



Autor: Anna Krzykawska

Nr albumu: 1079112

Afiliacja: Zakład Fizyki Nanostruktur i Nanotechnologii, Wydział Fizyki, Astronomii
i Informatyki Stosowanej, Uniwersytet Jagielloński, Kraków

Optimization of the Structure and Stability of Self-Assembled Monolayers of Biphenyl-Substituted Fatty Acid

Keywords: nanotechnology; self-assembled monolayer; organic molecule

The objective of this PhD thesis was to investigate the formation and optimisation of the structure and stability of organic self-assembled monolayers consisting of aliphatic-aromatic hybrid molecules with a carboxylic bonding group on Ag(111) substrates. As a first step, the structure of monolayers obtained for analogous molecules bound to the silver surface via a thiol or carboxylic group, in which a short aliphatic linker separates the binding group from the biphenyl aromatic moiety ($\text{CH}_3\text{-(C}_6\text{H}_4)_2\text{(CH}_2)_2\text{-SH}$ and $\text{H-(C}_6\text{H}_4)_2\text{(CH}_2)_2\text{-COOH}$) was compared. Then, in order to understand the influence of the aliphatic linker, this study was extended to a homologous series of carboxylic acids differing in the length of this linker defined by the number n of methylene groups ($\text{H-(C}_6\text{H}_4)_2\text{(CH}_2)_n\text{COOH}$, for $n = 1\text{--}4$). The third part of the work compares the structure and stability of analogous purely aromatic monolayers with a carboxyl and thiol bonding group for which the number $n = 0$ ($\text{H-(C}_6\text{H}_4)_2\text{-COOH}$ and $\text{H-(C}_6\text{H}_4)_2\text{-SH}$). The fourth, and final, part of the work consists of an extended analysis of the thermal stability of thiol and carboxyl monolayers on the silver surface, for which the borderline cases of purely aliphatic monolayers ($\text{C}_{16}\text{H}_{33}\text{COOH}$ and $\text{C}_{16}\text{H}_{33}\text{SH}$) as well as hybrid monolayers with increased length of the aliphatic linker ($n = 5$ and 6) were used from the point of view of the present study. Through detailed spectroscopic analysis (IRRAS reflectance-absorption infrared spectroscopy, X-ray photoelectron spectroscopy XPS) and microscopic analysis (scanning tunneling spectroscopy STM), information was provided on the formation of chemically pure and densely packed monolayers formed on the basis of the carboxylic group, which are formed 300 times faster and have about 10 times lower defect concentration compared to analogous thiol-based monolayers. It was shown that both the alignment of the molecules in the monolayer, the conformation of the binding group, as well as the packing density show an extremely strong pairing effect due to the parameter n leading for even monolayers to the formation of crystalline ordered structures, and for odd ones to disordered so-called quasi-ordered structures. By spectrometric analysis (temperature-programmed secondary ion mass spectrometry TP-SIMS), it was shown that the thermal stability of carboxyls and thiols changes dramatically depending on whether the binding group is linked to the rest of the molecule via an aromatic or an aliphatic group, and that the thermal stability of these systems does not depend directly on the length of the molecules (intermolecular interactions), but is controlled by the stability of the weakest bond at the molecule-metal interface. It has also been shown that in hybrid systems, the connection of the binding group through the aliphatic chain to the aromatic moiety exhibits a very strong and rapidly damped pairing effect on the thermal stability of the system. The results obtained for this work were used, among other things, to create a new type of chemically pure carbon nanomembranes by

electron beam irradiation and to extend the research on the use of the SIMS technique to study the stability of chemical bonds in SAM monolayers.