEM. Panels (a) and (c) in Figure 5. 15 shows 1µm x 1µm images of the CuPc 16-nm-thick layers deposited on n- and p-type native substrates. One can see typical for CuPc grain-like structure with randomly oriented crystallites. Panels (b) and (d) depict the corresponding topography analysis histograms.



Figure 5. 15 AFM images (1 um x 1 um) taken on the 16 nm CuPc films deposited on (a) n-type and (c) p-type Si(111) covered with native oxide substrates; (b) and (d) show corresponding topography analysis histograms.

A quantitative analysis of the AFM data shows that the RMS roughness of 16-nm CuPc layer is 1.15 nm on the n-type substrate and 0.67 nm on the p-type one. That is the latter is twice smoother than the former. The average lateral grain size is 75-150 nm for the n-type and 50-100 nm for p-type (in full consistency with SEM). The data for p-type substrate are in agreement with similar morphological studies reported in Refs. [52,108]. There are also significant differences in the parameters of the topography histograms shown on



Figure 5. 15 (b) and (d); the average (and maximum) height values are 3.8 (7.9) nm and 2.3 (5.1) nm, respectively.

Figure 5. 16 AFM images (1  $\mu$ m x 1  $\mu$ m) taken on the 16 nm CuPc films deposited on (a) n-type and (c) p-type RCA-treated Si(111); (c) and (d) show corresponding 3D images of the surface morphology while (e) and (f) depict profiles of roughness analysis. The image is not arranged in the same manner as Figure 5. 15 due to different software (not compatible with each other) used for analysis.

Figure 5. 16 depicts the 1  $\mu$ m x 1  $\mu$ m AFM images of 16-nm-thic CuPc layers deposited on n-type and p-type RCA-treated substrates (a and b respectively). Once again the grain-like structure with randomly oriented crystallites is well visible. Moreover, Figure 5. 16 (c) and (d) presents 3D

imagination of examined samples while Figure 5. 16 (e) and (f) shows the roughness analysis cross-sections of the n- and p-type sample respectively. A similar (to native samples) quantitative analysis of the AFM data made for the RCA samples exhibits the same tendencies as in case of native ones. The RMS roughness of CuPc layer is 1.47 nm on n-type substrate and 0.97 nm on p-type one. Again, the p-type substrate yielded smoother layer, however the difference is less pronounced than on Si/native-SiO<sub>2</sub> substrates. The average lateral grain size is 80-110 nm and 50-90 nm, while the average (and maximum) grain height values are 6.9 (9.7) nm and 4.7 (6.5) nm for n-type RCA-treated Si and p-type one, respectively. The tendencies agree with those observed on native substrates. Described above experimental results are gathered in Table 5. 5.

Parameter	Surface morphology parameters for 16 nm CuPc layers deposited on various substrates, nm					
substrate type	n-type native	p-type native	n-type RCA	p-type RCA		
Roughness	1.15	0.67	1.47	0.97		
Av. grain height	3.8	2.3	6.9	4.7		
Max. grain height	7.9	5.1	9.7	6.5		
Lateral grain size	75 - 150	50 - 100	80-110	50-90		

Table 5. 5 Results of AFM quantitative analysis of both sets of examined samples: 16-nm CuPc deposited on Si/native-SiO<sub>2</sub> and Si/RCA-SiO<sub>2</sub> substrates.

All the above experimental evidences indicate that n-type native substrates favor a growth of the CuPc film into larger, higher and less packed crystallites. Such morphological differences were described in the literature by Ling and Bao [197]. However, in that case, the variations resulted from growth at different substrate temperatures; more open structure and larger crystallite size were obtained for growth at higher temperature. Here we observe a different morphology of the CuPc organic film as originating from a subtle effect that can be only ultimately assigned to the substrate doping. No other explanations are likely, as the two Si substrate have the same initial roughness, the same oxide thickness and composition (only  $SiO_2$ ), they have been prepared under identical conditions (substrate temperature and evaporation rate). In particular it is evident from comparison of the experimental results (morphology and photoemission, shown in the following sections concerning CuPc - ambience interactions) that the n-type substrate is, as a matter of fact, less interacting than the p-type one. The smaller effect (difference in roughness) in the case of phthalocyanine deposited on the RCA-treated substrates may originate from the thicker oxide layer which partially buffers the impact of substrate conductivity. This could be one more, indirect evidence on above findings.

It has to be said that both AFM and SEM examinations were conducted exsitu; that is the CuPc samples had been exposed to the air during the examination. However, the all SEM-scanned thin films are in the  $\alpha$ -phase (as checked with XRD) so there is no reason for a preferential oxygen uptake in one case or another. Moreover, the CuPc thin film growth has been performed in UHV conditions, so the presence of water and oxygen induced dipole layers at the substrate surface cannot be claimed to be at the origin of a different molecule/substrate interaction strength and thus different film morphology.

In general the growth of organic molecules (and eventually the film morphology) onto inorganic substrates at the very initial stages of deposition (few nm thickness of the organic layer) is governed by: substrate type, substrate temperature during the film growth and deposition rate of the organic film [196]. Typically when (at fixed values of the above parameters) the molecule/substrate interaction dominates over the molecule/molecule interaction, the Pc molecules adsorb planarly on the substrate. Otherwise, (rather weak interaction with the substrate) the growth proceeds with the formation of organic crystallites. As a "rules of thumb", the higher is the substrate temperature during the deposition (i.e. increased molecular diffusivity), the larger is the resulting average crystallite size of the organic film and the surface morphology is more open. Similarly, the higher is the Pc evaporation rate (here particularly CuPc) or the smaller is the molecule/substrate interaction, once again the larger is the size of such crystallites. For example, with lowering the interaction strength with the substrate (e.g. at a given substrate temperature and molecular evaporation rate, passing from non-passivated Si substrates in UHV to passivated Si, then to Si covered with an oxide layer, and finally to weakly interacting substrates like graphite) the molecule diffusivity on the substrates is enhanced. Then the interaction with the other molecule becomes predominant and the Pc molecules typically pack into crystallites with increasing sizes [196].

In our case, the growth parameters of CuPc films for the n-type and p-type substrates were deliberately kept identical (the same substrate, thickness of the oxide layer, roughness of the substrate surface, substrate temperature during evaporation, pressure and evaporation rate during the film growth, and final thickness of the organic film). Nonetheless, growth on the p-type substrate led, if compared to the n-type case, evidently to crystallites with a significantly smaller average size. Hence, one can believe (especially taking under consideration that samples were exposed to air before AFM measurements) that the smaller average crystallite size is at the origin of the higher reactivity to ambient air of the p-type samples. More evidences in favor can be found in air-exposure studies discussed later in Section 5.4. This is very probable indeed if one consider the ratio between surface area and volume of a crystallite. The higher ratio observed in the CuPc film on p-type Si evidently favors a more efficient uptake of oxygen, water vapor, and carbon containing gases from the ambient air on the p-type sample rather than on the n-type one. This hypothesis will be discussed further in Section 5.4.

The stronger substrate/molecule interaction on p- compared to n-type substrates may be assigned to the possible formation of dipole layers. It can be expected that dipoles of different strength are likely formed as a function of the different substrate doping [93]. This is addressed in the following Sections 5.2.2 and 5.2.3 in which the careful core level and valence band investigations are conducted.

The experimental evidences presented in this Thesis indicate that not only the growth parameters and the substrate preparation, but also the substrate doping determines the properties of growing CuPc overlayers. The latter is a subtle tool to engineer the surface morphology and surface reactivity of CuPc thin films on inorganic substrates of utmost technological importance like  $Si/SiO_2$  but these statements will be discussed further in Section 5.3. Recalling what had already been discussed in Chapters 1 and 2, compact and smooth Pc thin films are desirable to increase the field effect mobility of the organic layer, as demonstrated by Ling and Bao [197]. On the other hand, in relevance to fabrication of CuPc-based gas sensing devices a more open structure (with larger specific surface) is preferable. Thus, the two types of morphology can be engineered by appropriate tuning the p- or n-type doping of the supporting Si substrate.

### 5.2.2 Chemical properties

The chemistry of the CuPc ultra-thin film was determined, similarly to the substrate, with the use of XPS and ARXPS methods. It has to be noted that the data and discussion presented in this section refer to the properties of final CuPc films rather than to interfacial effects which are described later.



Figure 5. 17 Growth of CuPc thin film on n-type native substrate depicted by evolution of XPS survey spectra. Substrate components (Si2p and Si2s) are not detectable when the CuPc layer is thicker than 8 nm.

The step-wise manner of investigations applied to this part of experiments aimed mainly to the understanding of the CuPc layer formation on the substrates with the presence of substrate carbon contaminants.

Figure 5. 17 depicts XPS survey spectra taken for different thicknesses of CuPc deposited on n-type native substrate. For brevity, only one sample was chosen – but in this scale it is representative for all samples. This figure presents well the whole process of the final 16-nm layer formation. One can observe the increase of the CuPc-related XPS peaks and the diminishing of the substraterelated ones. It has to be emphasized, that from the XPS investigations of the very first layer deposited onto the substrates, the spectra exhibited typical for CuPc features including Cu2p, C1s, N1s XPS peaks. The substrate characteristic peaks, the Si2p, Si2s and O1s, remained detectable up to CuPc layer thickness of about 8 nm which is shown in Figure 5. 17. As a general remark, it is worth stressing that the data gives information on the surface and "bulk" CuPc layer rather than the interfacial CuPc/SiO<sub>2</sub> layer. This is evident if one takes into considerations that the CuPc nominal layer thickness is 16 nm, and that, apart from significant but in any case small differences, the films are rather compact and both AFM and SEM do not show substrate areas which are not covered with the organic film. The substrate is thus significantly buried under the phthalocyanine layer.



Figure 5. 18 Comparison of "as deposited" 16 nm CuPc survey spectra. (a) – data recorded for CuPc deposited on native substrates, (b) – CuPc deposited on RCA-treated substrates. Only characteristic for copper phthalocyanine peaks are detectable. Substrate peaks are not visible.

As a confirmation that the substrate is completely covered with CuPc, one can take the XPS data recorded for freshly evaporated CuPc. Figure 5. 18 depicts the survey spectra recorded at normal take-off angle from final 16-nm CuPc layers on native samples (left panel) and on RCA-treated substrates (right panel). All main CuPc peaks are visible, whereas Si ones are not discernible any more. There are also no substantial differences between both spectra; the CuPc on the p-type substrate spectra show higher background intensity in the binding energy range from 100 to 400 eV. This range starts at about the energy of the Si2p and Si2s peaks which cannot be observed directly due to the coverage by the CuPc layers. However, the increasing background is due to inelastically scattered electrons arising from these Si electron orbitals. Following this, the CuPc layer covering the substrate should attenuate these electrons. Therefore, one might assume that the thickness of CuPc layer on the p-type sample is actually not identical with the nominal thickness determined by the quartz microbalance. Similar background effect on the n-type samples is much smaller, which could suggest different surface roughness of the layer.

The more detailed analysis of CuPc layers is based on the C1s core levels acquired for the stable final 16-nm films as well as their evolution as a function of layer thickness. Figure 5. 19 shows the C1s peak evolution for two low coverages of CuPc layer deposited on native Si substrates. These C1s spectra are similar to those recorded from alkyl-substituted phthalocyanine molecules [198,199]. They include the C-H contamination component located between C-C and C-N ones being due to the phthalocyanine. Qualitatively, the relative intensities between these components for the coverages in Figure 5. 19 are similar to those observed on (t-tert-Bu)<sub>4</sub> MgPc films on Au [199].



Figure 5. 19 Evolution of C1s XPS peaks from CuPc layers of low coverages deposited on the n- (left panel) and p-type native Si substrates (right panel). The final thickness of 16 nm is not shown due to its identity to the RCA samples (see Figure 5. 20). The labels follow the appearance order of components.

All recorded C1s spectra consist of three main different CuPc-related components (labeled C-C, C-N, and SC2). They can be attributed to the aromatic carbon of the benzene rings, pyrrole carbon linked to nitrogen and a  $\pi$ - $\pi$ \* satellite of the latter as in Ref. [200, 201]. In present studies, C1s signal referring to the carbon atoms of in CuPc was decomposed into two main components, C-C and C-N, and their shake-up satellites, SC1 (satellite from C-C) and SC2 (satellite from

C-N) [202,203]. The components arising from surface carbon contamination were introduced into the CuPc C1s region with relative intensities fixed at the values obtained on the substrates (see Section 5.1).

One can see that even for very thin CuPc layers the C1s peak exhibits a characteristic triple shape, which becomes more distinct with increasing thickness. It has to simultaneously remembered, that the carbon signal due to substrate contamination is being progressively attenuated as the CuPc overlayer thickness increases.



Figure 5. 20 Evolution of C1s XPS peaks with increasing thickness of CuPc layer deposited on the RCA-treated substrates. The labels follow the appearance order of components.

For thicknesses shown in Figure 5. 19, the C-H and C-OH contamination components are present in the spectra while the COOH one disappears even for 1.2 nm. The C-OH components at 1.2- and 1.5-nm layers are distinct

contributions. For 3 nm layers, the C-OH component diminishes almost completely and the C-H component is strongly reduced. Comparing ultra-thin CuPc layers (up to 3 nm) on n- and p-Si/native-SiO<sub>2</sub> samples the only visible difference is the slight energy shift by 0.2 eV of the C-OH component towards lower binding energies on the n-type substrate. Similar analysis of C1s peaks recorded from CuPc layers on the n- and p-type Si/RCA-SiO<sub>2</sub> substrates is shown in Figure 5. 20. It is seen that for initial ultra-thin layers (1.4 and 1.6 nm), contrary to native substrates, different contribution of C-H component is detected; relative to C-N component it is higher for CuPc on the n-type substrate than on the p-type one. This observation corresponds with the reduced carbon contamination on the RCA-treated Si samples (see C/O ratios in Table 5. 3). There are hardly any differences between the data sets. It can be suspected that RCA clean applied on n-type Si substrate removes eagerly the C-H and C-OH species from the silicon surface while the minute quantities of COOH are barely affected (however the differences are within an experimental uncertainty). For the p-type Si samples, only the C-H contribution changes by 3 % while the C-OH and COOH do not change after the RCA treatment. It is highly probable that the carbonaceous layer is reduced as a whole; however the composition is scarcely affected. Hence the relative concentrations of surface species might clarify the situation. The C/Si, C/O and O/Si relative concentrations calculated from the total areas under C1s, Si2p and O1s peaks/core levels are summarized in Table 5. 3 for all substrates. There are also some C-OH species detected as well as the traces of COOH can be noticed. For thicker 3-nm CuPc layers, the COOH signal fell below the detection limit while the C-H signal was still observed in the spectra without a significant variation in the intensity on n- and p-type substrates. Thus, the attenuation of the contamination signal is weaker when the p-type substrate was used, which indicates a less perfect (homogenous) growth of the CuPc film. This reflection agrees with the conclusions drawn from the preceding analysis of the inelastic background of the thickest films (16 nm). Finally, for the 16-nm-thick layers the C1s components originating from contamination were not found and only those coming from carbon atoms in CuPc are detected. Similarly, the contamination is not detected in the case of native Si substrates; C1s spectra of 16-nm CuPc are not shown.

In Section 5.1.2 it was pointed that the chemical differences between the substrates are rather small. However, even inconspicuous variations in the state of substrates can result in considerable differences in properties of CuPc ultrathin layers. Up to thickness of about 4-5 nm, which corresponds to about 9 monolayers of CuPc, there is a visible variance in the propagation of carbon contamination in CuPc. The C1s peak of the RCA-treated samples is more affected by carbon contaminants, which is probably due to mentioned in previous Section 5.1.2 segregation of the carbon contaminants. Possibly, the carbon species induce some inhomogeneous growth of the CuPc, at least until the contamination layer has been covered completely. This speculation, however, requires further investigations.

For the very first CuPc monolayers it seems that the growth on the n-type RCA sample is more influenced by surface contaminants, but for 3 nm it is clear that the C1s peak already resembles shape specific to CuPc. As expected, for
thicker CuPc layers, the differences induced by carbon contamination disappear completely. Summarizing, although there is no significant difference in carbon contamination influence on the composition of organic overlayer it seems to be necessary to anneal the Si substrate after the RCA technology if one desires to obtain carbon-contamination-free substrate before the deposition process. However it was not a goal of this work – the RCA samples should be treated as the reference samples for the native ones. Hence, besides the origin of the oxide (either native or RCA-prepared) the technological preparation of the samples should be the same. Within this work the non-annealed substrates were in the center of attention.

# 5.2.3 Electronic properties and Si/SiO<sub>2</sub>/CuPc interface characterization

In order to determine the electronic properties of CuPc layer the UPS measurements were taken after each step of evaporation. The layers on both native and RCA-modified silicon substrates of n- and p-type were investigated.



Figure 5. 21 Development of CuPc-related features on substrate UPS spectra on the course of overlayer evaporation on native n-Si(111) substrate and on native p-Si(111) one. High binding energy cutoff – (a) and (b); HOMO peak region – (c) and (d).

Figure 5. 21 presents the magnification of the high binding energy cut-off and the HOMO regions with respect to the Fermi level position ( $E_F$  was assigned to 0 eV on binding energy scale) of CuPc films at the initial stages of deposition on n-Si and p-Si. One can see the difference between the smooth line coming from substrate spectra and the "hilly" spectra recorded for CuPc. The CuPc-related features can be seen in the low-energy part of the spectra from the very first organic overlayers. The most significant of them – the HOMO peak has been marked and, playing the role of  $E_V$ , allows on determination of the CuPc electron properties. The high-energy part (cut-off region) does not change its shape together with the CuPc evaporation. However, the abrupt shift of high-energy cut-off between silicon substrate and first organic overlayer can be noticed. This shift suggests that the interface dipole  $\Delta$  has developed due to CuPc molecules. The value of the dipole potential is dependent on the substrate type and is 0.15 eV towards higher binding energy for native n-Si/SiO<sub>2</sub> substrate and 0.25 eV towards lower binding energy for native p-Si/SiO<sub>2</sub> one (left panels of Figure 5. 21). For clarity only substrate and two chosen thicknesses are shown.

Figure 5. 22 shows the same regions for CuPc evaporated on RCA-treated substrates. This time, no detectable interface dipoles exist between the substrate and first evaporated CuPc overlayer.



Figure 5. 22 A development of UPS spectra with increasing organic layer thickness for CuPc overlayer on RCA-treated n-Si(111) substrate and on RCA-treated p-Si(111) one. High binding energy cutoff – (a) and (b); HOMO peak region – (c) and (d).

Moreover, analyzing low binding energy region of the UPS spectra at the initial stages of CuPc deposition, the HOMO peak development was observed for all samples. Figure 5. 23 presents evolution of the HOMO peak with increasing CuPc thickness for both sets of substrates: native and RCA ones (only the magnification of the HOMO region is shown). For better clarity, only chosen thicknesses are shown. The HOMO peak of the very initial CuPc film (0.5 nm) on the native substrates (left panels) consists a broad band in with the full width at half maximum (FWHM) of around 0.70 eV. This value then decreases with film thickness to approximately 0.55 eV for 16-nm layer. Such an extended HOMO

peak was also observed by Peisert et al. in UPS investigations of CuPc deposited on polycrystalline Au foil and on oxidized silicon [75]. They related the broadening to the ill-defined adsorption sites on the polycrystalline substrate or to the formation of clustered standing molecules which demonstrate properties similar to the bulk phthalocyanine [75].



Figure 5. 23 UPS spectra of HOMO peak region evolution with increasing organic layer thickness for CuPc on native n-Si(111) substrate (upper) and on native p-Si(111) one (lower). The broadening of the HOMO bandwidth may be ascribed to the lateral inhomogenity in the molecular orientation [98].

Additionally, by application of polarization-dependent X-ray absorption spectroscopy that research group confirmed that for non-ordered substrates the standing orientation of organic molecules is preferable rather than the laying (planar) one. It has to be explained that by the standing orientation one should understand when the CuPc molecule plane is perpendicular to the substrates' surface. When planar orientation occurs, the CuPc molecule is "laying" on the substrate – the CuPc molecule plane is parallel to the substrate. Authors in Ref. [75] speculated that the reason is probably no well-defined adsorption sites due to the low symmetry of the substrate surface or to the surface roughness on a molecular scale. Considering these findings, one can expect that broad and asymmetrical HOMO peak indicates non well-ordered adsorption geometry of the CuPc molecules on Si(111) substrate covered by native oxide. Here, the HOMO peak was decomposed by the sum of Gaussian (70%) and Lorentzian (30%) curves. In the early stage of deposition two components were identified (number 1 and 2 in Figure 5. 23). However, when the CuPc thickness exceeds 3 nm the fitting returns only a single component. One can observe a slight difference in the behavior of the layers on n- and p-type native substrates. In the former the dominating component prevails and stabilizes earlier than in the latter. The relative area ratios of fitted HOMO components for CuPc deposited on native substrates are collected in Table 5. 6.

CuPc on n-type native substrate		CuPc on p-type native substrate		
CuPc layer thickness, nm	Component area ratio (area 2 / area 1)	CuPc layer thickness, nm	Component area ratio (area 2 / area 1)	
0.55	1.5 / 1	0.30	0.8/1	
0.82	1 / 13	1.30	1/2	
2.08	1/14	2.41	1/37	
4.00	0 / 1	5.00	0 / 1	

Table 5. 6 The area-to-area ratios for HOMO region components for chosen CuPc layers deposited on native substrates.

The components quantitatively described in Table 5. 6. correspond to the different adsorption geometry, and thus growth modes, on the substrate, i.e. the first to the standing CuPc molecular orientation and the second to the laying one. During the initial development of the film the laying adsorption was preferable whereas when its thickness exceeded 3 nm the laying adsorption of the initial layer became buried or rearranged. Similar effect of buried interfacial CuPc layer with orientation parallel to the substrate up to around 3 nm thickness was reported by Biswas et al. in near-edge X-ray absorption fine structure spectroscopy and XPS studies [204]. They stated that polycrystalline gold substrate used in their experiments interacts with organic molecule  $\pi$  electrons stronger at the interface than CuPc molecules with each other. However, during the further growth of the film the  $\pi$ - $\pi$  interaction predominates and at higher thickness only the standing orientation was observed [204].

On the other hand, the HOMO peak and consequently the initial formation of CuPc on RCA-treated substrates are much different (right panels Figure 5. 23). Firstly, the single component is observed and, secondly the HOMO shape is independent of the substrate doping. The FWHM of fitted component varies from 0.6 eV at extremely low coverages to 0.47 eV for the layers exceeding 3 nm thickness.

In the case of RCA-treated samples there is a single growth mode regardless of the type of substrate conductivity. The hypothesis could be that on thicker oxide (RCA) the molecules change their orientation continuously with the film growth giving one component in the HOMO region of the UPS spectra. Hence for given CuPc overlayer thickness there is common geometrical orientation for all molecules from the same layer. This statement can be sustained by the mentioned in Section 5.2.1 fact, that molecule/molecule interaction is predominant (instead of substrate/molecule interaction ) in case of thicker oxide layer. Thus for initial layer the laying orientation is preferable and then it is reorganizing with the increase of the film thickness.



Figure 5. 24 HOMO peak width (FWHM) evolution with progressively increasing thickness of CuPc on native and RCA-modified n- and p-Si(111) substrates.

Figure 5. 24 visualizes how the total FWHM of HOMO peak changes during the development of CuPc layer on the substrates. While the FWHM on RCA-treated samples coincides at the same value of about 0.47 eV for both conductivity types, the native substrates show lower final width for p- (0.45 eV) than n-Si (0.55 eV).



Figure 5. 25 Proposed schemes of different CuPc layer growth modes on various Si substrates. According to UPS and AFM investigations one can observe the differentiated arrangement of the molecules with increasing CuPc layer thickness.

Peisert et al. reported that the FWHM of around 0.45 eV corresponds to the formation of bulk-like CuPc layer [75]. In the present case the similar value could indicate the existence of continuous layer deposited on the substrate. Moreover different final FWHM values (between n- and p-type native samples as well as between native and RCA samples) may suggest slightly various standing adsorption mode projecting in different final morphological feature of CuPc. This hypothesis is confirmed by the AFM and SEM results which showed different

network of packed crystallites of CuPc thin films depending on the conductivity type of substrate [II]. However the AFM results for RCA samples are less coherent. Taking the same explanation (that FWHM values may indicate on the growth mode), the surface morphology should be the same in the case of n- and ptype RCA samples. Although the surfaces of both RCA-treated samples differ (from the topography point of view) less than corresponding native samples, the differences cannot be neglected.

The present results are summarized in Figure 5. 25, where schemes of CuPc growth modes on the various Si substrates are proposed. The CuPc on native samples exhibit two different growth modes (standing and lying) at the beginning of the deposition, however the influence of the conductivity is observed. That is the growth on the p-type one is more diversified – at very initial stage there are two adsorption modes and then the rearrangement occurs resulting in uniform standing molecule orientation with densely packed crystallites. In contrary, the CuPc on the n-type one is more preferentially deposited in the lying mode and with the increasing thickness the self rearrangement of the molecules causes the unification of the crystallite orientation. Although the unification occurs faster than in the case of p-type substrate, the orientation probably remains inclined. At the final stage, the CuPc crystallites deposited on n-type native substrate are seldom packed and recalling the AFM results the bigger crystallite sizes may be caused by preferential more-lying orientation at the surface.

The RCA samples are shown on one diagram due to similar results of HOMO region investigations. The growth mode appears to be the same in both RCA cases – the CuPc in succeeding monolayers are taking more and more standing orientation until the end of the deposition. Concerning the AFM results (different roughness), the only difference in RCA samples would be the distance between Pc molecules at the final stage of deposition – smaller in the case of p-type RCA substrate than for those deposited on n-type one. The growth mode for RCA samples looks to give more or less uniform orientation of the molecules for given deposition stage.

Applying formulas (5. 5) to the organic semiconductor conditions one obtains [187]:

$$\Phi = \hbar \omega - (E_{HOMO} - E_0),$$
  

$$\varphi = \hbar \omega - (E_F - E_0),$$
  

$$\chi = \Phi - E_g$$
(5.8)

where:  $E_g$  is the band gap,  $\hbar\omega$  is the energy of incident photons (here of He I radiation),  $E_0$  is the energy cut-off of the UPS spectra,  $E_{HOMO}$  is the energy onset of the HOMO peak corresponding to top of the valence band for inorganic materials, and  $E_F$  is the surface Fermi level position. With formulas (5. 8) it is possible to use UPS data in order to inspect how the energy levels at the CuPc/substrate interfaces align while the layers are growing.

Accordingly, Figure 5. 26 depicts the evolution of ionization energy and work function as a function of CuPc thickness for both n- and p-type native substrates. The cumulated data show the constant ionization energy ( $\Phi$ ) of 4.75 eV during whole deposition process regardless of substrate type. On the contrary, the work function ( $\varphi$ ) varies especially at the initial stages of deposition. The value at the

initial stages is 3.55 eV for n-type native substrate and 4.00 eV for p-type one, which makes a considerable difference.. During the CuPc overlayer growth, over the thickness of 3 nm, the work function tends to identical value of 3.75 eV for both native substrates.

Assuming constant CuPc transport band gap of 2.3 eV [205],  $E_{HOMO}$ - $E_F$  at CuPc on the n-Si native substrate is derived to be 1.20 eV at the extremely low coverage and decreases to 1.00 eV for the 9-nm phthalocyanine layer. These values correspond to the bending of the HOMO and LUMO levels downwards by 0.20 eV at the interface. On the other hand, for CuPc deposited on p-type native silicon,  $E_{HOMO}$ - $E_F$  being initially equal to 0.75 eV increases to 1.00 eV for the final layer indicating 0.25 eV upward bending of HOMO and LUMO energy levels.



Figure 5. 26 Ionization energy and work function changes as functions of thickness of CuPc layers on native n- and p-Si(111) substrates. The half-transparent lines are the guide to the eye only.

Figure 5. 27 depicts similar ionization energy and work function evolutions with thickness of CuPc grown on n- and p-type RCA-treated substrates. Contrary to native samples, the behavior of the work function follows the variation in the ionization. The ionization energy rapidly changes within the thickness up to 3 nm and then stabilizes at 4.9 eV. In the similar manner the work function tends to the constant value of 4.0 eV for the CuPc layers thicker than 3 nm. The same behavior of  $\Phi$  and  $\varphi$  suggests that there is no bending in HOMO and LUMO molecular energy levels. The only change then is the shift of the vacuum level until the complete CuPc monolayer is formed (up to 3 nm).

To confirm the electronic behavior of initial and final CuPc layers the XPS study of shifts in core levels was simultaneously carried out. Figure 5. 28 presents the changes of Cu2p and N1s core level positions during the deposition of CuPc films on Si native substrates of both doping types. At the n-type one both core levels moved around 0.40 eV towards the higher energy for the very first deposited layers. This shift confirms the downward bending of HOMO level. The shape of envelope in Figure 5. 27 is qualitatively consistent with that in Figure 5.



26 (for n-type) and the stable value is again reached at the thickness of around 3 nm.

Figure 5. 27 Ionization energy and work function changes as a function of thickness of CuPc layers on RCA-treated n- and p-Si(111) substrates. The half-transparent lines are the guide to the eye only.

At CuPc on p-type native Si substrate, however, no variations in core level positions were detected in disagreement with UPS data in Figure 5. 26. Nevertheless it should be emphasized that the XPS sensitivity to subelectronovolt shifts is much lower and the information depth is considerably larger than those of UPS. Moreover, the shapes and relative distances between core levels in both cases remained stable corresponding to non chemicalinteraction between CuPc molecules and native Si(111) during interface formation.



Figure 5. 28 Changes in Cu2p3/2 (left panel) and N1s (right panel) core level positions with thickness of CuPc layer on native n- (black squares) and p-Si(111) substrate (red dots). The half-transparent lines are the guide to the eye only.

In the case of RCA samples the situation is rather clear; as shown in Figure 5. 29 there are only insignificant changes (within 0.1 eV) in Cu2p and N1s core level positions. On one hand the lack of shift confirms the UPS findings (for layers thicker than 4 nm) for RCA-treated samples, while on the other hand it points to the lack of chemical interaction at the substrate/organic overlayer interface. The open question is if the changes really exist if the accuracy of the method is of the same order. However the changes correspond quite well to Si2p peak position changes which are described further.



Figure 5. 29 Changes in Cu2p3/2 and N1s core level positions with thickness of CuPc layer on native n- (black square) and p-Si(111) substrate (red circle). The half-transparent lines are the guide to the eye only.

In order to determine the influence of the deposited CuPc layer on electronic properties of silicon substrates, the Si2p core levels were investigated. Figure 5. 30 depicts binding energy shifts of Si2p peaks with the thickness of CuPc film. The left panel shows data for native silicon while the right one for RCA-treated silicon. In the case of the n-type native one, the Si2p peak shifts during the CuPc deposition by approximately 0.15 eV towards lower binding energy, indicating an increase in the upward band bending at the subsurface region of this substrate. At the p-type native Si the shift in opposite direction by 0.10 eV was detected demonstrating an increase in the downward band bending. Regardless of doping type the Si2p binding energy position stabilizes when the CuPc thickness exceeds 3 nm but the positions are rigidly shifted about 0.25 eV one to another. This shift is related to different position of Fermi level in the bulk of silicon as it was already mentioned in Section 5.1.

In the case of the n-type RCA-treated substrate, the Si2p peak shifts during the CuPc deposition by approximately 0.20 eV towards higher binding energy indicating an increase of downwards band bending in this substrate. The identical trend occurs at the p-type RCA-treated sample. The shift ceases to increase again over 3 nm of CuPc layer thickness, which is coherent with the native samples and with the UPS measurements. Once more the similar behavior



of the CuPc layers deposited either on n- or p-type RCA-treated Si substrates is clear.

Figure 5. 30 Evolution of Si2p core level positions with thickness of CuPc layer on native (left panel) and RCA-treated (right panel) Si(111) substrates of n (black square) p doping type (red circle). The half-transparent lines are the guide to the eye only.

In order to elucidate the substrate mutual influence on the CuPc layer, the energy distance between positions of N1s and Si2p peaks was analyzed. Figure 5. 31 depicts changes in N1s-Si2p energy distance with respect to the final 16 nm CuPc layer, i.e. the value of zero is assumed for the 16-nm-thick layer. This analysis can be performed only for layers not thicker than 8 nm due to the attenuation of substrate peaks by the overlayer.



Figure 5. 31 Changes of N1s-Si2p binding energy as a function of layer thickness. The half-transparent lines are the guide to the eye only. The value of zero corresponds to the final 16nm CuPc layer.

Significant variations between the RCA-treated and the native Si substrates. The N1s-Si2p differences are considerably varying with the thickness for the native substrates, while they remain relatively constant within 0.1 eV for the RCA ones. The most dynamic changes occur from 0 to 2 nm and then the binding energy

difference saturates. The trends observed at the CuPc on n- and p-type native or RCA-treated substrates are identical. Regardless of doping and the treatments the N1s-Si2p differences converge to the same absolute value of 299.3 eV. The convergence seems obvious as the substrate impact on overlayers should consecutively decrease with their thickness. The variations detected at the initial stages of CuPc growth give evidence that the CuPc/native-Si and CuPc/RCA-Si interfaces and, by implication, the very first CuPc monolayers are indeed electronically different. However, once the layers are thicker (over 3 nm) the differences disappear.

The information on electronic interaction between the substrate and the organic overlayer, obtained by monitoring the binding energy distance between the phthalocyanine N1s and substrate Si2p peaks may suggest different adsorption mode of CuPc molecule for differently prepared substrates. It seems that for thinner oxide layers (i.e. on native substrates) the CuPc molecule interacts more strongly with the Si substrate, which could result in more planar adsorption. Similar findings were reported earlier by Ottaviano et al. [206,196] for NiPc and FCuPc deposited on strictly defined and clean Si(111) 7x7 reconstructed substrates. This is also in good agreement with results of UPS studies presented at the beginning of this Section. On the other hand, the Si/CuPc system is completely dissimilar to Si/SiO<sub>2</sub>/CuPc one since the formation of latter requires a chemical interaction of incoming CuPc with the oxide first. Despite the dissimilarity, there is clear evidence of standing Pc orientation on  $SiO_2$  based on NEXAFS investigations [86,22]. The most probable conclusion is that due to the larger oxide thickness the wave functions of CuPc and Si can hardly overlap for the RCA samples, and therefore the CuPc establishes its own electronic properties from the beginning. In contrast, on the significantly thinner native oxide, for the first layers the overlap may be possible and the electronic states of Si may affect the initial CuPc electronically, until they are decoupled at greater CuPc thickness.

The important message is that the equivalence of the final stages (i.e. the same electronic positions) of deposition was obtained while there was the difference in the initial situation. It is presented in the core level shifts. The investigated variations in N1s-Si2p distance point that thicker oxide layer effectively buffers the CuPc from the residual influence caused by substrate doping type. Such influence has been previously reported in literature [II,93]. This observation lends useful technological direction for the preparation of low dimensional organic electronic devices where the organic layer is supposed to be less than 10 nm thick.

In conclusion, the use of the RCA technology allows obtaining ultra-thin CuPc films which are almost not affected electronically by the substrate doping.

The results of UPS and XPS investigations of electronic properties allow to construct tentative "band-like" diagrams. The half of the diagram concerning substrate is a band diagram. For the CuPc region the data were collected during stepwise evaporation, hence they are showing, in fact, the evolution of the molecular level position with increasing CuPc coverage. In real, together with investigating consecutive CuPc layers one can see the projection of the internal interfacial layer in the external layer.



Figure 5. 32 Compiled "semi-band-like" diagram of  $Si(111)/native-SiO_2/CuPc$  structure. The lines in the CuPc layer area should be treated as changes in molecular energy level position with the layer development (thickness). The top diagram shows the situation for n-and the bottom one for the p-type Si substrate.



Figure 5. 33 Compiled "semi-band-like" diagram of Si(111)/RCA-SiO<sub>2</sub>/CuPc structure. The lines in the CuPc layer area should be treated as changes in molecular energy level position with the layer development (thickness). The top diagram shows the situation for n- and the bottom one for the p-type Si substrate.

Figure 5. 32 and Figure 5. 33 present all collected results concerning energy level alignment at the Si/SiO<sub>2</sub>/CuPc double interface (Si/SiO<sub>2</sub> and SiO<sub>2</sub>/CuPc) for n- and p-type native and RCA-treated Si(111) substrates. The diagrams help to electronically characterize the double interface being the subject of the dissertation.

It has to be said that the proposed schemes are in fact the specific hybrids. The left side including the Si bulk up to  $Si/SiO_2$  interface is a 'classic' band diagram with the depth-dependence of energy levels. On the other hand, the right side from  $SiO_2/CuPc$  interface actually shows the changes in electronic properties with the thickness of CuPc layer.

The photoemission data, summarized in Figure 5. 32, suggest the existence of small interface dipole in case of CuPc deposited on the native substrates. The energy drop due to those dipoles is opposite, which indicates the different direction of negative charge displacement. In the case of the n-type substrate the displacement follows from the CuPc layer towards the Si substrate. Similar effect was observed by Chasse at al. in photoemission study of the CuPc/InP(110) interface [81], who suggested that each CuPc molecule acted as a "donor" on the inorganic semiconductor surface what corresponded to electron transfer from the molecule to the substrate. The formation of an interface layer corresponding to the negative charge transfer to the substrate was also reported and by Komolov et al. during CuPc film deposition on n-Si(100) and grown n-Si/SiO<sub>2</sub> substrates investigated by total current electron spectroscopy (TCS) [93]. The latter group explained that CuPc interaction with the substrate might lead to the deformation of the  $\pi$ -electron orbitals of CuPc molecules or the polarization of molecules. Negative charge of the first molecular layer is transferred over the interface, while its positive charge is partially compensated by the negative charge coming from the next molecular layer. Moreover, as it was found, this type of charge compensation occurs within the polarization layer existing in the Pc film (a layer with rearranged charge distribution) [93].

Electronic phenomena described in the literature may be identified in the case of CuPc on n-type native Si where downward bending (shift) of CuPc molecular levels and increasing depletion region in n-type native Si (blue regions in the diagram) confirms direction of negative charge transfer via tunnelable native SiO<sub>2</sub>.

The formation of band bending-like trend of CuPc near the interface however seems to be controversial when one invokes the 'traditional' formalism of inorganic semiconductors [98]. For organic semiconductors it becomes questionable if there is a sufficient number of charge carriers to obtain band bending originating from the formation of the space-charge layer within the Debye's screening length  $L_D$  under thermodynamic equilibrium. To evaluate if the  $L_D$  is within the reasonable range it has to be calculated. However to determine the  $L_D$  one needs the hole concentration in copper phthalocyanine. Since the concentration of the charge carriers in CuPc is not given, it has to be also calculated. Thus in order to determine the hole concentration in CuPc one can apply the formula [207]:

$$p = N_V \exp\left[-\frac{E_F - E_V}{kT}\right]$$
(5.9)

where:  $N_V$  is effective density of states in conduction band (for CuPc 4.1 ·10<sup>21</sup> cm<sup>-3</sup> [208]); k is the Boltzmann's constant and T - absolute temperature. Energetic distance  $E_V$ - $E_F$  here denoted  $E_{HOMO}$ - $E_F$  was taken as 1.00 eV (from UPS measurements). As a result the obtained concentration p equals approximately 10<sup>7</sup> cm<sup>-3</sup>. Corresponding value of Debye length  $L_D$  may be then calculated from equation [207]:

$$L_D = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{e^2 p}}$$
(5.10)

where:  $\varepsilon_0$  is vacuum permittivity constant,  $\varepsilon$  is relative dielectric constant (4.78 for CuPc [209]), and e is the elementary charge; p, k, T were defined above. Calculated L<sub>D</sub> value for above assumption is then around 1 mm. Comparing this value with evolution of the CuPc molecular levels within thickness of initial 3 nm (Figure 5. 32 and Figure 5. 33), this origin of band bending can be indeed excluded. The presence of band bending could be explained with the molecular reorganization during the development of organic film. Its analysis was already conducted within this Thesis (at the first part of current Section – where the UPS measurements of CuPc are considered). Up to the CuPc layer thickness of 3 nm the interface-induced polarization layer (nascent in CuPc) might cause continuous change of molecule orientation in the initial stages of deposition which finally manifests itself as the band bending-like shift. Similar effect was also detected by Yamane et al. at CuPc/HOPG interface during metastable-atom electron spectroscopy (MAES) measurements [98].

In the case of p-type native substrate (Figure 5. 32 bottom) one can observe the opposite phenomenon. The transfer of negative charge from Si substrate to the organic overlayer via thin tunnelable native oxide causes the increase of depletion in p-type silicon (under the oxide layer) and the upward shift of CuPc molecular levels. Also in this situation the shift could be related to the molecular rearrangement occurred as a result of possible CuPc layer polarization in the initial stages of deposition.

In the case of the RCA-treated samples there is no observable dipole at the interface. There is only a slight difference in the strength of the polarization effect between n-type and p-type samples. According to energy diagram in Figure 5. 33 one can assume that the polarization layer is located in the CuPc layer instead of dipole at the SiO<sub>2</sub>/CuPc interface.

The existence of polarization effect of the first organic layers is in agreement with already mentioned studies [93] for CuPc deposited on n-type Si(100) covered with 3-4 nm thick oxide. However the direction of polarization seems to be opposite than that described in Ref. [93].

Accounting for the consideration in Section 5.1 and the band diagrams of substrates one can claim that there is no charge transfer over the interface. For revealing this phenomenon the assumptions of the model of thick oxide (see Section 5.1.3) proposed by Mizsei [193] and existence of polarization layer in CuPc enclosed in Ref. [93] seems to be helpful. Then, one can state that shift in vacuum level (for the CuPc layers up to 3 nm) observed in Figure 5. 33 corresponds to attraction of the negative charge by the film. The negative charging can be related to the polarization of the CuPc molecules; hence, with the layer thickness increase the polarization becomes weaker. The average negative

charge in the polarization layer compensates the positive charge collected at the interface. The latter is introduced by the negatively charged silicon under the oxide layer what is additionally enhanced by the CuPc layer influence (the blue areas at the band diagram).

In summary, although an isolated CuPc molecule has no net electric dipole, in the CuPc film the electric dipoles are produced by the gradient of the intermolecular electronic interaction along the surface normal due to the continuous change in the molecular orientation of the film. As a consequence an incomplete overlapping of the CuPc molecules results in a partial superposition of the  $\pi$  orbitals, which in succession may result in change of intermolecular interaction. This interaction affecting the  $\pi$ -electron system is affecting then the HOMO and LUMO positions as they are the features originating from  $\pi$ molecular orbitals. Such change in molecular orientation and its influence on intermolecular interactions was found already reported in Ref. [88,89].

### 5.3 Interaction of CuPc ultra-thin layer with ambient air

As a short introduction it has to be recalled from Chapter 2, that CuPc layers are widely applied as sensing layers for gas sensors. In this section the effects 12hour and one-year exposure to the ambient air are monitored with X-ray Photoemission and Ultraviolet Photoemission Spectroscopies. The studies are focused on the chemical and electronic properties (rather than directly sensing ones) and include chemical stability/durability examinations, molecular energy level shifts ("band bending-like"), work function, electron affinity and their variations upon the air exposure and one-year aging. The short-time (12 hours) provides information on short-term chemical reactivity and change of electronic properties, while the long-time one (1-year on the air) gives information on CuPc layer stability and durability. The studies reported within current section concern the 16-nm (final) CuPc layers deposited on n- and p-type Si (111) substrates covered with the native oxide only. For clarity the n-Si and p-Si will designate here the corresponding n- and p-type native substrates. The information collected within presented studies seems to be important for evaluation of sensing properties of CuPc layers.

### 5.4.1 Short-term exposure to ambient air

The 16-nm CuPc layers were investigated freshly after the evaporation and then after 12 hours of air exposure. Figure 5. 34 depicts the respective XPS survey spectra acquired from the CuPc on the n-Si substrate; the one on p-Si is identical except the negative binding energy (BE) shift of 0.15 eV. Upon the exposure, only the slight shifts towards lower BE occur; by 0.10 eV for the CuPc on the p-type substrate and 0.15 eV on the n-type one. There is no clear evidence for existence of an air-driven oxidation.



Figure 5. 34 XPS survey spectra (take-off angle of 90°) recorded from fresh 16-nm CuPc layer on n-type native Si (111) substrate (lower line) and after subsequent 12-hour air exposure (upper line).

Furthermore, the N1s, Cu2p and C1s peaks recorded at higher resolution have not been altered. They all exhibit shapes typical to copper phthalocyanine. For brevity, Figure 5. 35 shows only C1s spectra as the most representative ones for copper phthalocyanine.

The C1s decomposition was conducted (conducted with similar restrictions as those described in Sections 5.1 and 5.2.2) with fixed FWHM values and fixed area ratio of C-C to C-N components equal to 3:1. The C-C contribution is attributed to 24 aromatic carbons of the benzene rings in the CuPc molecule, C-N one corresponds to 8 pyrrole carbons linked to nitrogen, whereas  $S_{C-C}$  and  $S_{C-N}$  signals are shake-up satellites of the C-C and C-N species [75,203]. There are no differences between the peaks recorded just after the deposition due to the type of substrate doping except the BE shift of 0.15 eV towards higher binding energies observed at the n-type substrate. Interestingly, the layers are not prone to carbon contamination as no additional carbon species (C-OH, C-OOH or others) were detected. It corresponds well to previous findings concerning propagation of substrate carbon contamination during CuPc layer development described in Section 5.1 and in [III]. The binding energy shift for C1s is consistent with those obtained for the Cu2p and N1s peaks.

Next, the UPS analysis has been done in order to determine the electronic parameters of subsurface area of the CuPc layers and their evolution upon the air exposure. For organic semiconductors, the ionization energy ( $\Phi$ ), work function ( $\phi$ ) and electron affinity ( $\chi$ ) are interrelated with the already defined formulas (see Eq.(5. 8) [187]). Just for clarity, it is worth to recall that their calculation using Eq. (5. 8) requires firstly determining the energy cut-off of the UPS spectra (E<sub>0</sub>), the energy onset of the HOMO peak (E<sub>HOMO</sub>), and the surface Fermi level position (E<sub>F</sub>-E<sub>HOMO</sub>). It is also necessary to know the transport band gap (E<sub>g</sub>, here 2.3 eV) and h $\omega$  (the energy of incident photons; here 21.22 eV - He I radiation).

As a general remind from Sections 5.1 and 5.2, the  $E_F$  was obtained as the center of Fermi edge slope of the reference Ag sample placed on the same manipulator as that of a CuPc sample under investigations. The low kinetic energy cut-off ( $E_0$ ) was located by the energy-axis intersection of a straight line fitted to the slope of the spectra (between 30% and 70% of its height). The energy onset  $E_{HOMO}$  was determined by fitting the straight line to the slope of the HOMO peak [159].

The variation of obtained work functions ( $\varphi$ ), the ionization energies ( $\Phi$ ) and HOMO level position in respect to position of Fermi level (E<sub>F</sub>-E<sub>HOMO</sub> energy distance) at as-deposited 16-nm CuPc films on native Si due to different doping type is insignificant. Their values are 3.70 eV, 4.80 eV and 1.10 eV for CuPc on n-Si, and 3.75 eV, 4.75 eV and 1.00 eV for CuPc on p-Si, respectively. Similar CuPc layers but 20 nm thick and deposited on hydrogen-passivated Si(111) substrates with unspecified doping were analyzed by Gorgoi et al. during combined UPS and IPES (inverse photoemission spectroscopy) investigations [87]. They reported  $\varphi$ =3.88 ± 0.07 eV,  $\Phi$ =4.82 ± 0.07 eV and E<sub>F</sub> - E<sub>HOMO</sub>=0.94 eV, all of which correspond well to values obtained in the present studies.



Figure 5. 35 Decomposed C1s XPS peaks (TOA of 90°) recorded from as-deposited and air-exposed 16-nm CuPc layers on the n- (left panel) and the p-Si native Si (111) substrates (right panel).

The effects of the air exposure on the electronic parameters of CuPc layers can be readily observed using the procedure suggested by Gopel [160]. It allows to determine the changes in the work function ( $\Delta \varphi$ ), and in the surface band bending  $(e\Delta V_s)$  directly from the UPS spectra recorded before and after the exposure (without the need of calculations via Eq. 5.8). Indeed, the variation in the energy cut-off stems from the  $\Delta \varphi$ , while the shift in the HOMO onset is equivalent to  $e\Delta V_s$ . Furthermore, the change in electron affinity ( $\Delta x$ ) is equal to the difference between  $e\Delta V_s$  and  $\Delta \varphi$ . In this order, Figure 5. 36 presents the magnification of the HOMO and cut-off areas of UPS spectra obtained from the freshly deposited and air-exposed CuPc on both Si(111) substrates. Basing on these spectra for CuPc on n-Si (Figure 5. 36 a and b) the air exposure induced the increase in the work function by  $\Delta \varphi = 0.55 \text{ eV}$ , in the band bending by  $\Delta eV_s=0.45 \text{ eV}$  and, consequently, the decrease in the electron affinity by  $\Delta x = 0.10 \text{ eV}$ . So that, assuming invariant transport CuPc band gap of 2.3 eV [205], the change in the ionization energy equals  $\Delta \Phi$ =-0.10 eV. Uncertainties are within 0.10 eV. In the case of air-exposed CuPc/p-Si (Figure 5. 36 c and d) the work function increased by  $\Delta \varphi = 0.25$  eV and the band bending raised by  $\Delta eV_s=0.30 \text{ eV}$ . These values yield the electron affinity change by  $\Delta x=-0.05 \text{ eV}$  and then the shift in the ionization energy by  $\Delta \Phi$ =-0.05 eV.



Figure 5. 36 The magnification of the HOMO (a and c) and cut-off regions (b and d) of UPS spectra obtained for as-deposited and air-exposed 16-nm CuPc on n- and p-type native Si(111).

The changes inferred from UPS correspond qualitatively with the rigid shifts in the XPS spectra (mentioned above), but the values differ slightly. However, it should be taken into account that the sensitivity of XPS to detect sub-electronovolt shifts is much lower and the information depth is different than UPS.

All the electronic parameters are summarized in Figure 5. 37 which illustrates the electronic surface structure of CuPc on n- and p-Si(111) before and after the exposure to the ambient air. It has to be emphasized that the data presented here neither indicate Si/SiO<sub>2</sub>/CuPc interfacial effects (these are shown in Figure 5. 32) nor provide the depth information, but refer only to the surface properties of the final 16-nm CuPc films.

In practice, the surfaces of phthalocyanine films present a range of different adsorption sites corresponding to different crystal faces edges, corners and structural defect sites. These properties are a consequence of presence of the occupied electron states in the upper part of HOMO band. These states decide about important electrical properties of subsurface layer including band bending (or change in molecular energy levels in case of organics).

It is a known fact that the interaction of oxidizing gases present in the ambient air (like oxygen, nitrogen dioxide or ozone) with the  $\pi$ -electron network of phthalocyanines causes the transfer of electrons from CuPc ring to the gas molecule [210] which may be written as:

$$CuPc + oxidizing gas(i.e.O_2, NO_2, O_3) \rightarrow CuPc^{\delta_+} + O_2^{\delta_-}, NO_2^{\delta_-}, O_3^{\delta_-} \rightarrow \\ \rightarrow CuPc + O_2^{\delta_-}, NO_2^{\delta_-}, O_3^{\delta_-} + hole^{\delta_+}$$
(5.11)

Thus, it could be regarded that the ambient oxidizing gases in the form of free ions, for example  $O_2^-$ , are electrostatically stabilized in the vicinity of the surface. This negative surface charge is compensated by a positive charge in the spacecharge region of the CuPc thin film. This region possesses reduced electron concentration compared to the bulk and provokes the upwards surface energy band bending [211]. Nevertheless, in contrast to inorganic semiconductors, the deliberation on band bending in organic ones is still controversial [212] as already mentioned within this Dissertation. In order to avoid terminology misunderstanding, the band bending in any organic semiconductor should be treated rather as a local deviation from neutrality resulting from occupation functions for electrons, holes, dopants, and traps. This deviation leads to an additional potential energy for all states, which is graphically represented by bent bands [213,214,215].



Figure 5. 37 Electronic surface structure of the 16-nm CuPc thin films on p- (left panel) and n-type (right panel) native Si (111) substrates.

When electrically active ("charged") species originate from the ionosorbed oxidizing compounds, then the resulting change in the band bending is reflected only in the work function alteration, that is  $\Delta eV_s = \Delta \phi$  [211,216]. In present studies, this relation is fulfilled to a greater degree for the CuPc layer deposited on p-Si (in the range of measurement uncertainty) and thus it is speculated that the ionosorption phenomenon occurs at this layer. The formation of  $CuPc^+$  and

 $NO_2^-$  ions after the interaction of CuPc with NO<sub>2</sub> was actually observed experimentally by Basova et al. using Raman and IR spectroscopies [210].

In the case of CuPc thin films deposited on n-Si, besides the ionosorption reflected in the change in surface band bending, the weak variation in the surface electron affinity was also detected, i.e.  $\Delta \chi$ =-0.10 eV. Here, we probably observe surface species undergoing a localized charge transfer. This local charge transfer causes a potential drop across the electric double layer created by an adsorbed gas molecule and the CuPc surface and could indicate the creation of an effective surface dipole [216]. On the other hand, such a slight shift in electron affinity is on the same order as the uncertainty and could be neglected. However, 0.10-eV difference observe at CuPc/n-Si is still twice larger than that at CuPc/p-Si; the latter is under the resolution of the measurement system.

Additionally, the presence of water vapor in the ambient air should be accounted for. Some authors proposed few explanations concerning the effects of moisture on the organic materials. For example,  $H_2O$  can diffuse into the crevices in organic thin films to enhance the conductivity of the sample [217,218] or the adsorption of  $H_2O$  can modify their morphology [219]. However, Yan et al. in atomic force microscopy studies did not observe the morphology change in the specific case of CuPc after the exposure to the air for a week [220]. Instead, they proposed that  $H_2O$  assists  $O_2$  adsorption on CuPc in accordance with the following relation:

$$CuPc + O_2 + 2H_2O \rightarrow 4CuPc^{\delta_+} + 4OH^{\delta_-} \rightarrow 4CuPc + 4OH^{\delta_-} + hole^{4\delta_+}$$
(5.12)

Accordingly, one can conclude that the interaction between  $O_2$  associated with  $H_2O$  and CuPc will generate even more charge carriers, i.e. holes. Then, the increasing hole concentration in the space charge layer of the film induces the shift of the Fermi level towards the HOMO level of CuPc [220,221]. Such an effect is observed in the present work as the surface Fermi level after the air exposure has approached the HOMO onset by 0.30 eV for CuPc on p-Si and 0.45 eV on n-Si. Similar results were already obtained in employing photoemission yield spectroscopy (PYS) studies aimed to investigate the electronic properties of 500-nm-thick CuPc layers deposited on native Si(111) and exposed to the air [222]. In Ref. [222] one could find that the position of surface Fermi level of CuPc film shifted by 0.12 eV towards the top of the valence band, while the HOMO position remained stable.

Analyzing the changes in the work function and surface band bending, i.e.  $\Delta \phi=0.55 \text{ eV}$  and  $e\Delta V_s=0.45 \text{ eV}$  for CuPc/n-Si, and  $\Delta \phi=0.25 \text{ eV}$  and  $e\Delta V_s=0.30 \text{ eV}$  for CuPc/p-Si, it follows that upon the short-term air-exposure the copper phthalocyanine on n-type Si substrate interacts more strongly with oxidizing agents.

The exposure period and its influence on the electronic behavior of CuPc layers appear in literature in the context of air reactivity of the CuPc-based electronics [220,223,224,225]. The crucial role has been assigned to the ambient air composition that, besides nitrogen, oxygen and water, consists also of ozone, nitrogen oxide and dioxide whose concentrations naturally fluctuate. On the long-time scale these oxidizing gases could slowly and irreversibly oxidize the phthalocyanine molecules, initially at the surface sites and then due to the diffusion in the bulk. This process eventually leads to the chemical reaction

between oxygen agents and carbon or nitrogen bonds of phthalocyanine macrocycle which has been detected by the XPS method and observed in the literature before [224, 225].

### 5.4.2 Long time air exposure - aging effects

In this subsection the XPS experiments on the 16-nm CuPc layers deposited on nand p-type native Si (111) substrates are summarized. The data presented here show the comparison of *in-situ* layers, 12-hour air-exposed ones and the samples aged for a year in the air. Again the considerations relate to the "bulk" CuPc layer rather than the interfacial  $SiO_2/CuPc$  layer. This is evident as the CuPc nominal layer thickness is 16 nm, and although there are some structure differences between the layers on n- and p-type substrates, both films are rather compact and AFM/SEM studies do not show substrate areas which are not covered with the CuPc film.

Figure 5. 38 shows the XPS survey spectra of examined 16-nm CuPc layer deposited on n- (upper line) and p-type (lower line) substrates. The spectra are still characteristic for CuPc films - N1s, C1s and Cu2p peaks are present. The spectra however exhibit the significant differences in comparison to "as-deposited" samples and those air-exposed for 12 hours (see spectra of C1s peak in Figure 5. 40). Contrary to short-term exposure, the O1s peak has appeared due to the contamination caused by coexistence of molecular oxygen and water vapors from the atmosphere. No other contaminants were detected. Interestingly, the O1s peak intensity depends on the doping type of the substrate, which will be discussed later on.



Figure 5. 38 Survey spectra of 16-nm CuPc films on n- (black line) and p-type native Si (blue line) substrates after 1-year air exposure.

Figure 5. 39 reports the corresponding Cu2p spectra after long-term air exposure. The spectra are identical in shape as those taken "in situ" from asdeposited CuPc films (not shown). The lack of air-induced changes demonstrates the integrity of the CuPc film (without detectable molecular fragmentation) even after long-term exposure to the air. Indeed, the figure shows the characteristic shape of the pure "CuPc-like" Cu2p peak; the satellite shake-up peaks at 6.4 and 9.0 eV above the main peaks that are specific spectroscopic fingerprints of copper bonded to the four pyrrole nitrogens of the Pc molecule [196,75,61]. This finding indicates no degradation of the organic molecule, which is far from being obvious. Indeed, in the case of more interactive substrates like Si substrates without oxide passivation it has been evidenced that, upon air exposure, the significant fragmentation of the Pc molecules occurs with the loss of the central metal atom of a MePc molecule [226,227].



Figure 5. 39 Cu2p <sub>3/2</sub> XPS peak acquired for 16-nm CuPc film evaporated on n- and p-type native Si substrates. Spectra take after 1-year exposure to air.

Figure 5. 40 reports the C1s spectra acquired for as-deposited 16-nm CuPc layers on n- and p-Si together with 12-hours and 1-year air exposed ones. To facilitate comparisons, all the spectra were normalized to unity and aligned to the same binding energy value. Now the air-exposure effects can be detected and quantified by the C1s peak shape analysis. The C1s spectra of fresh layers on n- and p-Si almost perfectly superimpose. This is likely, as the films are rather similar and the buried interface effects for the thickness of 16 nm are expected to be rather negligible. Here, the shape of the C1s peak is typical of pure bulk phthalocyanine [227,202,203] with the main (secondary) peak related to the benzene (pyrrole) carbon atoms of the Pc molecule and the peaks at higher binding energy assigned to a shake-up satellite excitations [226] (see Figure 5. 20).

According to Ottaviano et al. [227] who has shown that oxygen incorporates into Pc-like molecules mostly through bonding with pyrrole C atoms, the effects of air exposure can be monitored by changes in the relative intensities of the C-C (benzene) and C-N (pyrrole) components of C1s peak. After 12-hour air exposure (see Figure 5. 40) there is a slight increase in the intensity of the C-N components for both n- and p-type substrates, the C1s spectra are still substantially alike. After one-year exposure to air, the C1s spectrum of the n-type sample is essentially superimposing with that acquired only after 12-hour air exposure. On the other hand, there is a dramatic modification of the C1s spectrum of the p-type sample with a strong increase of the C-N related secondary peak.

The uptake of oxygen and carbon into the CuPc thin films as a function of air-exposure time can be determined by quantitative XPS analysis based on the C1s, N1s, and O1s detailed acquisitions. N1s and O1s spectra are not reported for brevity, but the results of such a quantitative analysis are summarized in Table 5. 7. It is noteworthy that after 12 hours in the air, there is still no detectable oxygen while the C/N ratio has increased. This points to an initial contamination (with similar amount) of small gaseous molecules like CH<sub>4</sub>, or C<sub>2</sub>H<sub>6</sub> with a similar sticking probability on both (n-type and p-type) CuPc films. In line with the trends shown in Figure 5. 40 for the C1s data after one-year in the air, the ratios in the table clearly indicate that the CuPc on p-Si sample is by far more chemically reactive to adsorbed air species, both in terms of oxygen and of gases containing carbon atoms.

The oxygen uptake for the p-type substrate (on average 2 adsorbed oxygen atoms per Pc molecule) is about 2.5 times higher than for the n-type one (5-6 atoms/Pc). Hence, the difference in the intensities of O1s peaks of survey spectra in Figure 5. 38 are related to various degree of interaction between CuPc layers and oxidizing ambience (oxygen and water vapors). The various oxygen interaction and incorporation is due to somewhat different structure of these layers which has arisen due to different substrate doping (see Section 5.2). The C/N ratio increases from 4.4 (the expected for pure Pc molecule value is 4.0) to 5.1 for n- and 6.0 for p-type substrate.

	n-type substrate		p-type substrate	
Procedure	C/N	O/N	C/N	O/N
as deposited	4.4	-	4.4	-
air exposure 12h	4.6	-	4.7	-
air exposure 1year	5.1	0.24	6	0.67

Table 5. 7 C:N and O:N elemental ratios (as determined from quantitative XPS analysis) for 16-nm CuPc layer on n- and p-type Si substrates. Values are calculated from C1s, N1s, and O 1s spectra from: as-deposited, 12-hour and 1-year air-exposed layers.

Unfortunately the UPS data are not available for 1-year air-exposed samples. However, the supplementary experiment was conducted with the use of PYS method. Figure 5. 41 presents photoemission yield spectra obtained for discussed layers on n- and p-Si substrates. The data cannot be treated directly as the complete substitute of the UPS method due to reasons discussed in Section 4.2.3 (mainly the different information depth) and due to lack of the comparative data from "as-deposited" and 12-hour exposed samples. Nevertheless, the differences of electronic values detected by this method can point to some distinctions between reactivity of CuPc/n-Si and CuPc/p-Si samples.



Figure 5. 40 XPS C1s spectra for 16-nm CuPc films on n- and p- native Si substrates. Top panel depicts comparison of C1s spectra for as-deposited layers. Medium and bottom panels: (solid line) as-deposited, (dotted line) after 12-hour air exposure and (dashed line) after 1-year air exposure.

Indeed, as one can see there are considerable variations in work function and ionization energy values. They can be easily traced in Figure 5. 41 with the onset of the photoemission (black lines) and the onset of the Kane fit to the high-energy region of the data (green line), respectively. The work function is 4.65 eV for n-

type substrate and 4.80 eV for p-type one, while the corresponding ionization energy is 5.20 eV and 5.23 eV, respectively. These values cannot be directly and unanimously related with any of above discussed phenomena. However, the results are an indirect evidence for different behavior upon air exposure of copper phthalocyanine related to the substrate conductivity type. The lack of PYS data concerning freshly evaporated films does not allow the determination whether the variations are induced only by the substrate type before the exposition or by the different absorption of gaseous molecules by CuPc layers on n- and p-type Si substrates.



Figure 5. 41 Photoemission Yield spectra for CuPc 16 nm layers deposited on n-type native Si (a) and p-type native Si (b) substrates after long-term air exposure. Black lines corresponds to obtained experimental curve, greenish curves depict the effective density of occupied states while yellowish ones show the approximation made by Kane's function.

In general, due to the rather open structure of the organic crystals (here, particularly CuPc), oxygen and water vapor from ambient air likely diffuse into the Pc organic layers [220]. Indeed, the diffusion of oxygen and dissociation of water vapor into Pc crystallites is so probable, that it is at the origin of doping (an  $O_2$  plays a role of a doping agent for CuPc molecules) and gas sensitivity of considered ultra-thin layers. In particular, CuPc oxygen doping, through water vapor dissociation, admits the relation discussed earlier (5. 12) [220].

In terms of oxygen uptake, it is also well known that the α-phase of CuPc adsorbs a larger amount of the oxygen than any other phase [49,228,229]. Such property is one of the bases of the potential of CuPc as a gas sensing material.

Another phenomenon which needs to be considered here is that, if the CuPc deposition occurs in the presence of oxygen and water vapor a  $CuPc^+:O_2^-$  dipole layer is created at the substrate surface [230]. This is well observable in the case of phthalocyanine layers on p-type Si substrates (in contrast to the n-type ones). As one can find in Ref. [230], existence of such feature is likely increasing the substrate-molecule interaction and accordingly can hamper the molecule diffusivity onto the substrate surface. Nonetheless, above facts cannot explain completely experimental findings presented within this work.

The considered CuPc films deposited on n- and p-type substrates are all in the α-phase (as checked with XRD) so there is no reason for a preferential oxygen uptake in one case or another. Moreover, the CuPc thin film growth has been performed in UHV conditions, so the presence dipole layers due to water and oxygen at the substrate surface cannot be claimed as the origin of different molecule/substrate interaction strength.

The conclusion drawn above seems, at first sight, to contradict previous results on the short-term (12 hours) air exposure which indicated higher affinity to oxygen of less compact CuPc surface obtained on n-type Si substrate (see Section 5.3.1). However, taking into account the AFM results presented in Section 5.2.1 one can claim that network of densely packed crystallites exhibited by the CuPc on p-Si provides more active species for the prolonged bulk-like chemical reactions with oxidizing agents. Contrary, for the short 12-hour exposure, the open network present on n-Si/CuPc is more inclined to initial surface oxidation due to the provision of the electronically active sites.



## **SUMMARY AND CONCLUSIONS**

In the Thesis the CuPc layers with the thickness up to 16 nm were studied in order to characterize their properties relevant to application in organic electronics, photovoltaics and sensor devices. The ultra-thin CuPc films were thermally evaporated in UHV conditions onto n- and p-type Si (111) substrates. The substrates were covered with oxide layer formed both natively (Si/native-SiO<sub>2</sub>) and on the course of the standard RCA clean (Si/RCA-SiO<sub>2</sub>). Significantly, before the deposition the substrates were only pre-cleaned without further elaborate in-situ treatments aimed to remove contaminants. The investigations were focused on surface morphology, surface chemistry and surface electronic properties of CuPc layers and the determination of the energy level alignment at the Si/SiO<sub>2</sub>/CuPc double interface. In order to facilitate reproducibility and reliability of the data the Si substrates were carefully examined prior to the CuPc deposition. The examinations of the substrates and the layers were conducted with the same research methods (i.e. XPS, UPS, PYS, AFM, SEM and XRD) and within the same experimental systems so that the number of interfering factors was greatly reduced.

In the framework of this Thesis the following conclusions about the ultrathin CuPc layers deposited on the  $Si/SiO_2$  substrates are drawn:

- ⇒ The main difference between the native and RCA-prepared substrates is the oxide layer thickness (0.8 nm for native and 1.3 nm for RCA). They have almost atomically flat surface as shown by morphology AFM investigations. The oxide layer in both cases consists mainly of stable SiO<sub>2</sub>. Surface chemistry of native substrates is almost similar regardless of the type of conductivity. The RCA clean seems to remove more likely the carbon contaminants with OH groups from n- rather than p-type substrates. Furthermore, on the n-type substrates there is always more carbon contamination species independently of a treatment. Electronically, the native and RCA-prepared substrates vary in both the surface and Si/SiO<sub>2</sub> interface electronic structure. The native substrates tend to be consistent with theoretical thin-oxide model while the RCA ones with the thick-oxide model assumptions proposed by Mizsei;
- ⇒ SEM and AFM studies show that the sizes of crystallites forming CuPc layers on the native substrates are 50-100 nm when deposited on p-Si and 100-150 nm on n-Si. Furthermore, regardless of the origin of the oxide (native or RCA-formed) the CuPc layers on n-type substrates possess more open structure and lower specific surface (surface-to-volume crystallite ratio) than the ones on p-type substrates. The morphology investigations are supported by the photoemission studies (UPS) which indicate two different growth modes (standing and lying CuPc molecules) on the native substrates. In particular, the growth on the p-Si is more diversified, that is at very initial stage (below one monolayer) there are both adsorption orientations, then there is a region with gradual change towards the standing position, and finally (over approx. 10 nm) molecules are adsorbed only in the standing position forming densely packed crystallites. In contrary, on the n-Si the CuPc molecules are more preferentially deposited in the lying mode and with the increasing thickness the self rearrangement of the molecules results in

uniformly inclined crystallite orientation. In the case of RCA substrates, the growth mode appears to be the same no matter the doping type – there is a gradual rearrangement from the initial lying orientation to the final standing one.

- $\Rightarrow$  The impact of substrate doping on CuPc layers is reflected in the distance between CuPc molecules at the final stage of deposition. It is smaller for pthan n-type Si substrates. As the substrate conductivity interestingly affects the layer morphology, these observations constitute important hints for the fabrication of low-dimensional organic electronic structures and for subtle engineering of surface morphology;
- $\Rightarrow$  Carbon contaminants present on the native and RCA-treated Si substrates affects the chemistry of ultra-thin CuPc layers up to the thickness of about two monolayers (approx. 6 nm). Thicker CuPc layers are not chemically affected by these contaminants at all. Consequently, the elimination of extra in-situ treatments to remove the carbon species simplifies the CuPc deposition process without corrupting considerably the layer purity and stoichiometry unless the layer is thinner than 6 nm.
- ⇒ The electronic structure of Si/SiO<sub>2</sub>/CuPc double interface depends both on the origin of oxide layer (native or RCA-formed) and the conductivity type. In the case of CuPc deposited on the native Si substrates, there is a small interface dipole effect as inferred from the photoemission studies. The directions of those dipoles are opposite for n- and p-type doping, which indicates the different direction of negative charge displacement. The displacement is towards Si substrate for the former and CuPc layer for the latter. After CuPc deposition on the RCA-treated samples the dipole is not observed at the interface. Instead, there is only a slight difference in the strength of the polarization effect between n- and p-type sample suggesting that the polarization layer exists in the CuPc film;
- ⇒ The short-term (12-hour) air exposure does not affect the surface chemistry (or the changes are below the detection level of XPS) of the CuPc layers as inferred from studies of 16-nm CuPc layers deposited on p- and n-type native Si(111) substrates. However, the UPS results indicate the air-driven increase in the CuPc work function by 0.55 eV on n- and 0.25 eV on p-Si. The corresponding band bending changes were 0.45 eV and 0.30 eV, respectively. A slight dipole effect at CuPc on n-Si was found after the exposure.. The changes in electronic parameters of 16-nm-thick layer are provoked by ambient air-introduced ionic species and the subsequent generation of charge carriers related to the adsorption of oxidizing gases on the CuPc surface;
- $\Rightarrow$  The effects of long-term (one-year) air exposure are evidently more pronounced for CuPc layers deposited on native p-Si at which greater carbon and oxygen contents are observed. This is due to the difference in the surfaceto-volume ratio of the CuPc crystallites between the films deposited on n- and

p-type native substrates. Nevertheless, XPS examinations show that 16-nmthick CuPc films are chemically stable and durable upon this long term exposure to air.

The directions for further investigations of examined within this Thesis structures should include the optimization of the CuPc layer deposition process (e.g. evaporation and substrate temperature) as the parameters having crucial impact on the surface morphology. Further, the possible correlations between morphology and electronic properties should be studied in details. The thorough analysis of substrate/overlayer interface electronics should be performed and the charge flow ought to be modeled as they are crucial for optimization of future organic devices and their performance. More systematic studies of the environmental influence on the Si/SiO<sub>2</sub>/CuPc structures are also necessary particularly for the operation of gas sensors based on CuPc thin films and in the aspect of time-durability of organic electronic devices.

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