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Badanie efektów morfologicznych  
podczas bombardowania powierzchni  
atomami oraz klastrami o energiach  
keV-owych

Praca doktorska  
na kierunku Fizyka

Praca wykonana pod kierunkiem  
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## Oświadczenie autora pracy

Ja niżej podpisany Dawid Maciążek (nr indeksu: 1064310) doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. „Badanie efektów morfologicznych podczas bombardowania powierzchni atomami oraz klastrami o energiach keV-owych” jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem prof. dr. hab. Zbigniewa Postawy. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

Jestem świadom, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

.....

Kraków, dnia

.....

Podpis autora pracy

## Oświadczenie kierującego pracą

Potwierdzam, że niniejsza praca została przygotowana pod moim kierunkiem i kwalifikuje się do przedstawienia jej w postępowaniu o nadanie tytułu zawodowego.

.....

Kraków, dnia

.....

Podpis kierującego pracą

# Podziękowania

*Przede wszystkim chciałbym podziękować mojemu promotorowi prof. dr hab. Zbigniewowi Postawie za zaangażowanie oraz wsparcie we wszystkich moich naukowych dążeniach. Szczególnie doceniam udostępnione mi możliwości rozwoju takie jak staże, wyjazdy oraz współprace międzynarodowe.*

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# Rozdział 1

## Wstęp

### 1.1 Forma pracy doktorskiej

Niniejsza rozprawa została napisana jako podsumowanie wcześniejszych działań naukowych opublikowanych w następujących artykułach [1–7]:

1. **Dawid Maciążek**, Robert J. Paruch, Zbigniew Postawa, Barbara J. Garrison „*Micro- and Macroscopic Modeling of Sputter Depth Profiling*“ J. Phys. Chem. C, 2016, 120, 25473-25480
2. Sloan J. Lindsey, Gerhard Hobler, **Dawid Maciążek**, Zbigniew Postawa „*Simple model of surface roughness for binary collision sputtering simulations*“ Nucl. Instrum. Methods Phys. Res., 2017, 393, 17-21
3. Hua Tian, **Dawid Maciążek**, Zbigniew Postawa, Barbara J. Garrison, Nicholas Winograd „*C-O Bond Dissociation and Induced Chemical Ionization Using High Energy  $(\text{CO}_2)_n^+$  Gas Cluster Ion Beam*“ J. Am. Soc. Mass Spectrom., 2018, 30, 476-481
4. Gerhard Hobler, **Dawid Maciążek**, Zbigniew Postawa „*Crater function moments: Role of implanted noble gas atoms*“ Phys. Rev. B, 2018, 97, 155307
5. Gerhard Hobler, **Dawid Maciążek**, Zbigniew Postawa „*Ion bombardment induced atom redistribution in amorphous targets: MD versus BCA*“ Nucl. Instrum. Methods Phys. Res., 2019, 447, 30-33

6. Nunzio Tuccitto, **Dawid Maciążek**, Zbigniew Postawa, Antonino Licciardello „*MD-Based Transport and Reaction Model for the Simulation of SIMS Depth Profiles of Molecular Targets*“. Phys. Chem. C, 2019, 123, 20188–20194
7. **Dawid Maciążek**, Michał Kański, Zbigniew Postawa „*Intuitive Model of Surface Modification Induced by Cluster Ion Beams*“ Anal. Chem., 2020, 92, 10, 7349–7353

Praca podzielona jest na trzy części. W pierwszej części przedstawiam podejmowane przeze mnie zagadnienie badawcze wraz z kontekstem naukowym. W drugiej części po krótko opisuję artykuły składające się na tę pracę. W ostatniej części zamieściłem przedruki opisywanych publikacji, które umożliwiają dogłębne zapoznanie się z treścią opisywanych prac.

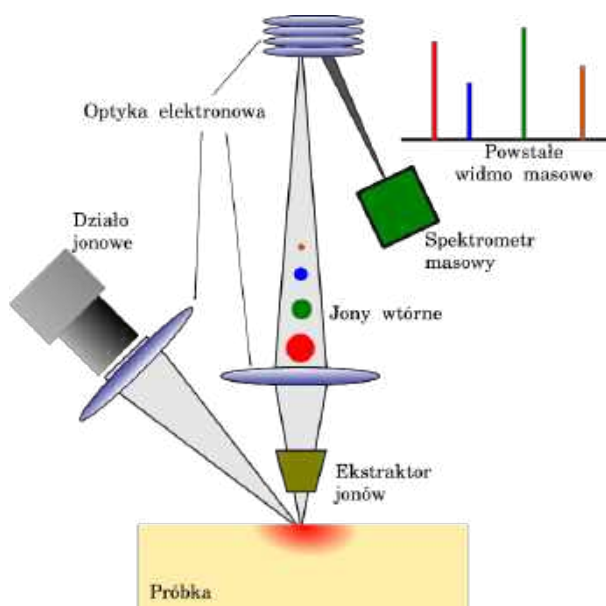
## 1.2 Zagadnienie badawcze

Celem niniejszej pracy doktorskiej jest zbadanie efektów morfologicznych (kształt powierzchni próbki) pojawiających się podczas bombardowania powierzchni pociskami atomowymi oraz klastrowymi. Ponieważ przyczynowość tych efektów może działać w dwie strony, opis moich działań naukowych podzieliłem na dwie sekcje tematyczne, które zgłębiają następujące zagadnienia:

- Jak **morfologia** próbki *wpływa* na zachodzący na jej powierzchni proces **bombardowania** i emisji cząstek.
- Jak **bombardowanie** próbki *wpływa* na wytwarzaną na jej powierzchni **morfologię**.

Zrozumienie wyżej przedstawionych zagadnień jest bardzo istotne, ponieważ bombardowanie wiązką jonową jest fundamentalną częścią wielu technik badawczych oraz procesów technologicznych [8]. Przykładem takiej techniki badawczej jest spektrometria masowa jonów wtórnych (SIMS), która jest najczulszą metodą badania składu chemicznego powierzchni [9]. W tym przypadku wiązka jonów służy do emisji atomów lub molekuł próbki z wybranego obszaru na jej powierzchni. Wyemitowane na skutek uderzenia pocisku zjonizowane cząstki trafiają następnie do spektrometru masowego, gdzie mierzone jest widmo masowe. Schematyczne przedstawienie tej techniki znajduje się na **rysunku 1.1**.

W standardowym układzie mierzymy tylko te cząstki, które uległy jonizacji podczas uderzenia. Dostępna jest również odmiana tej techniki, w której wyemitowane cząstki obojętne są jonizowane za pomocą wiązki laserowej [9]. Kolejnym przykładem zastosowania wiązki jonów jest usuwanie materiału z badanej próbki, aby odsłonić jej wnętrze. Jeśli połączymy ten proces z technikami takimi jak spektroskopia fotoelektronów (XPS) [8], spektroskopia elektronów Augera (AES) [8] lub wspomniany SIMS, to uzyskamy możliwość zbierania informacji o składzie chemicznym z całej objętości próbki. Podejście takie nazywa się profilowaniem głębokościowym. Najlepszym przykładem wykorzystania wiązki jonowej w przemyśle jest proces domieszkowania półprzewodników, który jest jednym z kroków podczas wytwarzania układów scalonych [8], które są podstawą dzisiejszej cywilizacji.



**Rysunek 1.1:** Schemat działania aparatury SIMS z detektorem czasu przelotu.

### 1.3 Kontekst naukowy

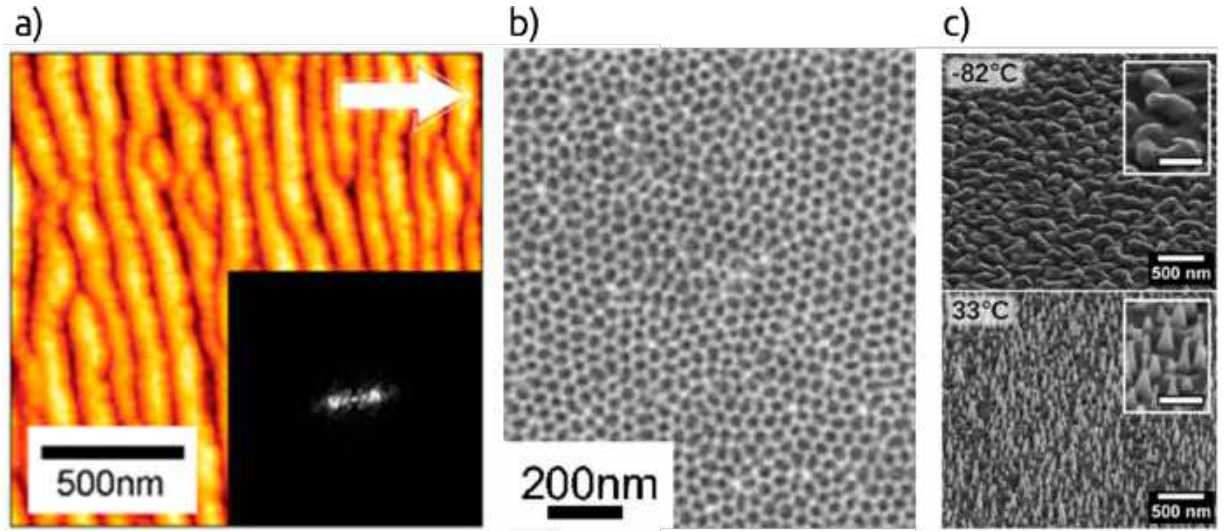
W procesie bombardowania powierzchni pociskami atomowymi lub klastrowymi dochodzi do szeregu zjawisk zachodzących na powierzchni bombardowanej próbki pod wpływem uderzenia pocisku. Do najważniejszych z nich należą rozpylanie, jonizacja oraz redystrybucja masy. Rozpylanie opisuje zjawisko erozji próbki z jednoczesną emisją cząstek stanowiących jej integralną część przed uderzeniem. Przyczyną tego zjawiska jest deponowanie energii kinetycznej pocisku w rozpylanym materiale. Energia ta może być zdeponowana bezpośrednio do układu jądrowego na skutek elastycznych zderzeń pomiędzy atomami pocisku oraz próbki, jak i do struktury elektronowej układu [10]. Jeśli ilość elastycznych zderzeń wywołanych bombardowaniem jest na tyle mała, że możemy założyć iż zderzenia następują wyłącznie pomiędzy atomem będącym w spoczynku a atomem obdarzonym energią kinetyczną, to mówimy wtedy o liniowej kaskadzie zderzeń [10]. Kiedy to założenie

przestaje obowiązywać, a do zderzeń dochodzi również między atomami w ruchu, to mówimy wtedy o efektach nieliniowych [10]. W trakcie propagacji kaskady zderzeń, na skutek wzbudzeń elektronowych część atomów lub molekuł ulega jonizacji [10]. Jeśli taka cząstka zostanie wyemitowana nim utraci uzyskany ładunek, to nazywamy ją jonem wtórnym. Propagująca się w próbce kaskada zderzeń prowadzi również do trwałego przemieszczenia się materiału w jej obrębie w procesie nazywanym redystrybucją masy.

Ważnym czynnikiem dyktującym przebieg procesu bombardowania jest typ stosowanego pocisku. Pociskami mogą być pojedyncze atomy, molekuły, klastry atomowe oraz klastry molekularne. Wybór pocisku dla danego eksperymentu ma wpływ na współczynnik rozpylania, prawdopodobieństwo jonizacji oraz fragmentację molekuł bombardowanego podłoża [11]. Ważnym momentem w historii rozwoju dział jonowych generujących wspomniane pociski było wprowadzenie dział klastrowych [11]. Redukcja fragmentacji molekuł podłoża oraz mechanizm „samoczyszczenia” (self-cleaning) w porównaniu do pocisków mono-atomowych miała bardzo duży wpływ na jakość uzyskiwanych profili głębokościowych [11].

Morfologia bombardowanej powierzchni ma znaczący wpływ na zachodzące na niej procesy. Wielkość amplitudy, jaki i kształt struktur na powierzchni wpływają na współczynnik rozpylania [2], rozkład kątowy emitowanych cząsteczek [12], prawdopodobieństwo dysocjacji molekuł pocisku [3] oraz jakość uzyskiwanych profili głębokościowych [12]. Próbka może posiadać określoną morfologię przed rozpoczęciem procesu bombardowania, jak również morfologia może być na jej powierzchni indukowana na skutek tegoż bombardowania. Bardzo ciekawym przykładem takiego zjawiska jest powstawanie samoorganizujących się struktur wykazujących uporządkowanie dalekiego zasięgu [13]. Fascynujące w tym procesie jest to, że z perspektywy powierzchni miejsce uderzenia pocisku jest całkowicie losowe, natomiast powstające na skutek tych pojedynczych uderzeń struktury cechują się uporządkowaniem w skali znacznie większej niż skala pojedynczego uderzenia. Różne przykłady takiego zjawiska przedstawione są na **rysunku 1.2**. Strukturami, które mogą powstać są: nano-zmarszczki [14–16] (nanoripples) nazywane również riplami, które wyglądem przypominają makroskopowe falki powstające na piasku pod wpływem działania wiatru, nano-dziury (nanohole) [17], nano-kropki (nanodots) [14] oraz nano-pilary [18].

Ponieważ proces bombardowania jest bardzo złożony, jego opis za pomocą modeli analitycznych nie daje pełnego obrazu sytuacji. Do pełnego zrozumienia zjawisk zachodzących

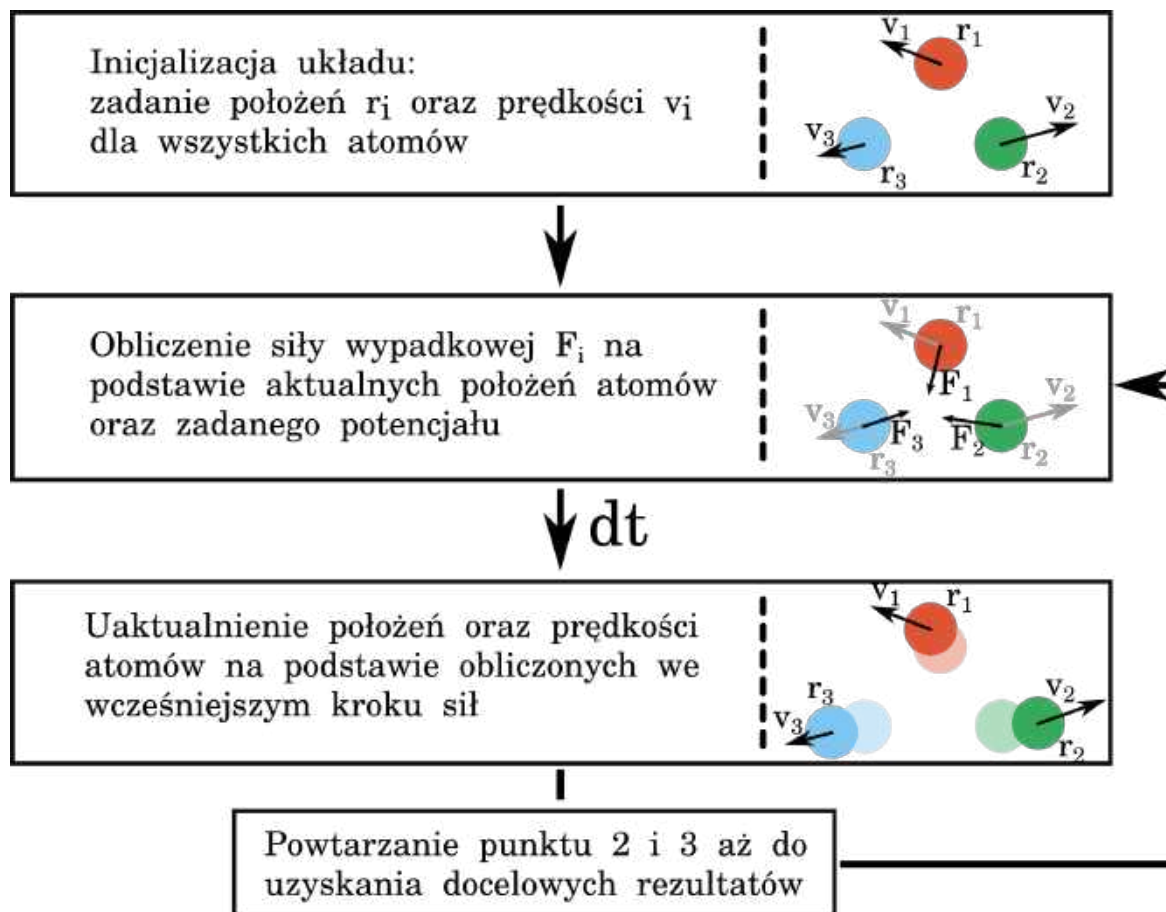


**Rysunek 1.2:** Przykłady samoorganizacji powierzchni indukowanej wiązką jonową. a) Riple na powierzchni złota bombardowanej wiązką  $\text{Ar}_{3000}$  pod kątem  $\theta=60^\circ$   $E_k=30$  keV [16]. b) Nano-dziury na powierzchni germanu bombardowanej wiązką galu pod kątem  $\theta=0^\circ$   $E_k=5$  keV [17]. c) Nano-pilary na powierzchni  $\text{InSb}(001)$  bombardowana wiązką argonu pod kątem  $\theta=0^\circ$   $E_k=3$  keV [18]

na powierzchni próbki niezbędne jest zastosowanie metod numerycznych, takich jak symulacje komputerowe. Przykładem metody, która wykorzystywana jest do modelowania zjawiska bombardowania jest dynamika molekularna. W dynamice molekularnej modelowane atomy są reprezentowane jako punkty materialne o określonej masie, których ruch dyktowany jest drugą zasadą dynamiki Newtona [19]. Sprowadza się to do tego, że aby uzyskać informację o położeniach tych atomów w czasie, co nazywamy trajektorią układu, należy rozwiązać sprzężony układ klasycznych równań ruchu Newtona:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \sum_{i < j} \vec{F}_{ij}, \quad i, j = 1, \dots, N, \quad (1.1)$$

gdzie  $N$  to liczba modelowanych cząstek,  $m_i$  jest masą atomu  $i$ ,  $F_{ij}$  jest siłą jaką atom  $i$  oddziałuje na atom  $j$  (wyrażenie  $\sum_{i < j} \vec{F}_{ij}$  jest po prostu siłą wypadkową działającą na atom  $i$ ). W toku symulacji, siły obliczane są na podstawie funkcji nazywanej potencjałem oddziaływania [19]. Właściwe zdefiniowanie tej funkcji jest krytycznym elementem całej metody, ponieważ od tego będzie zależało, w jakim stopniu wykonywane symulacje odzwierciedlać będą rzeczywistość. Na szczęście, w literaturze istnieje bogata baza zdefiniowanych i przetestowanych potencjałów dla szerokiej gamy związków i struktur.



**Rysunek 1.3:** Schematyczne przedstawienie algorytmu dynamiki molekularnej.

Algorytm dynamiki molekularnej można sprowadzić do trzech następujących po sobie kroków, których schemat znajduje się na **rysunku 1.3**. W pierwszym kroku definiujemy układ, zadajemy liczbę atomów, ich położenia oraz prędkości początkowe. Proces ten nazywa się ustaleniem warunków początkowych. W następnym kroku obliczamy wypadkową siłę działającą na każdy atom, korzystając z zadanego potencjału. Trzecim krokiem jest rozwiązanie równań Newtona i uaktualnienie położeń oraz prędkości wszystkich atomów. Z perspektywy układu powoduje to progresję czasu o zadaną wartość  $dt$ . Parametr  $dt$  nazywany jest krokiem czasowym. Powtarzamy iteracyjnie krok drugi i trzeci tak długo, aż całkowity czas symulacji badanego zjawiska będzie spełniał nasze oczekiwania.

Pomimo prostoty koncepcji algorytmu dynamiki molekularnej, napisanie implementacji tego algorytmu jest zadaniem bardzo trudnym. Na szczęście nie musimy tego robić, ponieważ dziedzina dynamiki molekularnej jest już bardzo dojrzałą dyscypliną. Istnieje wiele publicznie dostępnych programów służących do przeprowadzania symulacji tą metodą. Programy te tworzone są przez grupy badawcze z całego świata. W moich badaniach

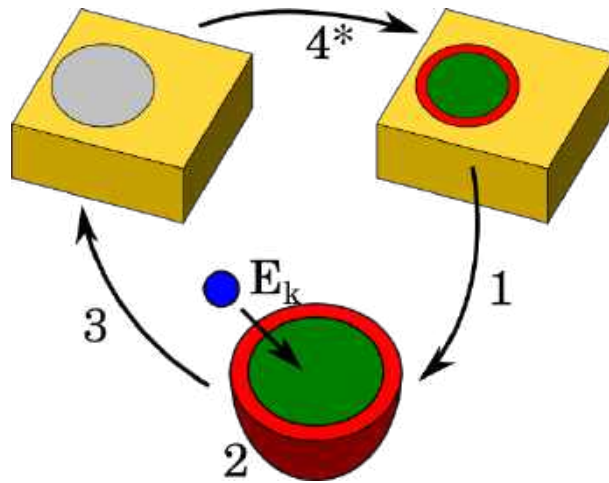
wykorzystuję program LAMMPS [20], który jest aktywnie rozwijany od ponad 25 lat przez wiele grup badawczych, włączając naszą grupę. Jego największymi atutami są mnogość dostępnych potencjałów oraz bardzo efektywna implementacja symulacji uruchamianych na wielu procesorach. LAMMPS do rozwiązywania równań ruchu wykorzystuje wariant prędkościowy algorytmu Verleta [21].

Przed rozpoczęciem symulacji, musimy podjąć szereg decyzji dotyczących założeń oraz uproszczeń, które przyjmujemy tworząc model badanej próbki. Należą do nich: kształt próbki, warunki brzegowe, struktura wewnętrzna próbki i użyte potencjały. Ponieważ jesteśmy ograniczeni mocą obliczeniową, nie możemy stworzyć dowolnie wielkiego układu. W praktyce górny limit na liczbę symulowanych atomów jest rzędu kilku milionów atomów, co przekłada się na wymiary próbki rzędu dziesiątek nanometrów.

Wybór kształtu geometrycznego próbki zależy od typu symulacji jaki chcemy przeprowadzić. W przypadku pojedynczego uderzenia stosowałem kształt półkuli. Dla takiego układu symulacja jest przeprowadzana w taki sposób, że bombardujące pociski uderzały w płaską stronę. Takie rozwiązanie pozwala na swobodną propagację fali uderzeniowej powstałej na skutek uderzenia, która następnie jest wygaszana na brzegach półkuli poprzez odpowiednio nałożone warunki brzegowe [22]. Natomiast jeśli chcemy badać efekt wielu uderzeń, to w takim przypadku musimy stworzyć większą próbkę o prostopadłościennym kształcie. Próbka ta powinna mieć okresowe warunki brzegowe w kierunkach równoległych do powierzchni. W moich badaniach wykorzystywałem procedurę „divide and conquer“ dla symulacji rozpylania [23], którego schemat przedstawiony jest na **rysunku 1.4**. W tej metodzie przed rozpoczęciem symulacji wycinamy z niej wyżej wspomnianą półkulę i przeprowadzamy symulację tak, jak dla pojedynczego uderzenia. Po zakończeniu, zmodyfikowaną uderzeniem półkulę wklejamy z powrotem w miejsce wycięcia.

Schemat tworzenia struktury wewnętrznej próbki zależy od tego, czy chcemy otrzymać próbkę krystaliczną czy amorficzną. W pierwszym przypadku wygenerowanie atomów składających się na próbkę jest bardzo proste. Można to zrealizować poprzez odpowiednie kopiowanie i translację atomów lub molekuł [19]. Dla układów amorficznych sytuacja się komplikuje, ponieważ z samej definicji, układy te nie powinny mieć uporządkowania dalekiego zasięgu. Generowanie tego typu układów realizuje się w dwóch krokach. W pierwszym tworzymy układ krystaliczny o oczekiwanej gęstości. Następnie przeprowadzamy symulację, w której stopniowo podnosimy temperaturę aż do zadanej wartości.

Utrzymujemy symulowany układ w podwyższonej temperaturze aż ulegnie amorfizacji. Po tym kroku stopniowo ochładzamy układ do początkowej temperatury w efekcie otrzymując próbkę, którą możemy wykorzystać w symulacjach rozpylania.

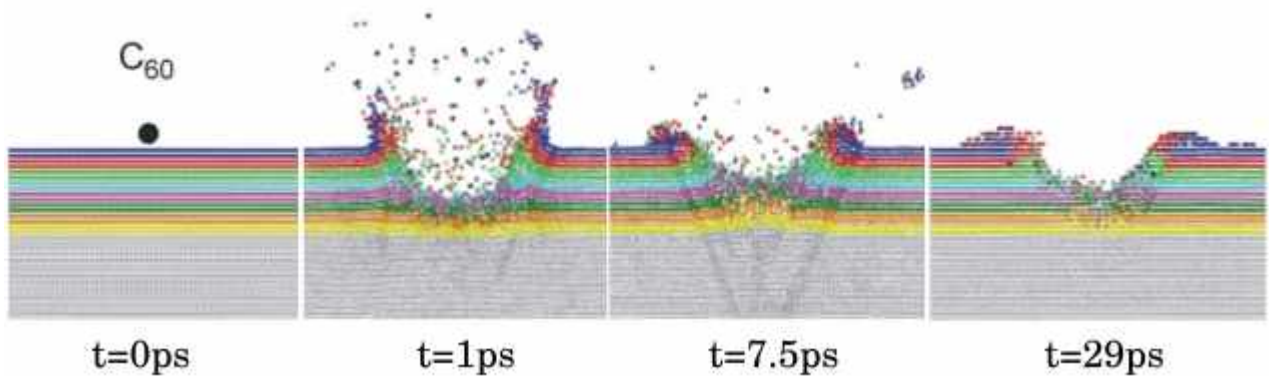


**Rysunek 1.4:** Schemat procedury „divide and conquer“ dla symulacji procesu ciągłego rozpylania [23]. 1. Wycięcie fragmentu próbki, 2. przeprowadzenie symulacji, 3. wklejenie zmodyfikowanego fragmentu, 4\*. powtarzanie procesu do uzyskania odpowiedniej fluencji.

W kontekście symulacji komputerowych mówimy o potencjale oraz jego parametryzacji. Potencjał to formuły matematyczne, natomiast parametryzacja to już konkretne wartości liczbowe wykorzystywane w tych formułach. Raz definiowany potencjał może zostać sparametryzowany przez inne grupy badawcze dla różnego typu materiałów. Informację o tym, czy dana parametryzacja potencjału nadaje się do naszych celów, możemy znaleźć w publikacji opisującej proces jej tworzenia. Poniżej przedstawiam listę potencjałów, które wykorzystywałem w moich badaniach:

- Potencjał *ZBL* [24]: służy do opisu oddziaływań bliskiego zasięgu, ma charakter wyłącznie odpychający.
- Potencjał *Lennard-Jones* [25]: wykorzystywany do opisu oddziaływań pomiędzy atomami gazów szlachetnych, na przykład w symulacjach uderzenia klastrowego pocisku gazowego.
- Potencjał *Embedded-atom method* (EAM) [26]: stosowany do opisu oddziaływań w metalach.

- Potencjał *Tersoff* [27]: używany przede wszystkim do opisu oddziaływań w półprzewodnikach.
- Potencjał typu *ReaxFF* [28]: potencjał o bardzo szerokich możliwościach, stosowany głównie do opisu układów organicznych. Niestety jego skomplikowana formuła matematyczna powoduje, że koszt obliczeniowy jest parokrotnie większy niż w wyżej opisanych potencjałach.



**Rysunek 1.5:** Wizualizacja przebiegu uderzenia 15 keV C<sub>60</sub> w próbkę srebra [29].

Typowy przebieg symulacji uderzenia pocisku klastrowego w próbkę pokazany jest na **rysunku 1.5**, w tym przykładzie pocisk C<sub>60</sub> o energii 15 keV uderza w powierzchnię srebra pod kątem 0° w stosunku do normalnej. W pierwszych paru pikosekundach obserwujemy bardzo dynamiczne zachowanie się układu na skutek depozycji energii kinetycznej pocisku. Część atomów podłoża uzyskuje energię kinetyczną na tyle dużą, że przewyższa energię wiązania i zostaje wyemitowana. Uderzenie powoduje zdefektowanie powierzchni oraz przemieszczenia atomów w stosunku do ich początkowej pozycji, co nazywamy mieszaniem jonowym. W powyższym przykładzie widać, że po upływie 30 ps wszystkie interesujące nas zjawiska dobiegły końca, co jest równoznaczne z zakończeniem symulacji.

## Rozdział 2

# Opis badań składających się na pracę doktorską

W tej części pracy przedstawiam opis prowadzonych przez mnie badań. Opis podzielony jest na dwie sekcje tematyczne. W pierwszej sekcji zgłębiam temat wpływu morfologii próbki na procesy zachodzące podczas bombardowania. Druga sekcja jest naturalną kontynuacją tego tematu, gdzie badam zjawiska prowadzące do powstania oraz ewolucji morfologii próbki podczas bombardowania. Każda z sekcji bazuje na skróconym opisie publikacji zawierającej opublikowane wyniki moich badań. Publikacje te ujęte są w osobnej podsekcji, aby umożliwić łatwe nawigowanie pomiędzy skróconym opisem a publikacją źródłową. Dla każdej z publikacji przedstawiam lokalny oraz globalny kontekst naukowy prowadzonych badań. Następnie opisuję zastosowaną przeze mnie metodologię w części badań, za którą byłem odpowiedzialny. Ostatnim elementem każdego opisu jest przedstawienie głównych wniosków, które były efektem przeprowadzonych badań.

### 2.1 Wpływ morfologii powierzchni na proces bombardowania

#### 2.1.1 Modelowanie profili głębokościowych

Sekcja oparta na publikacji: „*Micro- and Macroscopic Modeling of Sputter Depth Profiling*“.

## Motywacja

Ważnym narzędziem do badania trójwymiarowego składu chemicznego próbek jest profilowanie głębokościowe metodą SIMS. W technice tej za pomocą jonowej wiązki rozpylającej, w miarę postępu eksperymentu odsłania się coraz głębiej leżące obszary badanej próbki. Równocześnie odsłonięta powierzchnia próbki bombardowana jest wiązką analizującą. Prowadzi to do emisji jonów wtórnych, których intensywność mierzona jest za pomocą spektrometru mas (układ SIMS). Intensywność mierzonych jonów w funkcji czasu, lub po odpowiednich przeliczeniach w funkcji głębokości, nazywamy profilem głębokościowym.

Pierwsze przeprowadzone przeze mnie badania miały na celu określenie wpływu morfologii powierzchni na proces uzyskiwania profili głębokościowych. Jeśli chcielibyśmy modelować proces profilowania głębokościowego bezpośrednio za pomocą dynamiki molekularnej, szybko przekonamy się że jest to technicznie niewykonywalne. Przykładowo, profilowanie głębokościowe próbki NiCr o grubości 500 nm za pomocą wiązki 15 keV  $\text{Ga}^+$  [30], wymaga osiągnięcia fluencji o wartości  $3.6 \cdot 10^{19} \frac{\text{jonow}}{\text{cm}^2}$ . Aby uniknąć artefaktów symulacyjnych związanych ze zbyt małą próbką, powierzchnia modelowanej próbki musi mieć wymiary co najmniej 10 nm  $\times$  10 nm, co przy wcześniej wspomnianej fluencji, daje konieczność wykonania  $1.5 \cdot 10^{12}$  symulacji. Jeśli za czas jednej symulacji przyjmiemy jedną godzinę, co jest możliwe tylko w przypadku najprostszych potencjałów, daje nam to ponad 11 milionów lat!

Jednym ze sposobów pokonania tego ograniczenia jest podział badanego zjawiska na dwie domeny czasowe. Pierwsza domena czasowa opisuje efekty związane z uderzeniem pojedynczego pocisku. Dla tego przypadku, za pomocą symulacji metodą dynamiki molekularnej, uzyskałem ilościowe dane o współczynniku rozpylania oraz o mieszaniu materiału wywołanym uderzeniem. W drugiej domenie czasowej, wykorzystałem dane uzyskane w poprzednim kroku do sparametryzowania cząstkowego równania różniczkowego adwekcji-dyfuzji zaproponowanego w publikacji Tuccitto [31]:

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left( D(x) \frac{\partial c}{\partial x} \right), \quad (2.1)$$

gdzie  $c(x, t)$  to stężenie modelowanego składnika w próbce na głębokości  $x$  oraz w czasie  $t$ ,  $v$  to aktualny współczynnik rozpylania,  $D(x)$  to funkcja opisująca mieszanie jonowe, wywołane uderzeniem pocisku. Jeśli modelujemy próbkę składającą się z wielu składni-

ków, to każdemu składnikowi przypisujemy osobne równanie w powyższej postaci. Rozwiązaniem takiego układu równań jest ewolucja czasowa koncentracji składników próbki. Na podstawie koncentracji składników próbki obliczam profile głębokościowe, wykorzystując funkcję  $S(x)$ . Funkcja ta opisuje liczbę cząstek emitowanych z głębokości  $x$  pod powierzchnią.

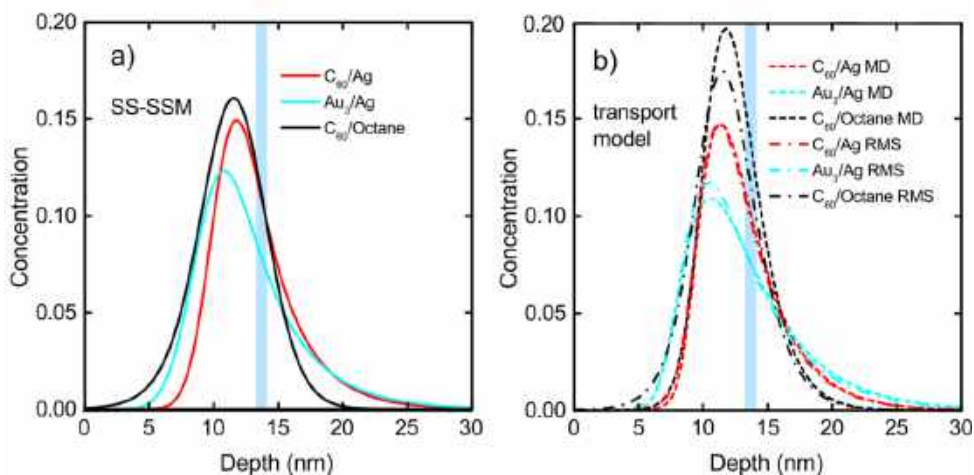
## Metodologia

Parametryzacja modelu sprowadza się do wyznaczenia funkcji  $D(x)$  oraz  $S(x)$  na podstawie symulacji komputerowych. Pierwszą z nich obliczyłem, korzystając z przemieszczeń jakich doznały atomy próbki na skutek uderzenia pocisku, a drugą na podstawie liczby rozpylonych atomów z głębokości  $x$ . Ze względu na naturę symulacji komputerowych, obliczone na ich podstawie funkcje mają wartości dyskretne. Jednak, aby algorytm rozwiązujący równanie różniczkowe działał stabilnie, funkcje te powinny być wyrażone za pomocą funkcji analitycznej. Dlatego na potrzeby modelu, na podstawie dyskretnych wartości  $S(x)$  oraz  $D(x)$  obliczyłem ich formę analityczną, zakładając, że jest realizowana poprzez funkcję sigmoidalną:

$$Sig(x) = \frac{a}{1 + e^{s \cdot (x - x_0)}}, \quad (2.2)$$

gdzie  $a$  to amplituda,  $x_0$  punkt przegięcia,  $s$  jest nachyleniem. Jeśli modelujemy układ wieloskładnikowy, to konieczne jest otrzymanie funkcji  $S(x)$  oraz  $D(x)$  dla każdego składnika osobno.

W pierwszej części badań sprawdziłem, jak zaproponowany model radzi sobie z symulowaniem profili głębokościowych dla próbek z cienką warstwą mierzonego substratu (warstwa delta). W tym celu obliczyłem wartości parametrów funkcji  $S(x)$  i  $D(x)$ , posługując się wynikami symulacji wielokrotnych uderzeń w systemach: 20 keV C<sub>60</sub>/Ag(111), 20 keV Au<sub>3</sub>/Ag(111) oraz 10 keV C<sub>60</sub>/oktan. Symulacje te zostały wcześniej przeprowadzone w grupie profesora Postawy [32–34]. Wygenerowany profil głębokościowy warstwy delta porównałem z profilem otrzymanym za pomocą modelu SS-SSM [33], który również może być użyty do uzyskania profili głębokościowych. Jednak model ten cechuje się dużą złożonością obliczeniową oraz skomplikowaną procedurą obliczania kształtu profili z przeprowadzonych obliczeń. Prezentowany tutaj model jest znacznie łatwiejszy pod kątem interpretacji wyników oraz szybkości obliczeń. Parametryzacja obu modeli była oparta na

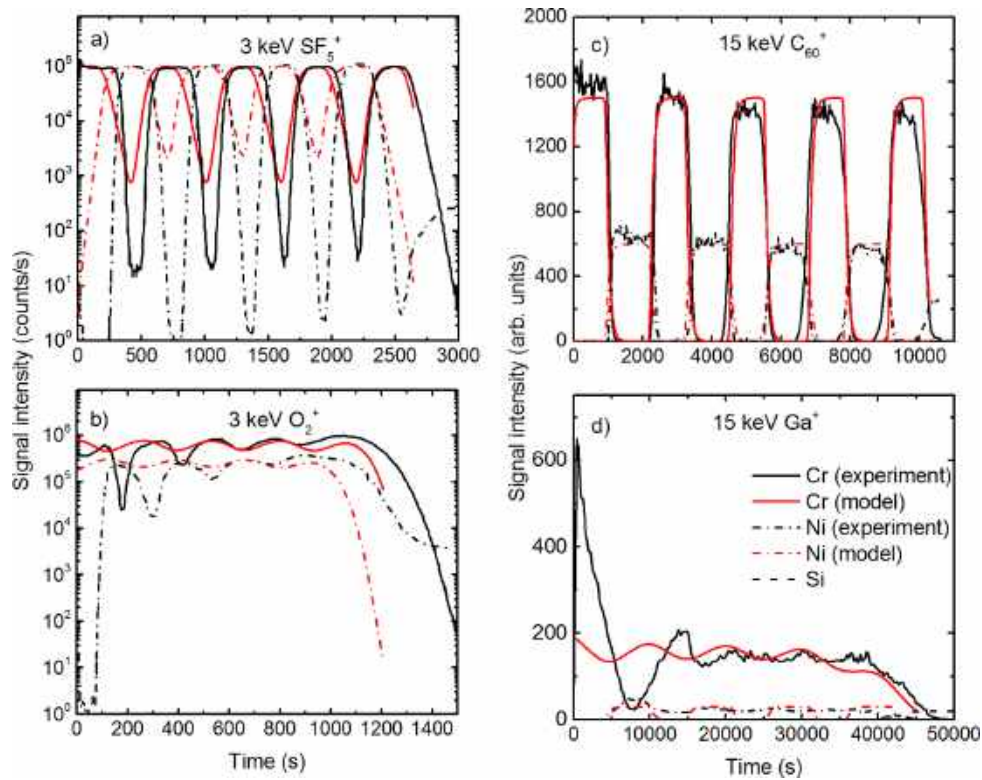


**Rysunek 2.1:** Porównanie profili głębokościowych warstwy delta o grubości 1 nm na głębokości 13.2 nm otrzymanych za pomocą: a) modelu SS-SSM, b) modelu opracowywanego w tej publikacji.

tym samym zestawie symulacji. Wygenerowane za pomocą obu modeli profile głębokościowe były jakościowo zgodne (**rysunek 2.1**).

Kolejnym krokiem było sprawdzenie zdolności proponowanego modelu do symulowania profili głębokościowych próbek, w których grubość mierzonych warstw wynosiła kilkanaście nanometrów. Do tego celu wybrałem wielowarstwową próbkę NiCr składającą się z na przemian ułożonych warstw Ni oraz Cr o całkowitej grubości 500 nm. Wybór tego systemu uzasadniony jest tym, że w literaturze istnieje dla niego bogaty zasób badań eksperymentalnych z różnymi typami pocisków. W trakcie prac okazało się, że model sparametryzowany bezpośrednio na podstawie symulacji, tak jak w poprzednim przypadku, nie dawał zgodności generowanych profili głębokościowych z eksperymentalnymi. Spowodowane jest to tym, że symulacje wielokrotnych uderzeń modelują tylko początkowy etap eksperymentu profilowania głębokościowego, w którym chropowatość osiąga wartość co najwyżej kilku nanometrów. Natomiast w eksperymentach z próbką NiCr chropowatość powierzchni sięgała dziesiątek nanometrów. Aby uwzględnić to zjawisko, podczas parametryzacji zastosowałem nowatorskie podejście hybrydowe, gdzie część informacji pochodziła z symulacji komputerowych, a część z odtwarzanego eksperymentu. Funkcje  $S(x)$  oraz  $D(x)$  dalej były reprezentowane za pomocą funkcji sigmoidalnych, których punkt przegięcia oraz nachylenie obliczałem na podstawie chropowatości eksperymentalnej, natomiast amplitudę obliczyłem na podstawie wyników z symulacji komputerowych.

Profile wygenerowane przez model porównałem z profilami eksperymentalnymi uży-



**Rysunek 2.2:** Porównanie eksperymentalnych profili głębokościowych (czarna linia) z symulowanymi za pomocą modelu (czerwona linia) dla próbki NiCr rozpylanej wiązkami: a) 3 keV  $\text{SF}_5^+$ , b) 3 keV  $\text{O}_2^+$ , c) 15 keV  $\text{C}_{60}^+$ , d) 15 keV  $\text{Ga}^+$ .

skanymi za pomocą wiązek [30, 35, 36]: 3 keV  $\text{SF}_5^+$ , 15 keV  $\text{C}_{60}^+$ , 3 keV  $\text{O}_2^+$  oraz 15 keV  $\text{Ga}^+$  (rysunek 2.2).

## Wnioski

W opisywanej w tej sekcji publikacji udało mi się zademonstrować działanie modelu zdolnego do przewidywania profili głębokościowych na podstawie wyników uzyskanych z symulacji dynamiką molekularną. Ważnym wkładem naukowym, wynikającym z powyższej publikacji, jest wprowadzenie metodologii uzyskiwania parametryzacji modelu na podstawie symulacji oraz danych eksperymentalnych. Pomimo swojej prostoty, stworzony model uzyskał bardzo dobrą zgodność z profilami referencyjnymi. Model skutecznie odtworzył profile głębokościowe dla różnych typów pocisków oraz poradził sobie z szerokim spektrum chropowatości powierzchni badanych próbek (2.5 nm - 100 nm). Bardzo dobre odwzorowanie profili głębokościowych przy zastosowaniu hybrydowej parametryzacji, w której kluczowym czynnikiem jest chropowatość badanego układu, wskazuje na to, że morfologia

badanej próbki ma dominujący wpływ na kształt uzyskiwanych profili głębokościowych. W literaturze sugerowano, że efekt mieszania jonowego może być równie istotny. Moje badania pokazały jednak, że efekty związane z mieszaniem jonowym mają wpływ drugorzędny.

### 2.1.2 Modelowanie profili głębokościowych rozszerzone o reakcje chemiczne

Sekcja oparta na publikacji: „*MD-Based Transport and Reaction Model for the Simulation of SIMS Depth Profiles of Molecular Targets*“

#### Motywacja

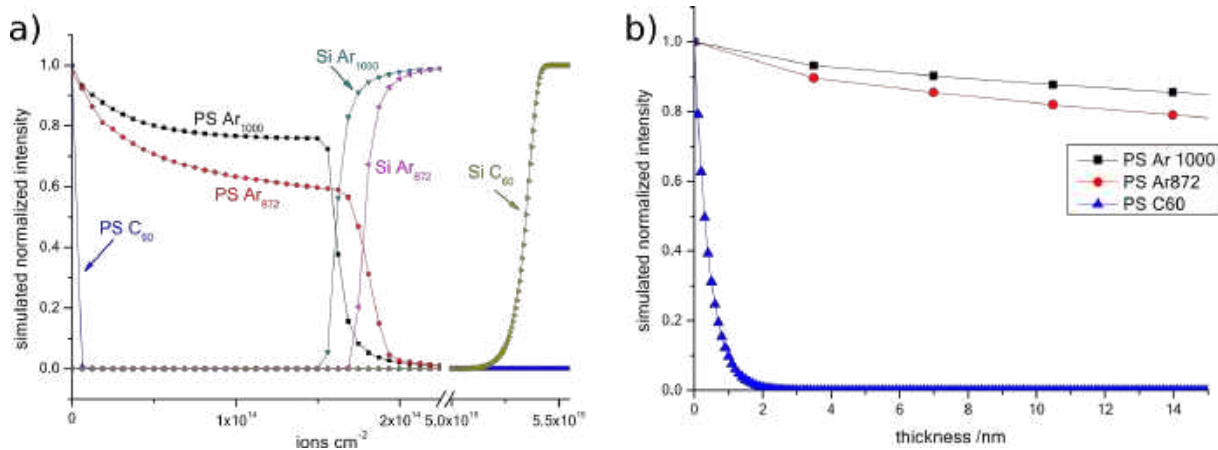
Badania zawarte w tym artykule stanowią kontynuację prac nad omawianym wcześniej modelem adwekcji-dyfuzji. Model rozszerzyłem o efekty wywołane reakcjami chemicznymi pierwszego rzędu, dla których stała szybkości reakcji, zależna od głębokości pod powierzchnią  $x$ , opisywana jest funkcją  $R(x)$ . Weryfikację modelu przeprowadziłem na próbce polistyrenu osadzonej na podkładzie krzemowym. Układ ten jest interesujący dla moich badań, ponieważ polistyren pod wpływem bombardowania wiązką jonów ulega procesowi sieciowania [37]. Efekt sieciowania silnie zależy od typu użytej wiązki. Na przykład, przy zastosowaniu wiązki  $C_{60}$  indukowane sieciowanie jest na tyle duże, że sygnał pochodzący od polimeru podczas profilowania głębokościowego spada praktycznie do zera [38]. Jeśli wiązka bombardująca składa się z klastrów argonowych, to uzyskiwany sygnał od polimeru nie znika wraz z głębokością mierzonego profilu głębokościowego [38]. Proces sieciowania można zredukować lub nawet wyeliminować jeśli na powierzchnię bombardowanego układu dostarczane są cząsteczki tlenku azotu (NO) [39]. Molekuła ta działa jako eliminator wolnych rodników powstających na skutek uderzenia pocisku w powierzchnię próbki.

#### Metodologia

Aby modelować ewolucję koncentracji składników badanej próbki konieczne było stworzenie parametryzacji ( $S(x)$ ,  $D(x)$ ,  $R(x)$ ) dla polistyrenu, krzemu oraz usieciowanego polistyrenu. Układy te były bombardowane pociskami  $Ar_{1000}$ ,  $Ar_{872}$  oraz  $C_{60}$  o energii  $E_k=20$  keV i kącie padania  $\theta=45^\circ$ . Takie parametry wiązki odpowiadają wartościom stosowanym w

eksperymentcie. W symulacjach usieciowany polistyren został przybliżony przez system składający się wyłącznie z atomów węgla. Jest to przykład ekstremalnego usieciowania. Tak jak w poprzedniej pracy, na podstawie przeprowadzonych symulacji bombardowania badanych próbek, wyznaczyłem parametry funkcji  $D(x)$  oraz  $S(x)$ . Funkcję opisującą efekt chemiczne  $R(x)$ , które w badanym układzie opisywały proces sieciowania polistyrenu, wyznaczyłem na podstawie liczby wolnych rodników tworzących się podczas uderzenia. W tych obliczeniach brałem pod uwagę liczbę niezwiązanych atomów wodoru, atomów węgla z niewysyconymi wiązaniami oraz liczbę wiązań C-H, które uległy konwersji w C-C.

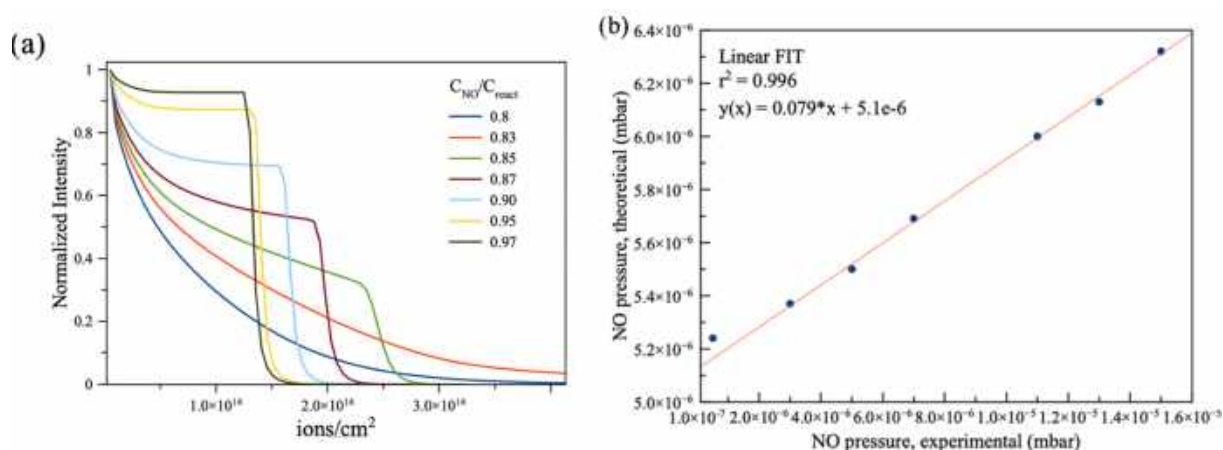
Na podstawie tak sparametryzowanego modelu wyznaczyłem profile głębokościowe dla badanego układu polistyrenu rozpylanego wiązkami  $\text{Ar}_{1000}$ ,  $\text{Ar}_{872}$  oraz  $\text{C}_{60}$ . W symulacjach uderzenie pociskiem  $\text{C}_{60}$  skutkowało produkcją wolnych rodników o rząd wielkości większą niż w przypadku klastrow argonowych. Fakt ten znajduje odzwierciedlenie w wyznaczonych profilach głębokościowych. W przypadku wiązki  $\text{C}_{60}$  sygnał od polistyrenu szybko spada na skutek sieciowania (**rysunek 2.3**), natomiast profile głębokościowe uzyskane za pomocą pocisków argonowych utrzymywały dużą intensywność sygnału na całej szerokości analizowanej warstwy dla polistyrenu (**rysunek 2.3**).



**Rysunek 2.3:** Profile głębokościowe dla wiązek  $\text{Ar}_{1000}$ ,  $\text{Ar}_{872}$  oraz  $\text{C}_{60}$  o energii  $E_k = 20$  keV i kącie padania  $\theta = 45^\circ$ , wyznaczone za pomocą modelu dla polistyrenu osadzonego na krzemie. a) cały przebieg profilu głębokościowego, b) zbliżenie na pierwsze 15 nm.

Kolejnym krokiem było zbadanie wpływu eliminatora wolnych rodników na zachowanie się profilu głębokościowego dla przypadku zastosowania pocisku  $\text{C}_{60}$ . Zgodnie z oczekiwaniem, degradacja sygnału od polistyrenu była tym mniejsza im więcej cząsteczek

NO było podawane na powierzchnię (**rysunek 2.4a**). W tych obliczeniach założyliśmy, że prawdopodobieństwo reakcji NO z wolnym rodnikiem jest równe jeden. Aby obliczyć dokładnie jakie jest to prawdopodobieństwo dla przypadku polistyrenu rozpylanego  $C_{60}$ , skorelowaliśmy ciśnienie cząstkowe NO w modelu (teoretyczne) z eksperymentalnym ciśnieniem cząstkowym NO (**rysunek 2.4b**). Dla danego, eksperymentalnie zmierzonego współczynnika rozpylania, które było otrzymane przy określonym ciśnieniu cząstkowym NO, w modelu szukaliśmy takiej wartości teoretycznego ciśnienia cząstkowego NO, które dawało taki sam współczynnik rozpylania jak w doświadczeniu. Z dopasowania linii prostej do tak wyznaczonych punktów (**rysunek 2.4b**) ustaliliśmy, że rzeczywista efektywność działania cząsteczek NO w tym układzie jest na poziomie 10%. Oznacza to, że spośród 10 zaadsorbowanych cząsteczek NO tylko jedna spowoduje zniknięcie rodnika. Jest to pierwsze ilościowe oznaczenie efektywności działania NO na powierzchni sieciowanego polistyrenu.



**Rysunek 2.4:** a) Profile głębokościowe dla wiązki  $C_{60}$  w zależności od stosunku liczby cząsteczek NO do liczby wolnych rodników. b) Korelacja teoretycznego (użytego w modelu) oraz eksperymentalnego ciśnienia cząstkowego NO wraz z dopasowaniem liniowym.

## Wnioski

Udało się stworzyć model do symulowania profili głębokościowych, w których ważną rolę odgrywają reakcje chemiczne. Model ten dobrze odwzorował zachowanie się profili głębokościowych w zależności od typu wiązki [38]. Dla pocisku  $C_{60}$  model poprawnie przewidywał, że cząsteczki NO dostarczane na bombardowaną powierzchnię znacząco zwiększą jakość uzyskiwanych profili. Zmiany te były proporcjonalne do ilości dostarczanych cząste-

czek. Wykorzystanie modelu pozwoliło oszacować, że wydajność cząstek NO w reagowaniu z wolnymi rodnikami powstającymi podczas bombardowania polistyrenu wiązką  $C_{60}$  jest na poziomie 10%.

### 2.1.3 Efekty chemiczne podczas bombardowania wywołane morfologią powierzchni

Sekcja oparta na publikacji: „*C-O Bond Dissociation and Induced Chemical Ionization Using High Energy  $(CO_2)_n^+$  Gas Cluster Ion Beam*“

#### Motywacja

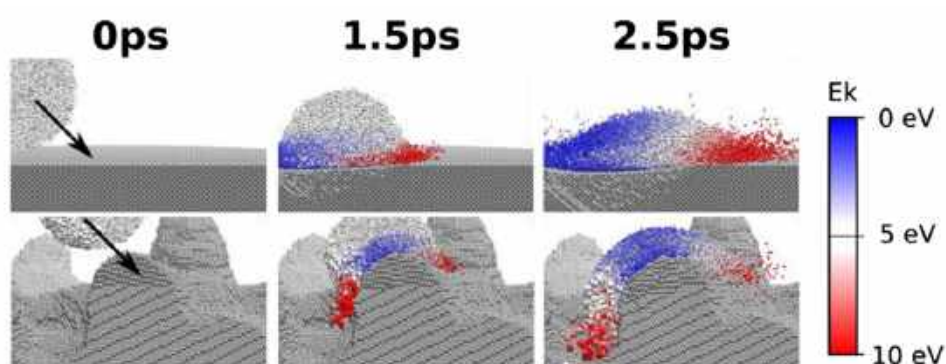
Badania zawarte w tej sekcji stanowią kontynuację pracy nad nowym typem klastrowej wiązki  $(CO_2)^+$ , które prowadziłem we współpracy z laboratorium Prof. N. Winograda ze Stanowego Uniwersytetu Pensylwanii. W pierwszej części badań [40] pokazaliśmy, że wiązka klastrowa oparta na molekułach  $CO_2$  posiada lepsze właściwości niż wiązka klastrowa oparta na atomach argonu. Przewagą wiązki opartej na  $CO_2$  jest to, iż można było ją skupić do mniejszego rozmiaru plamki na powierzchni, co przekładało się na dwukrotnie lepszą rozdzielczość poprzeczną. Uzyskanie bardziej skupionej wiązki spowodowana jest tym, że molekuły  $CO_2$  posiadają znacznie większą energię kohezji (0.27 eV) niż atomy argonu (0.065 eV), dzięki czemu utworzone klastry mają mniejszą szansę na metastabilny rozpad w kolumnie działa [40].

Podczas przeprowadzania dalszych badań nad klastrową wiązką  $(CO_2)^+$  pojawiło się pytanie, dlaczego podczas bombardowania, część molekuł wchodzących w skład klastra ulegała fragmentacji, pomimo tego, że energia kinetyczna przypadająca na molekułę klastra była znacznie mniejsza niż energia dysocjacji  $CO_2$  (8.3 eV)? Prawdopodobną przyczyną tego zjawiska jest proces zachodzący podczas uderzenia klastra o powierzchnię, co nie jest bezpośrednio mierzalne za pomocą technik eksperymentalnych. Aby dowiedzieć się, co spowodowało taki efekt, niezbędne było przeprowadzenie symulacji komputerowych.

#### Metodologia

Pierwszym układem który stworzyłem na potrzeby omawianej publikacji, była próbka Au(100) o idealnie gładkiej powierzchni. Próbka była bombardowana klastrami  $(CO_2)_n$  o

energii 50 keV pod kątem  $45^\circ$ . Wielkości klastrow wybrałem tak, aby odpowiadały pociskom wykorzystywanym w eksperymencie [3]. W rezultacie użyłem pocisków o rozmiarach 4000, 6000, 8000 oraz 10000 cząsteczek  $\text{CO}_2$ , co po przeliczeniu na energię kinetyczną na molekułę, daje odpowiednio: 12.5 eV/n, 8.33 eV/n, 6.25 eV/n, 5 eV/n. Symulacje wykonane na płaskiej powierzchni Au(100) pokazały, że fragmentacja molekuł  $\text{CO}_2$  następuje tylko dla pocisku o największej energii kinetycznej na molekułę (12.5 eV/n). Wynik ten potwierdza, intuicyjne założenie, iż, aby doszło do fragmentacji molekuły podczas uderzenia, energia kinetyczna na molekułę powinna być większa niż jej energia dysocjacji. Jednak wynik ten nadal nie tłumaczy zjawiska obserwowanego w eksperymencie.



**Rysunek 2.5:** Przebieg uderzenie pocisku 20 keV  $(\text{CO}_2)_{10000}$  dla płaskiej powierzchni (górny panel) oraz dla powierzchni z wytworzoną morfologią (dolny panel). Kolorem oznaczono aktualną energię kinetyczną molekuły  $\text{CO}_2$ .

Po bliższej inspekcji trajektorii zaobserwowałem, iż część molekuł klastra po uderzeniu w powierzchnię posiada energię kinetyczną większą niż przed uderzeniem (**rysunek 2.5**). Proces ten przebiega w dwóch etapach. Najpierw podczas uderzenia klastery ulega kompresji, a następnie tak zmagazynowana energia zostaje przekazana do molekuł z czoła klastra, które zostają wyrzucone ze zwiększoną energią kinetyczną (**rysunek 2.5**). Wektor prędkości molekuł o zwiększonej energii kinetycznej jest jednak zwrócony w kierunku przeciwnym do powierzchni. Dlatego też, w przypadku płaskiej powierzchni, te molekuły nie miały już możliwości na oddziaływanie z podłożem i były emitowane do próżni. Na podstawie tej obserwacji stworzyłem drugi układ symulacyjny. Było to srebro o chropowatej powierzchni, której morfologia wykształciła się na skutek wielokrotnych uderzeń [32]. Parametry pocisków  $(\text{CO}_2)_n$  były takie same jak dla płaskiej powierzchni. Dla takiego układu wyniki symulacji jednoznacznie pokazały, że dysocjacja molekuł klastra następuje

nawet dla tak niskich energii jak 5 eV/n. Śledząc ewolucję czasową procesu uderzenia pocisku w podłoże, zjawisko to można wytłumaczyć jako dwa następujące po sobie zdarzenia. Najpierw występuje transfer energii do molekuł z czoła klastra, tak jak to miało miejsce w przypadku płaskiej powierzchni. Następnie molekuły o zwiększonej energii, przez to że morfologia próbki jest chropowata, mają szansę na zderzenie się z jej powierzchnią (**rysunek 2.5**). Podczas takiego zderzenia część molekuł CO<sub>2</sub> ulega fragmentacji. Symulacje przeprowadziłem dla dwóch punktów uderzenia o różniącą się lokalnej morfologii: uderzenie w „dolinę” oraz uderzenie w „górze”. Wyniki uzyskane dla obu punktów uderzenia były ze sobą jakościowo zgodne.

## Wnioski

Dzięki zastosowaniu dynamiki molekularnej, udało się wytłumaczyć obserwowane zjawisko fragmentacji molekuł CO<sub>2</sub> podczas bombardowania powierzchni klastrem (CO<sub>2</sub>)<sub>n</sub>. Korzystając tylko z technik eksperymentalnych bezpośrednio pokazanie przyczyny fragmentacji molekuł CO<sub>2</sub> w przypadku klastrow, których energia na molekułę była mniejsza niż energia potrzebna na fragmentację tej molekuły, nie byłoby możliwe. Uwidacznia to fakt, że symulacje komputerowe są komplementarną częścią eksperymentu. Bardzo ważnym wnioskiem z tych badań jest obserwacja, iż morfologia powierzchni próbki ma bezpośredni wpływ na zjawiska chemiczne zachodzące podczas bombardowania. Powstałe na skutek fragmentacji CO<sub>2</sub> wolne rodniki mogą wchodzić w reakcję ze składnikami podłoża.

## 2.2 Wpływ bombardowania na morfologię powierzchni

### Formalizm funkcji krateru

Ze względu na fakt, że w dalszej części niniejszej pracy opisuję publikacje opierające się na tak zwanym formalizmie funkcji krateru (crater function formalism) [41], w tej sekcji przedstawiam minimalną ilość informacji wymaganą do zrozumienia metodologii stosowanej w tym formalizmie. W tej sekcji koncentruję się na procesie tworzenia się periodycznych struktur na powierzchni bombardowanego materiału, czyli ripli. W literaturze istnieje wiele modeli, które zostały stworzone do opisu procesu powstawania ripli indukowanych wiązką jonową [13]. Ich podstawowym zadaniem jest przewidzenie, dla jakich kątów padania wiązki ( $\theta$ ) możemy spodziewać się indukowania na powierzchni ripli (efekt

destabilizujący), a dla jakich kątów padania, bombardujące pociski będą powodować wygładzenie powierzchni (efekt stabilizujący). Formalizm funkcji krateru jest przykładem takiego modelu, w którym ewolucja kształtu powierzchni opisywana jest kinematycznym równaniem ruchu w postaci [42]:

$$\frac{1}{J} \frac{\partial h}{\partial t} = C_0(\theta) + C_1(\theta) \frac{\partial h}{\partial x} + C_2(\theta) \frac{\partial h}{\partial y} + C_{11}(\theta) \frac{\partial^2 h}{\partial^2 x} + C_{22}(\theta) \frac{\partial^2 h}{\partial^2 y} + C_{12}(\theta) \frac{\partial^2 h}{\partial x \partial y}, \quad (2.3)$$

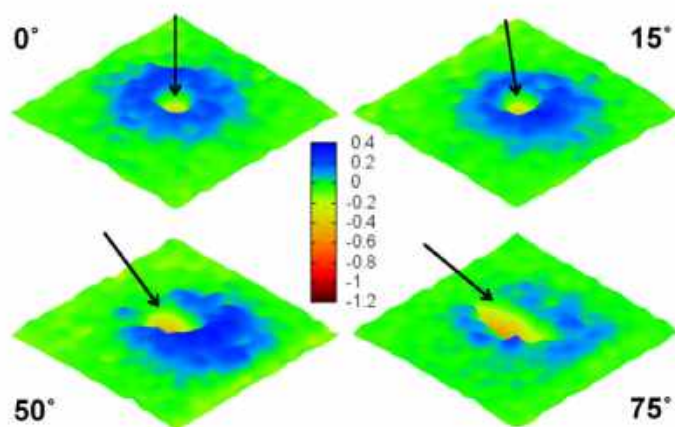
gdzie  $J$  to strumień cząstek padających na powierzchnię,  $h(x, y, t)$  jest funkcją opisującą wysokość powierzchni próbki w punkcie  $(x, y)$  i czasie  $t$ ,  $C$  to współczynniki, które determinują ewolucję układu. Według przyjętej konwencji kierunek  $x$  jest równoległy do rzutu wiązki padającej na powierzchnię, natomiast kierunek  $y$  jest prostopadły do tego rzutu. Powyższe równanie jest wyprowadzone przy założeniu tak zwanego reżimu liniowego. Oznacza to, że równanie to można stosować w przypadku, w którym płaska powierzchnia podlega tylko minimalnej perturbacji [42]. W związku z tym, nie można tego równania wykorzystać do bezpośredniego modelowania ewolucji powierzchni. Niemniej jednak, wnioski uzyskiwane na skutek analizy tego równania pozwalają przewidzieć, dla jakiego kąta padania w badanym układzie możemy spodziewać się powstawania ripli. W analizie stabilności powierzchni interesują nas parametry współczynników  $C_{11}(\theta)$  oraz  $C_{22}(\theta)$ , które nazywane są współczynnikami krzywizny (curvature coefficients). Jeśli współczynnik  $C_{11}(\theta)$  lub  $C_{22}(\theta)$  jest mniejszy niż zero, to model przewiduje powstanie ripli dla danego kąta padania  $\theta$ .  $C_{11}$  opisuje powstanie ripli w kierunku prostopadłym do bombardującej wiązki, natomiast  $C_{22}$  opisuje powstanie ripli w kierunku równoległym do bombardującej wiązki. Współczynniki  $C_{11}$  oraz  $C_{22}$  oblicza się na podstawie równań [42]:

$$C_{11}(\theta) = \frac{\partial}{\partial \theta} \left( M^{(1)}(\theta) \cos \theta \right) + \frac{\partial}{\partial K_{11}} \left( M^{(0)}(\theta) \cos \theta \right), \quad (2.4)$$

$$C_{22}(\theta) = \cot \theta \left( M^{(1)}(\theta) \cos \theta \right) + \frac{\partial}{\partial K_{22}} \left( M^{(0)}(\theta) \cos \theta \right), \quad (2.5)$$

gdzie  $K_{11}$  oraz  $K_{22}$  to krzywizna powierzchni w miejscu uderzenia pocisku ( $K_{ij} = \frac{\partial^2 h}{\partial x_i \partial x_j}$ ), a  $M^{(0)}(\theta)$  i  $M^{(1)}(\theta)$  to odpowiednio: zerowy oraz pierwszy moment funkcji krateru. Funkcja krateru opisuje średnią zmianę wysokości powierzchni wywołaną uderzeniem pocisku (**rysunek 2.6**). Kształt tej funkcji oblicza się na podstawie przemieszczeń atomów (mieszanie oraz rozpylanie) wywołanych uderzeniem pocisku. Dane na temat przemieszczeń

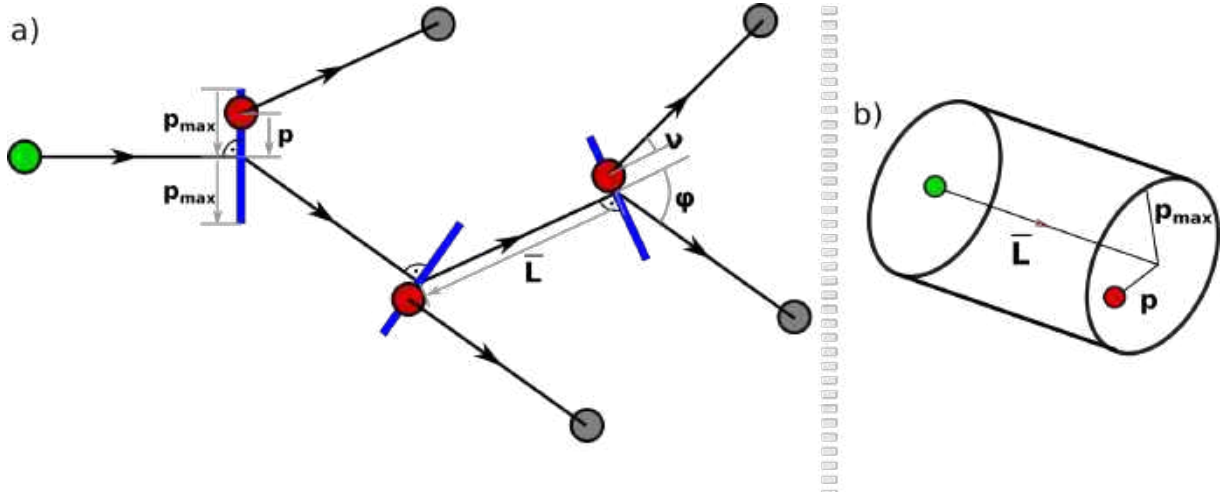
dla badanego układu uzyskuje się na podstawie symulacji komputerowych metodą dynamiki molekularnej lub metodą Monte Carlo.



**Rysunek 2.6:** Wizualizacja funkcji krateru dla różnych kątów padania pocisku. Kolorem oznaczono średnią zmianę wysokości powierzchni wywołaną uderzeniem. Przedstawionym układem jest pocisk Ar o energii 500 eV bombardujący próbkę krzemu [43].

Część publikacji [2, 4, 5] przedstawianych w dalszym opisie moich badań, powstała we współpracy z grupą doktora Gerharda Hoblera z Uniwersytetu Technicznego w Wiedniu. Badania te opierały się na zastosowaniu symulacji metodą dynamiki molekularnej oraz metodą Monte Carlo do badania zjawisk prowadzących do powstawania morfologii powierzchni na skutek bombardowania wiązką jonów. Symulacje metodą dynamiki molekularnej były w całości wykonywane przeze mnie na Uniwersytecie Jagiellońskim, natomiast symulacje metodą Monte Carlo wykonywane były przez grupę doktora Hoblera.

Grupa doktora Hoblera do symulacji wykorzystuje modele IMSIL [44] własnej implementacji. Metoda ta opiera się na przybliżeniu zderzeń binarnych (binary collision approximation), co oznacza, że uderzenie pocisku w próbkę przebiega w reżimie liniowej kaskady zderzeń (zderzenia zachodzą wyłącznie między atomem poruszającym się a atomem w spoczynku). Jeśli symulowana próbka jest amorficzna (wszystkie badania opisywane w tej rozprawie dotyczyły takich próbek) to w metodzie Monte Carlo rezygnuje się ze śledzenia atomów próbki i zastępuje się je regionem opisywanym gęstością atomową. **Rysunek 2.7** przedstawia przebieg trajektorii zachodzącej w takim regionie. Symulację trajektorii rozpoczyna utworzenie atomu pocisku o zadanej energii kinetycznej. Następnie atom ten przebywa w linii prostej dystans nazywany drogą swobodnego przelotu ffp (free flight path), który w przypadku ciał amorficznych jest odwrotnie proporcjonalny do gę-



**Rysunek 2.7:** Wizualizacja (2D dla przejrzystości) przebiegu trajektorii w symulacji Monte Carlo dla próbki amorficznej. Zielone koło reprezentuje atom pocisku, czerwone koło atom wtórny „utworzony“ podczas zderzenia, czarne linie to droga swobodnego przelotu (free flight path), która dla ciał amorficznych jest stała  $\bar{L}$ ,  $\phi$  oraz  $\nu$  to kąt rozproszenia atomu pocisku oraz tarczy,  $p$  to parametr zderzenia (impact parameter), który jest realizacją rozkładu losowego obliczanego na podstawie  $p_{max}$ . Szare koło to finalna lokacja danego atomu. Atomy wtórne też mogą generować zderzenia jednak dla przejrzystości rysunek tego nie przedstawia. b) Wizualizacja drogi wolnego przelotu w 3D, oznaczenia jak w a).

stości atomowej. Po przebyciu ffp atom „zderza“ się z atomem tarczy, który jest tworzony na płaszczyźnie prostopadłej do ffp (na **rysunku 2.7** niebieska linia). Oddalenie atomu tarczy od osi ffp jest nazywane parametrem zderzenia (impact parameter). Dla danego uderzenia jego wartość obliczana jest z rozkładu  $p = p_{max}\sqrt{N}$ , gdzie  $N$  to jednorodny rozkład prawdopodobieństwa, a  $p_{max}$  to parametr zadawany w symulacji (maximum impact parameter). Przekaz energii kinetycznej w takim zderzeniu jest elastyczny, a jej wartość wraz z kątami rozpraszania ( $\phi, \nu$ ), obliczane są na podstawie całki rozpraszania (scattering integral) [45]. Po zderzeniu atom tarczy zyskuje energię kinetyczną dzięki czemu staje się atomem „pocisku“ zdolnym do dalszych zderzeń. Na każdy poruszający się atom w próbce działa siła hamująca (electronic stopping power), która stopniowo redukuje jego energię kinetyczną. Trajektoria układu jest obliczana do momentu, aż energia kinetyczna wszystkich śledzonych atomów, spadnie poniżej zadanej wartości progowej. Wykonując tysiące tego typu symulacji, możemy uzyskać informację na temat rozkładu implantowa-

nich atomów pocisku, współczynnika rozpylania oraz mieszania jonowego wywołanego uderzeniem.

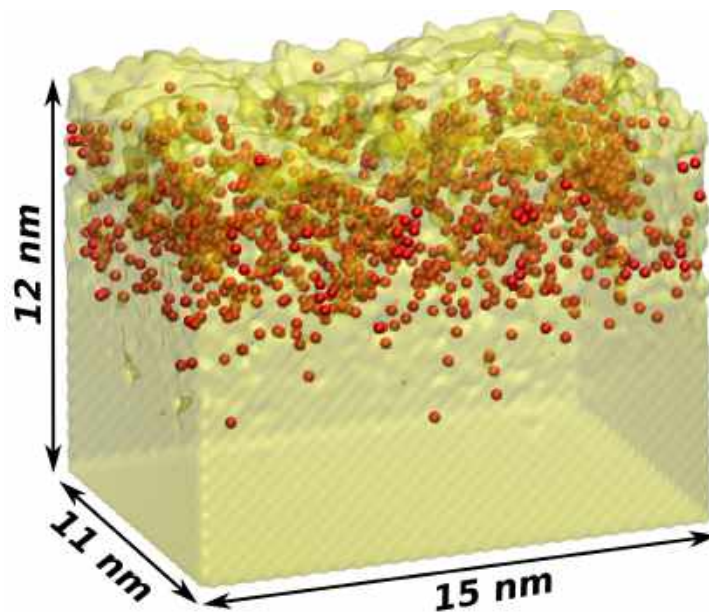
Podstawową zaletą metody Monte Carlo w stosunku do metody dynamiki molekularnej jest jej szybkość. Symulacje wykonywane z jej pomocą są wielokrotnie szybsze. Przez szereg zastosowanych przybliżeń metoda Monte Carlo nie może być stosowana do wszystkich przypadków bombardowania. Podstawowym ograniczeniem jest to, że symulowane zjawisko musi spełniać założenia liniowej kaskady zderzeń oraz symulacje muszą stosować przybliżenie zderzeń binarnych. Oznacza to, że metoda ta nie może być zastosowana np. do modelowania efektów nieliniowych, takich jak uderzenie pocisku klastrowego. Jednak metoda Monte Carlo jest bardzo skutecznym narzędziem do symulowania procesu bombardowania próbek nieorganicznych pociskami monoatomowym o energiach co najmniej 1 keV [46].

### 2.2.1 Wpływ implantowanych atomów gazów szlachetnych na morfologię powierzchni w formalizmie funkcji krateru

Sekcja oparta na publikacji: „*Crater function moments: Role of implanted noble gas atoms*“

#### Motywacja

Jak przedstawiłem we wstępie do tego rozdziału, formalizm krateru jest ważnym narzędziem stosowanym do badania zjawiska indukowania morfologii powierzchni zachodzącej podczas bombardowania wiązką jonową. Jednak wszystkie dotychczasowe badania wykorzystujące formalizm krateru, ignorowały wpływ implantowanych atomów gazów szlachetnych z wiązki rozpylającej powierzchnię. Dlatego celem opisywanej tutaj publikacji było sprawdzenie poprawności takiego podejścia. Do badań wybrałem próbkę krzemu, ponieważ jest to najczęściej stosowany układ w tego typu badaniach. Natomiast pociskami bombardującymi były: argon, krypton oraz ksenon. Badania koncentrowały się na wykorzystaniu metody dynamiki molekularnej oraz metody Monte Carlo do obliczenia wpływu implantowanych atomów gazów szlachetnych na momenty funkcji krateru, które, jak to było wcześniej omówione, są podstawą analizy stabilności powierzchni.

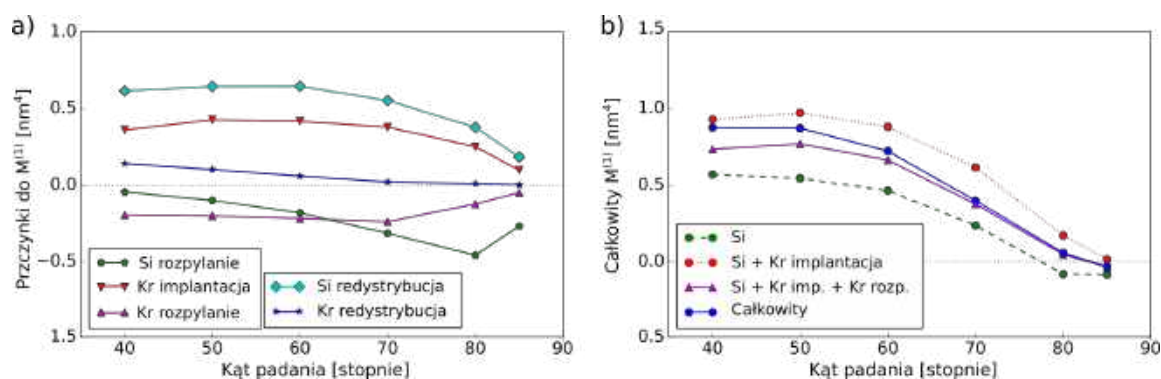


**Rysunek 2.8:** Wizualizacja próbki krzemu symulowanej za pomocą dynamiki molekularnej, powstałej po 6000 uderzeń pociskiem 2 keV Kr pod kątem  $60^\circ$ . Żółta, półprzezroczysta powierzchnia reprezentuje atomy krzemu, czerwone sfery reprezentują implantowane atomy Kr uwięzione w próbce.

## Metodologia

Ponieważ koncentracja implantowanych atomów w próbce może mieć wpływ na przebieg procesu rozpylania, ważną częścią moich badań było stworzenie próbki, która dobrze odwzoruje rzeczywistą koncentrację gazów w bombardowanym krzemie. Aby uzyskać taką próbkę, przeprowadziłem symulację wielokrotnego bombardowania aż do momentu, w którym koncentracja uwięzionych atomów pocisku w próbce uległa stabilizacji. W przypadku badanej próbki krzemu o wymiarach powierzchni 15 nm x 11 nm, wymagało to przeprowadzenia około 6000 symulacji uderzenia pocisku. **Rysunek 2.8** przedstawia wizualizację próbki krzemu po przeprowadzeniu 6 tysięcy symulacji.

Podstawą badań składających się na tę publikację były symulacje metodą dynamiki molekularnej procesu bombardowania krzemu atomami Kr o energii kinetycznej równej 2 keV dla kątów padania równych:  $40^\circ$ ,  $50^\circ$ ,  $60^\circ$ ,  $70^\circ$ ,  $80^\circ$  oraz  $85^\circ$ . Każdy kąt padania to osobna seria symulacji, rozpoczynająca się od krystalicznej próbki krzemu. Na podstawie ostatnich 1500 uderzeń (gdy koncentracja implantowanych atomów w próbce jest już stała), dla każdego kąta padania obliczyłem momenty funkcji krateru. **Rysunek 2.9a** przedstawia wartości przyczynków do pierwszego momentu funkcji krateru od rozpylania,

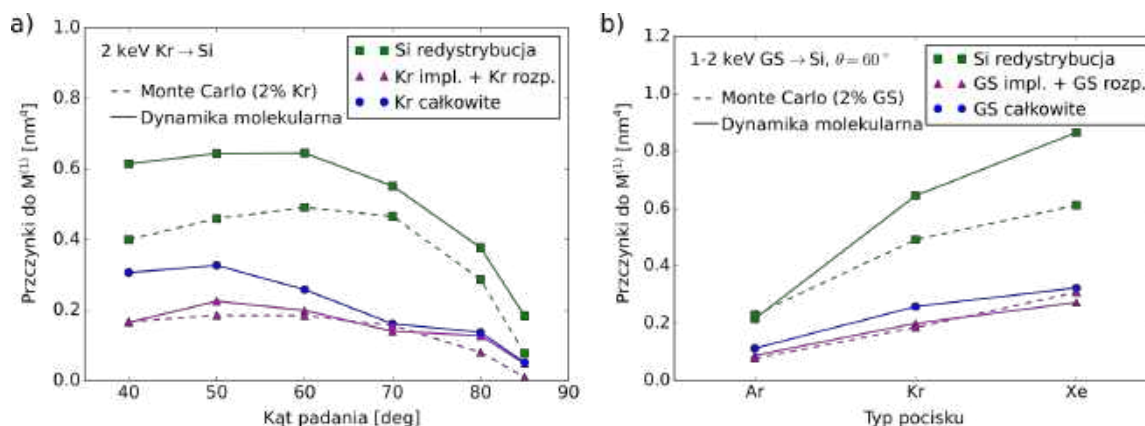


**Rysunek 2.9:** a) Przedstawienie wszystkich przyczynków składających się na pierwszy moment funkcji krateru. b) Przedstawienie różnych kombinacji tych przyczynków.

implantacji i redystrybucji dla atomów krzemu oraz atomów pocisku. Na **rysunku 2.9b**, który przedstawia różne kombinacje przyczynków, można zauważyć, że uwzględnienie implantowanych atomów Kr ma istotne znaczenie dla pierwszego momentu funkcji krateru. Natomiast dla zerowego momentu funkcji krateru wkład od implantowanych atomów jest pomijalnie mały.

**Rysunek 2.10a** przedstawia porównanie wyników otrzymanych metodą dynamiki molekularnej z wynikami uzyskanymi metodą Monte Carlo. Wyniki te pokazują, że metoda Monte Carlo mocno nie doszacowuje wkładu do pierwszego momentu funkcji krateru od redystrybucji atomów krzemu. Różnica spowodowana jest tym, że przy niskich energiach (końcowa część trajektorii) poruszający się atom wprawia w ruch kolektywnie wiele atomów próbki jednocześnie. Prowadzi to do tego, że założenie liniowej kaskady zderzeń przestaje obowiązywać i obserwujemy efekty nieliniowe, które mogą być dokładnie modelowane tylko za pomocą dynamiki molekularnej. Dalsze porównanie, wykonane dla różnych typów pocisków 1 keV Ar, 2 keV Kr, 2 keV Xe padających pod kątem  $\theta = 60^\circ$  przedstawia **rysunek 2.10b**, na którym widać, że niedoszacowywanie redystrybucji atomów krzemu przez metodę Monte Carlo jest tym większe, im większa jest masa pocisku.

**Rysunek 2.11** przedstawia koncentrację procentową atomów Ar w krzemie na skutek bombardowania wiązką 1 keV Ar dla wyników eksperymentalnych [47], otrzymanych metodą dynamiki molekularnej oraz metodą Monte Carlo. Metoda dynamiki molekularnej dobrze odwzorowuje rozkład głębokościowy, nieznacznie przeszacowując koncentrację dla głębokości powyżej 3 nm. Natomiast metoda Monte Carlo kilkakrotnie przeszacowuje procentową koncentrację atomów Ar. Wynik ten potwierdza, że metoda dynamiki molekularnej jest bardziej dokładna niż metoda Monte Carlo.



**Rysunek 2.10:** Porównanie metody dynamiki molekularnej z metodą Monte Carlo dla bombardowania krzemu a) pociskiem 2 keV Kr pod różnymi kątami, b) różnymi gazami szlachetnymi (GS): 1 keV Ar, 2 keV Kr, 2 keV Xe pod kątem  $\theta = 60^\circ$ .

## Wnioski

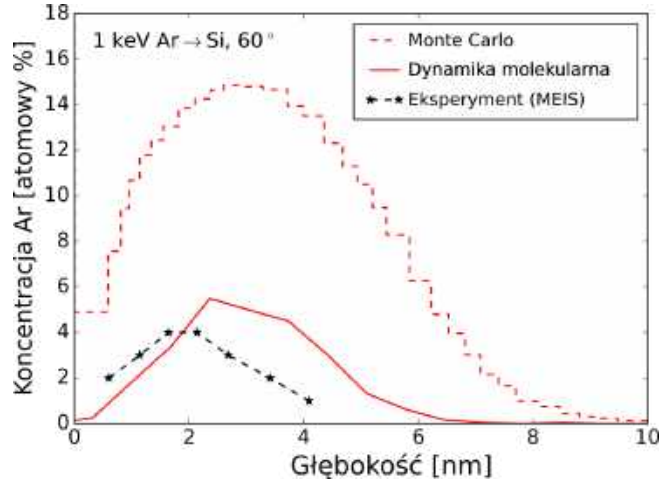
Podstawowym wnioskiem uzyskanym z prowadzonych badań jest to, że uwzględnienie implantowanych pocisków z wiązki rozpylającej ma istotny wpływ na pierwszy moment funkcji krateru, a co za tym idzie na proces formowania się morfologii powierzchni. Dodatkowo, porównanie otrzymanych wyników metody dynamiki molekularnej z metodą Monte Carlo pokazało, że metoda Monte Carlo nie doszacowuje wkładu do pierwszego momentu od redystrybucji atomów krzemu. Spowodowane jest to efektami nieliniowymi powstającymi podczas niskoenergetycznych zderzeń międzyatomowych.

## 2.2.2 Porównanie metody dynamiki molekularnej oraz metody Monte Carlo w ramach formalizmu krateru

Sekcja oparta na publikacji: „*Ion bombardment induced atom redistribution in amorphous targets: MD versus BCA*”

## Motywacja

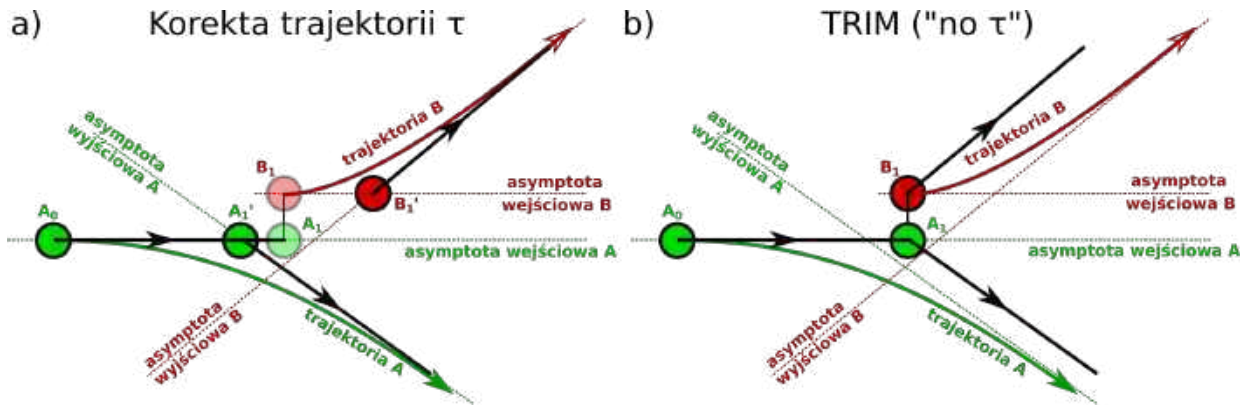
Opisywana tutaj publikacja jest bezpośrednią kontynuacją badań opisywanych w poprzedniej sekcji. Wcześniej przedstawione wyniki pokazywały, że metoda Monte Carlo nie doszacowuje redystrybucji masy dla atomów krzemu. Dlatego celem przeprowadzonych prac było zbadanie wpływu parametrów symulacji Monte Carlo na uzyskiwane za jej pomocą wartości pierwszego momentu funkcji krateru (suma przesunięć wszystkich atomów) dla



**Rysunek 2.11:** Porównanie koncentracji implantowanych atomów argonu dla pocisku 1 keV Ar bombardującego krzem przewidywanych przez metodę Monte Carlo oraz przez metodę dynamiki molekularnej do wyników eksperymentalnych [47].

niskiego zakresu energetycznego ( $<100$  eV). Taka energia kinetyczna odpowiada końcowemu stadium rozwoju kaskady zderzeń. W symulacjach Monte Carlo, realizowane to było w taki sposób, że atom próbki z pierwotną energią rozpoczynał trajektorię na zadanej głębokości wewnątrz próbki. Natomiast w symulacjach dynamiką molekularną, atom próbki był wybierany losowo z zadanego obszaru, a następnie przydzielana mu była odpowiednia energia kinetyczna.

Kontrolowanym parametrem w metodzie Monte Carlo była energia przemieszczenia  $E_d$ . Na jej podstawie obliczany był parametr  $p_{max}$  w taki sposób, że dla zadanej  $E_d$  żadna kolizja z energią wyższą niż  $E_d$  nie była pominięta. Dodatkowo porównane są trzy sposoby obliczania poprawki dla pozycji atomu pocisku oraz atomu tarczy po zderzeniu (**rysunek 2.12**), czyli pozycje z których atomy rozpoczynają przemieszczanie do następnego zderzenia. Domyślna metoda modelu IMSIL oblicza poprawkę do pozycji po zderzeniu na podstawie przecięć wynikających z asymptot trajektorii obliczonych na podstawie całki czasowej  $\tau$  (time integral) [48] (**rysunek 2.12**). Jednak w przypadku niskich energii, korekcja ta może doprowadzić do ujemnego ffp, co jest niefizyczne. Dlatego drugi model „ffp>0” wprowadza ograniczenie na taki przypadek. Trzecim sprawdzanym sposobem konstrukcji trajektorii po zderzeniu jest TRIM („no  $\tau$ ”), dla którego pozycje atomów po zderzeniu nie są korygowane na podstawie całki czasowej  $\tau$  (**rysunek 2.12b**).

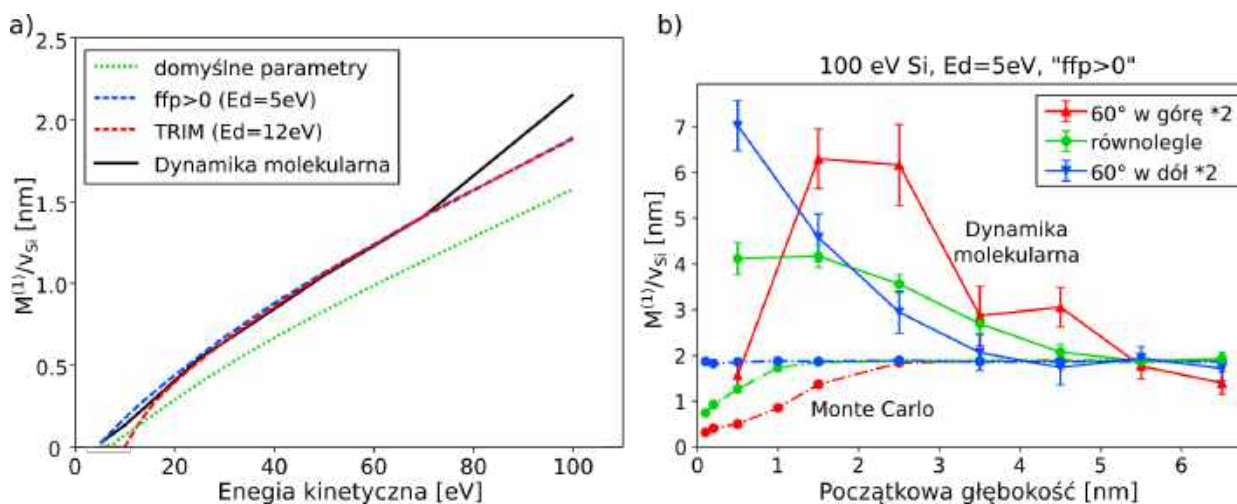


**Rysunek 2.12:** Schematyczne przedstawienie trajektorii zderzających się atomów pocisku  $A$  (kolor zielony) oraz tarczy  $B$  (kolor czerwony) obliczonymi na podstawie całki czasowej. Czarną strzałką oznaczono drogę swobodnego przelotu.  $A_0$  oznacza pozycję atomu pocisku przed zderzeniem, natomiast pozycja atomu tarczy oraz atomu pocisku po zderzeniu, a przed kontynuowaniem dalszej drogi to a)  $A_1'$ ,  $B_1'$  po uwzględnieniu poprawki wynikającej z przecięcia asymptot wchodzącej oraz wychodzącej, b)  $A_1$ ,  $B_1$  bez uwzględnienia tej poprawki.

## Metodologia

Aby jak najlepiej odwzorować rzeczywistą strukturę powstałą wewnątrz bombardowanej próbki krzemu, w symulacjach metodą dynamiki molekularnej wykorzystałem próbkę krzemu uzyskana na skutek bombardowania wiązką 2 keV Kr  $\theta = 60^\circ$  w poprzedniej publikacji. W badaniach interesował mnie wpływ pierwotnej energii kinetycznej nadawanej atomowi próbki na pierwszy moment funkcji krateru. Badane energie kinetyczne znajdowały się w zakresie 5 eV do 100 eV. Dla każdej badanej energii kinetycznej przeprowadziłem 300 symulacji, w których atom, któremu przypisywałem pierwotną energię kinetyczną losowany był z regionu 3-6 nm pod powierzchnią próbki. Każda symulacja wykonywana była na nowej kopii badanej próbki, dzięki czemu wszystkie przeprowadzone symulacje były wykonane na identycznym układzie. Uśrednione wyniki symulacji uzyskane metodą dynamiki molekularnej dla różnych energii pierwotnych przedstawione są na **rysunku 2.13a**, wraz z wynikami metody Monte Carlo dla trzech badanych metod poprawek pozycji po zderzeniu. W symulacjach Monte Carlo, parametr  $E_d$  został tak dobrany, aby uzyskać najlepsze dopasowanie do wyników symulacji metodą dynamiki molekularnej. Jak widać, symulacje wykorzystujące metodę „ffp>0” oraz TRIM do korekcji pozycji atomów po zderzeniu, uzyskały bardzo dobre dopasowanie do wyników uzyskanych

metodą dynamiki molekularnej.



**Rysunek 2.13:** a) Porównanie wyników trzech metod wprowadzenia poprawki do pozycji atomów po zderzeniu, domyślny sposób modelu IMSIL, „ffp>0” oraz TRIM. Wartości  $E_d$  zostały tak dobrane, aby uzyskać najlepsze dopasowanie do wyników dynamiki molekularnej. b) Zależność pierwszego momentu  $M^{(1)}$  od początkowej głębokości pierwotnego atomu o energii 100 eV dla metody „ffp>0” dla trzech zwrotów wektora prędkości początkowej względem kierunku równoległego do powierzchni.

Następnie zbadałem wpływ głębokości na jakiej położony jest atom z początkową energią na wartość pierwszego momentu. Wyniki dla energii 100 eV oraz trzech różnych orientacji wektora prędkości przedstawia **rysunek 2.9b**. Jeśli oś  $x$  skierowana jest równoległe do powierzchni, to wybranymi kierunkami były: równoległy do  $x$ , pod kątem  $60^\circ$  do  $x$  w kierunku powierzchni oraz pod kątem  $60^\circ$  od powierzchni w głąb próbki. Ponieważ pierwszy moment obliczany jest w kierunku  $x$ , to aby można było porównać otrzymane wyniki, na **rysunku 2.9b** wyniki dla kierunków w stronę powierzchni oraz od powierzchni pomnożone są razy dwa ( $\cos(60^\circ) = 0.5$ ). Każdy punkt na **rysunku 2.9b** został obliczony na podstawie 300 symulacji. Jak widać na wykresie, dla głębokości powyżej 4 nm wartości pierwszego momentu nie zależą od kierunku. Natomiast im bliżej powierzchni znajduje się atom, któremu nadajemy początkową prędkość, tym większa jest różnica w otrzymanych momentach w zależności od kierunku prędkości. Spowodowane jest to tym, że przy powierzchni kolektywny ruch atomów może propagować się w jej kierunku zmieniając jej kształt (efekty nieliniowe). Dla kierunku w stronę powierzchni, dla pomiaru najbliżej powierzchni (0.5 nm) wartość pierwszego momentu nagle spada, co spowodowane jest tym, że

duża część atomów zostaje po prostu rozpylona i nie ma wkładu do procesu redystrybucji. Dodatkowo, dla porównania, na wykres zostały naniesione wyniki metody Monte Carlo o parametrach „ffp>0“,  $E_d=5$  eV. Dla tej metody, dla głębokości powyżej 2.5 nm, obserwujemy stałą wartość pierwszego momentu, natomiast dla głębokości bliżej powierzchni następuje spadek wartości pierwszego momentu. Ponownie jest to spowodowane tym, że metoda Monte Carlo nie jest w stanie symulować efektów nieliniowych (odkształcanie powierzchni), a spadek tej wartości podyktowany jest tym, że część atomów zostaje rozpylona i nie ma wkładu do momentu. Dla głębokości powyżej 4 nm wartości otrzymane obiema metodami zbiegają się.

## Wnioski

Otrzymane wyniki pokazały, że odpowiednio sparametryzowana metoda Monte Carlo, wykorzystująca model IMSIL może uzyskać wyniki zgodne z symulacjami metodą dynamiki molekularnej. Dla badanego zakresu niskich energii ( $E_k < 100$  eV), aby model IMSIL generował poprawne wyniki, konieczne było wprowadzenie modyfikacji do metody obliczania pozycji atomów po zderzeniu.

### 2.2.3 Prosty model szorstkości dla metody Monte Carlo

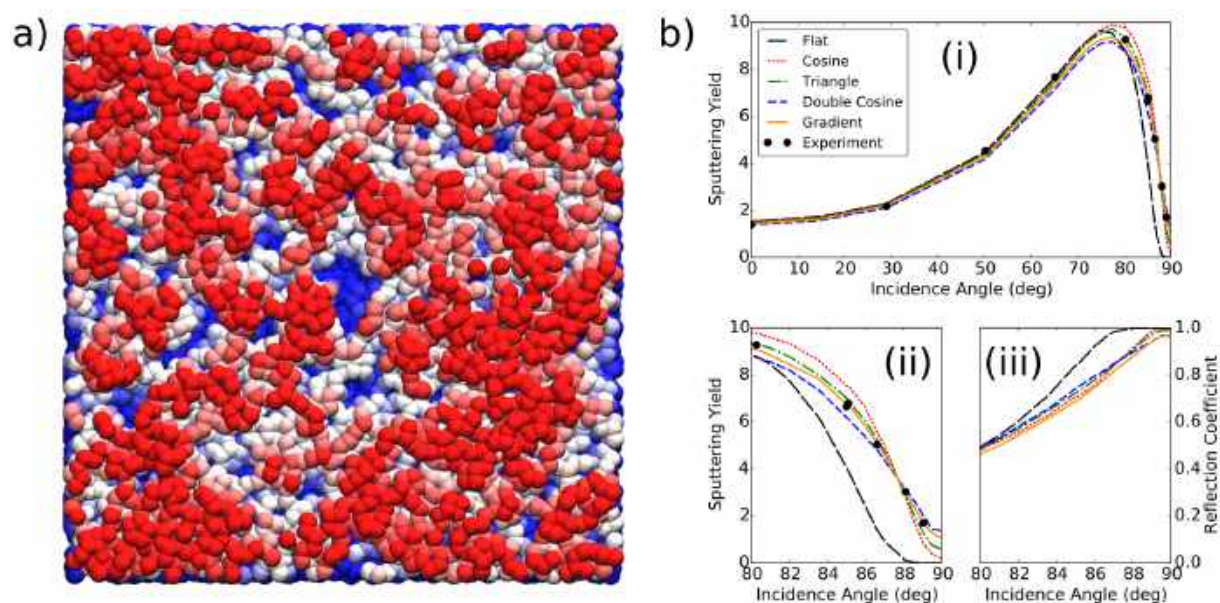
Sekcja oparta na publikacji: „*Simple model of surface roughness for binary collision sputtering simulations*“

#### Motywacja

Jak przedstawiłem to we wcześniejszych publikacjach, metoda Monte Carlo jest ważnym narzędziem wykorzystywanym do badań procesu bombardowania próbki pociskami atomowymi. Jednak dla dużych kątów padania ( $\theta > 80^\circ$ ) morfologia bombardowanej powierzchni zaczyna mieć dominujący wpływ na dokładność uzyskiwanych tą metodą wyników [49]. Bombardowania powierzchni pod takimi kątami jest bardzo istotne w wytwarzaniu nanostruktur za pomocą techniki FIB [50]. Celem opisywanej tutaj publikacji było zbadanie czterech modeli szorstkości zaimplementowanych na potrzeby symulacji metodą Monte Carlo. Trzy z nich, nazywane modelami geometrycznymi, wprowadzają szorstkość bezpośrednio poprzez zmianę kształtu powierzchni modelowanej próbki: sinus, podwójny sinus oraz kształt trójkątny. Każdy z tych modeli zdefiniowany był poprzez dwa parametry,

amplitudę oraz długość fali. Za pomocą dynamiki molekularnej wyznaczyłem rzeczywistą długość fali struktur, które powstają na powierzchni krzemu podczas bombardowania pod kątami ślizgowymi. Czwarty model szorstkości modelował chropowatość tylko poprzez szerokość warstwy przejściowej pomiędzy próżnią a próbką. W tej warstwie gęstość materiału zmieniała się od zera, na powierzchni, do gęstości materiału właściwego w głębi próbki.

## Metodologia



**Rysunek 2.14:** a) Powierzchnia krzemu symulowana metodą dynamiki molekularnej, utworzona na skutek 2100 uderzeń pociskiem 5 keV Ga pod kątem  $\theta=89^\circ$ . Kolor atomu reprezentuje wysokość atomu Si w kierunku normalnym do powierzchni. b) Porównanie wyników eksperymentalnych z metodą Monte Carlo wykorzystującą różne modele szorstkości powierzchni: i) współczynnik rozpylania w zakresie  $0^\circ$ - $90^\circ$ , ii) współczynnik rozpylania w zakresie  $80^\circ$ - $90^\circ$ , iii) współczynnik odbicia pocisku.

Dla tak dużych kątów padania, krytycznym parametrem, jaki należy zapewnić w symulacjach metodą dynamiki molekularnej, jest odpowiedni potencjał oddziaływania pomiędzy pociskiem a atomami podłoża. Jako potencjał oddziaływania galu z krzemem wybrałem potencjał Lennarda-Jonesa [25] o głębokości studni potencjału  $\epsilon=0.9$  eV. Wartość ta została wybrana na podstawie szeregu niezależnych symulacji wielokrotnego bombardowania krzemu galem o energii 5 eV pod kątem  $89^\circ$ . W symulacjach zmieniałem wartość  $\epsilon$ , aż do momentu, w którym obliczony na podstawie symulacji współczynnik rozpylania,

zgadzał się z wartością eksperymentalną ( $Y_{exp}=1.7$  [2]). Tak znaną wartość parametru  $\epsilon$  zweryfikowałem symulacjami wykonanymi dla kąta padania  $85^\circ$ . Otrzymana z tych symulacji wartość współczynnika rozpylenia  $Y_{sim}=6.49$  pokrywała się niemal idealnie z wartością eksperymentalną  $Y_{exp}=6.66$  [2]. Potwierdza to, że wartość  $\epsilon$  jest wybrana poprawnie.

Na podstawie stanu powierzchni po bombardowaniu pod kątem  $85^\circ$  (**Rysunek 2.14a**), obliczyłem długość fali odpowiadającą strukturom na powierzchni, która wyniosła około  $\lambda=3$  nm. Wartość ta została wykorzystana w modelach geometrycznych w metodzie Monte Carlo. Optymalna amplituda chropowatości dla modeli geometrycznych oraz w modelu gradientowym została wyznaczona na podstawie wielu symulacji z różnymi wartościami tej amplitudy. **Rysunek 2.14b** przedstawia uzyskane wyniki współczynnika rozpylenia dla badanych modeli z zadaną optymalną amplitudą chropowatości.

Dla dużych kątów padania (**rysunek 2.14b.ii**) symulacje Monte Carlo wykorzystujące modele opisujące chropowatość próbki uzyskują znacznie dokładniejsze wartości współczynnika rozpylenia niż symulacje Monte Carlo bazujące na podstawowym modelu płaskiej powierzchni. Jest to spowodowane tym, że w modelach implementujących chropowatość powierzchni, atom pocisku ma mniejszą szansę na odbicie się od próbki bez spowodowania rozpylenia (**rysunek 2.14b.iii**).

## Wnioski

Zastosowanie modeli chropowatości powierzchni w symulacjach metodą Monte Carlo przełożyło się na dokładniejsze obliczenia współczynnika rozpylenia. Zwiększenie dokładności otrzymywanych wyników było szczególnie widoczne dla dużych kątów padania ( $\theta>80^\circ$ ), dla których obliczenia bez chropowatości dawały bardzo niedokładne wyniki. Opracowany w tej publikacji model gradientowy dzięki swojej prostocie (jeden parametr) oraz wydajności obliczeniowej może być efektywnie wykorzystywany w symulacjach Monte Carlo.

### 2.2.4 Intuicyjny model opisujący zjawisko indukowania morfologii powierzchni wiązką jonową

Sekcja oparta na publikacji: „*An Intuitive Model of Surface Modification Induced by Cluster Ion Beams*“

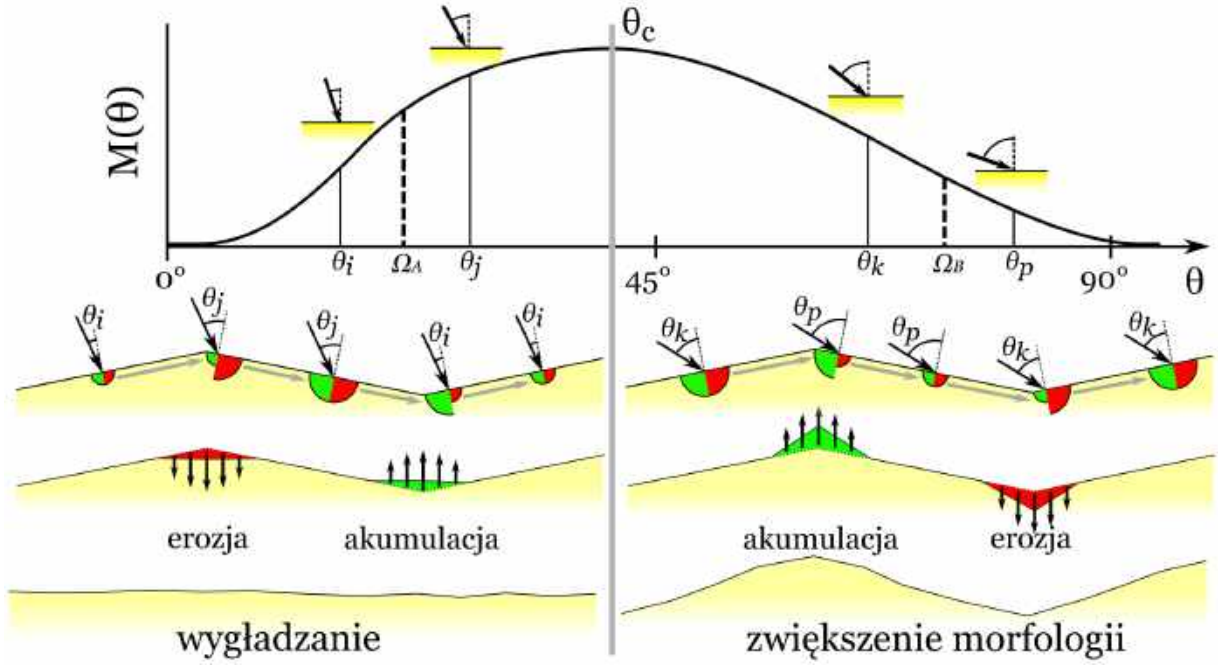
## Motywacja

Istnieje wiele modeli opisujących zjawisko powstawania ripli podczas bombardowania powierzchni wiązką jonów [13]. Modele te jednak mają bardzo złożoną definicję matematyczną, co nie jest korzystną cechą, ponieważ im większy poziom abstrakcji matematycznej, tym ciężiej jest zrozumieć występujące zjawiska. Dobrze demonstrowe to wykorzystywany w wyżej opisywanych publikacjach formalizmu krateru, gdzie powstawanie ripli tłumaczone jest na podstawie wartości parametru  $C$ , natomiast parametr ten jest w złożony sposób obliczany na podstawie momentów funkcji krateru. Jeśli czytelnik nie ma wystarczająco obszernej wiedzy na tematy matematyki wykorzystywanej przez model, to uzyskiwane na podstawie tego podejścia wnioski mogą wydawać się nie do końca uzasadnione. Taki stan rzeczy zmotywował mnie do zaproponowania modelu, który bazowałby na bezpośredniej fizycznej interpretacji, dając łatwy do zrozumienia obraz zjawiska powstawania ripli. Dodatkowym wymogiem dla tworzonego przeze mnie modelu było to, by pozwalał przewidywać, przy jakich parametrach wiązki (energia pocisku, kąt padania) możemy spodziewać się powstania ripli.

## Metodologia

Myślą przewodnią proponowanego przeze mnie modelu jest zwrócenie uwagi na to jak lokalny kąt padania wiązki, a co za tym idzie lokalna redystrybucja masy wywołana uderzeniem pocisku, przekłada się w skali całej powierzchni próbki na zwiększanie lub zmniejszanie morfologii indukowanej bombardowaniem. Przy czym opisywany tutaj lokalny kąt padania to taki, który wstępuje w miejscu padania pocisku, a jego wartość zależy od globalnego kąta padania pocisku oraz od lokalnego nachylenia powierzchni. Z kolei globalnym kątem padania jest kąt eksperymentalny, czyli taki jaki padająca wiązka tworzy z powierzchnią próbki w skali makroskopowej. **Rysunek 2.15** przedstawia wizualizację przykładowych globalnych kątów padania  $\Omega_A$ ,  $\Omega_B$  (przerywana linia na wykresie  $M(\theta)$  oraz towarzyszących im lokalnych kątów padania  $(\theta_i, \theta_j)$  oraz  $(\theta_k, \theta_p)$ ).

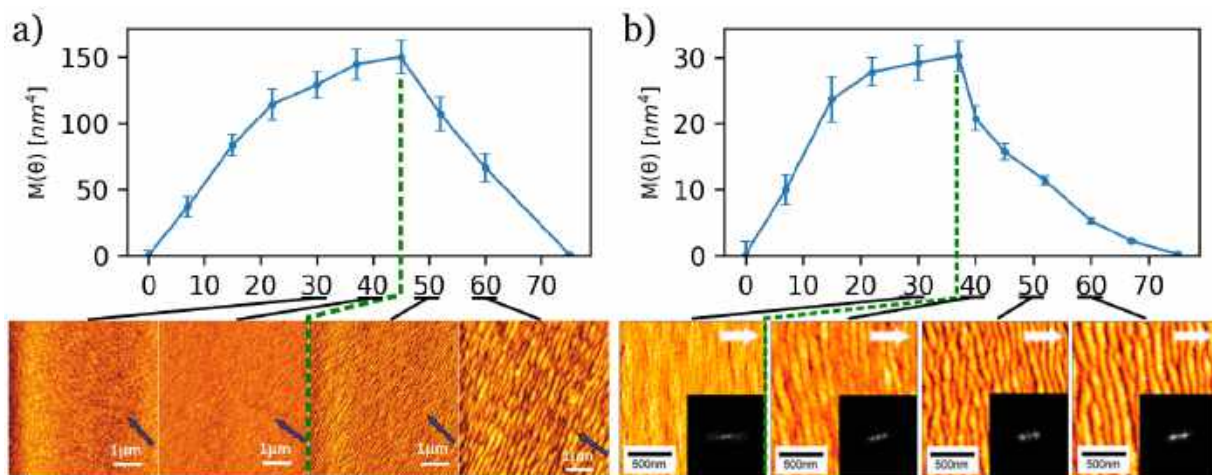
Przedmiotem analizy jest wpływ lokalnej redystrybucji masy na morfologię powierzchni, dla dwóch przypadków globalnego kąta padania, korzystając z uproszczonego schematu przedstawionego na **rysunku 2.15**. W pierwszym przypadku globalny kąt padania  $\Omega_A$  znajduje się w regionie, w którym wartość funkcji redystrybucji masy  $M(\theta)$  rośnie wraz z lokalnym kątem padania. Oznacza to, że redystrybucja masy dla kąta padania  $\theta_i$  jest



**Rysunek 2.15:** Wizualizacja wpływu kształtu kątowej zależności redystrybucji masy ( $M(\theta)$ ) wywołanej uderzeniem pocisku na ewolucję morfologii powierzchni. W przedstawionych rozważaniach powierzchnię traktuję jako serię dyskretnych węzłów, między którymi dochodzi do wymiany masy. Wielkość transferu masy uzależniona jest od lokalnego kąta padania. Na ilustracji wartość ta zobrazowana jest wielkością ćwiartki koła. Czerwony kolor reprezentuje wypływ masy z węzła, a zielony przypływ masy do węzła.

mniejsza niż dla kąta padania  $\theta_j$ , jeżeli  $\theta_i > \theta_j$ . Śledząc lokalne przemieszczanie się masy, obserwujemy erozję masy na wzniesieniach oraz akumulację masy w depresjach. Przeprowadzając takie samo rozumowanie dla przypadku, gdy globalny kąt padania  $\Omega_B$  znajduje się w regionie, gdzie  $M(\theta)$  maleje wraz ze wzrostem  $\theta$ , otrzymamy odwrotny efekt. Oznacza to, że będziemy obserwować akumulację masy na szczytach, natomiast erozję masy w depresjach. Łącząc oba efekty, możemy wnioskować, że wygładzanie lub zwiększanie szorstkości powierzchni zależy od kąta krytycznego  $\theta_C$ , dla którego funkcja redystrybucji masy ma wartość maksymalną. Jeśli kąt padania wiązki w eksperymencie znajduje się pomiędzy  $0^\circ$  a  $\theta_C$ , to bombardowanie będzie miało wygładzający efekt. Natomiast jeśli będzie powyżej  $\theta_C$ , to będą powstawały riple.

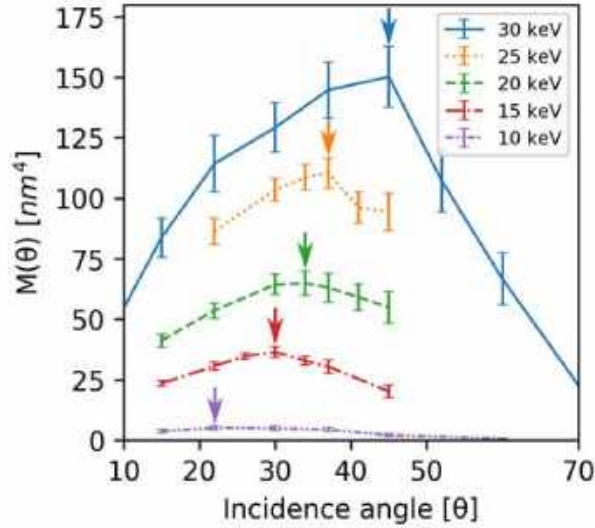
Aby sprawdzić przewidywania mojego modelu wybrałem dwa eksperymenty jako punkty odniesienia. W tych doświadczeniach krzem [15] oraz złoto [16] były bombardowane wiązką 30 keV  $\text{Ar}_{3000}$ . Są to przykłady idealne, ponieważ autorzy przeprowadzili proces bombar-



**Rysunek 2.16:** Porównanie wyników eksperymentalnych [15,16] (obrazy AFM) z funkcją redystrybucji masy obliczoną na podstawie symulacji metodą dynamiki molekularnej, zielona przerywana linia oznacza kąt krytyczny  $\theta_C$ . a) Próbka krzemu, b) próbka złota, bombardowane pociskiem  $\text{Ar}_{3000}$   $E_k=30$  keV.

dowania dla różnych kątów, a po zakończonym eksperymencie, dla każdego przypadku, zmierzili obrazy AFM, na których podstawie można wnioskować czy pojawiły się riple czy też nie. Za pomocą dynamiki molekularnej techniką wielokrotnych uderzeń obliczyłem funkcję redystrybucji masy dla różnych kątów padania (**rysunek 2.16**). Dla obu przypadków maksimum znajdowało się dokładnie w miejscu, dla którego w układach eksperymentalnych zachodziło przejście z gładkiej powierzchni do pojawienia się ripli, co jednoznacznie potwierdzało skuteczność mojego modelu.

Dodatkowo sprawdziłem, jak funkcja redystrybucji masy zależeć będzie od energii kinetycznej pocisku (**rysunek 2.17**). W tym przypadku badaną próbką był krzem bombardowany pociskiem  $\text{Ar}_{3000}$  o energiach 10 keV, 15 keV, 20 keV, 25 keV i 30 keV. Każda energia to osobna seria symulacji wielokrotnego bombardowania dla różnych kątów padania. Położenie maksimum dla najmniejszej energii pocisku  $E_k=5$  keV znajdowało się w  $\theta_c = 23^\circ$ , w miarę zwiększania tej energii położenie maksimum przesunęło się w kierunku wyższych kątów  $\theta_c$ , osiągając największą wartość  $\theta_c = 45^\circ$  dla najwyższej badanej energii  $E_k=30$  keV. Oznacza to, że wraz ze wzrostem energii kinetycznej pocisku, położenie maksimum przesunęło się w kierunku większych kątów. Taki trend był obserwowany w pracy [51]. W tym eksperymencie próbkę organiczną bombardowano wiązką klastrową  $\text{Ar}_{5000}$  o różnych energiach (5 keV, 10 keV, 20 keV). Dla energii 5 keV zaobserwowano, że jakość profilu (rozdzielczość głębokościowa mierzona warstwy delta) pogarsza się wraz



**Rysunek 2.17:** Kątowa zależność funkcji redystrybucji masy dla różnych energii pocisku  $\text{Ar}_{3000}$  bombardujących próbkę krzemu. Położenie maksimum funkcji redystrybucji dla każdej energii kinetycznej pocisku oznaczone jest strzałką.

z głębokością, a degradacja ta była spowodowana powstaniem morfologii powierzchni (riple), natomiast dla energii 10 keV oraz 20 keV jakość profilu pozostaje stała (efekt wygładzający). Ponieważ kąt padania dla wszystkich energii był taki sam  $\theta = 45^\circ$ , oznacza to, że dla energii wiązki pomiędzy 5 keV a 10 keV powinna nastąpić zmiana położenia maksimum na funkcji redystrybucji z  $\theta_c < 45^\circ$  do  $\theta_c > 45^\circ$ .

## Wnioski

W opisywanej pracy pokazałem, że bombardowanie powodujące redystrybucję masy zawsze powoduje wzmacnianie lub wygaszanie chropowatości powierzchni. To, w którym z tych dwóch reżimów znajduje się bombardowana próbka, zależy od dwóch głównych czynników: pod jakim globalnym kątem wiązka pada na powierzchnię i jaka jest kątowa zależność redystrybucji masy dla badanego układu. Redystrybucja masy musi mieć wartość zero dla skrajnych kątów padania  $\theta = 0^\circ$  (całkowita symetria uderzenia, czyli tyle samo masy jest przemieszczone w prawo i w lewo) oraz  $\theta = 90^\circ$  (pocisk porusza się prostopadle do powierzchni, więc nie może powodować żadnej redystrybucji masy). Maksimum tej funkcji musi więc leżeć gdzieś pomiędzy tymi wartościami. W prezentowanych badaniach wartości kąta krytycznego zawierały się w przedziale  $23^\circ - 50^\circ$ . Fakt ten ma duże znaczenie dla technik, w których bombardowanie wykorzystywane jest do warstwowego

usuwania próbki. W tych przypadkach zależy nam na tym, aby być w regionie wygładzającym ( $\theta < \theta_C$ ). Na przykład w układach SIMS, większość komercyjnej aparatury ma na stałe zamontowane działo jonowe pod kątem  $\theta = 45^\circ$  do normalnej do powierzchni badanych układów. Co oznacza, że dla części próbek będziemy indukować niepożądaną morfologię powierzchni. Dzięki zrozumieniu zjawiska dostarczanemu przez niniejszy model widzimy, że zmiana kąta padania wiązki nawet o kilka stopni w kierunku mniejszych wartości skutkowałoby przejściem do reżimu wygładzającego. A co za tym idzie, znaczną poprawą otrzymywanych profili głębokościowych. Dodatkowo, zwiększenie energii padającej wiązki przesuwa kąt krytyczny w kierunku mniejszych wartości. Oznacza to, że dla przypadków kiedy mamy problem z chropowatością, a nie możemy zmienić kąta padania, to jednym z możliwych rozwiązań jest zwiększenie energii kinetycznej padającej wiązki.

## 2.3 Podsumowanie pracy

Celem niniejszej pracy było zbadanie efektów morfologicznych zachodzących podczas bombardowania powierzchni pociskami atomowymi oraz klastrowymi. W pierwszej części przedstawiłem prace, w których badania koncentrowały się na wpływie morfologii powierzchni na proces bombardowania i emisji cząstek. W publikacji „*Micro- and Macroscopic Modeling of Sputter Depth Profiling*” wprowadziłem model służący do symulowania profili głębokościowych uzyskiwanych w technice SIMS na podstawie danych eksperymentalnych oraz informacji uzyskanych z symulacji komputerowych. Stworzone za pomocą modelu profile głębokościowe dobrze odtwarzały wyniki eksperymentalne. Analizując wyniki generowane przez model, można zaobserwować, że na kształt otrzymywanych profili dominujący wpływ ma chropowatość próbki, natomiast wpływ mieszania jonowego ma wpływ drugorzędny. W kolejnej pracy „*MD-Based Transport and Reaction Model for the Simulation of SIMS Depth Profiles of Molecular Targets*”, wspomniany model rozwijam o efekty chemiczne zachodzące podczas bombardowania. Badanym układem był polistyren bombardowany klastrami argonowymi oraz  $C_{60}$ . Układ ten przechodzi proces sieciowania, który można redukować, doprowadzając cząsteczki NO na bombardowaną powierzchnię. Model dobrze odwzorował jakościowy wpływ ilości podawanych cząsteczek NO na kształt profili głębokościowych, jednak najważniejszą wnioskiem z tej pracy było uzyskanie ilościowej informacji, że wydajność cząsteczek NO w reakcji z wolnymi rodnikami powstającymi na powierzchni podczas bombardowania pociskiem  $C_{60}$  wynosi 10%. W ostatniej publikacji poruszanej w tej części pracy „*C-O Bond Dissociation and Induced Chemical Ionization Using High Energy  $(CO_2)_n^+$  Gas Cluster Ion Beam*” za pomocą symulacji metodą dynamiki molekularnej pokazałem, jak morfologia powierzchni wpływa na proces fragmentacji molekuł  $CO_2$  podczas bombardowania klastrami  $(CO_2)_n$ .

Druga część niniejszej pracy koncentrowała się na wpływie bombardowania na powstającą morfologię powierzchni. W tym celu w części prac wykorzystywałem formalizm funkcji krateru, który przewiduje efekt wygładzania lub zwiększenia chropowatości w oparciu o momenty funkcji krateru obliczane na podstawie symulacji metodą dynamiki molekularnej lub metodą Monte Carlo. W pierwszej pracy „*Crater function moments: Role of implanted noble gas atoms*” pokazałem, że implantowane atomy pocisku mają istotny wkład do pierwszego momentu funkcji krateru. Jest to istotny wniosek, ponieważ wszystkie dotychczasowe badania ignorowały ten wpływ. Dodatkowo porównanie wyników z symulacji

metodą dynamiki molekularnej z metodą Monte Carlo, pokazało, że ta druga nie doszacowuje wkładu do pierwszego momentu od redystrybucji atomów próbki. Problem ten został zbadany w publikacji „*Ion bombardment induced atom redistribution in amorphous targets: MD versus BCA*“, w której badałem wpływ parametrów metody Monte Carlo na dokładność otrzymywanych za jej pomocą pierwszych momentów funkcji krateru. Wartościami odniesienia dla tych symulacji były wartości uzyskane za pomocą dynamiki molekularnej. Wyniki pokazały, że możliwe jest takie dobranie parametrów metody Monte Carlo, aby rozwiązać problem niedoszacowywania wkładu od redystrybucji atomów próbki. W kolejnej opisywanej publikacji „*Simple model of surface roughness for binary collision sputtering simulations*“ badałem efekt wprowadzenia różnych modeli chropowatości w metodzie Monte Carlo na dokładność wyników uzyskiwanych za pomocą tej metody, ze szczególnym naciskiem dla ślizgowych kątów padania wiązki. Zastosowanie modeli chropowatości, które były parametryzowane na podstawie symulacji metodą dynamiki molekularnej, skutkowało znacznym zwiększeniem dokładności otrzymywanych wyników, w szczególności dla kątów ślizgowych. W ostatniej opisywanej publikacji „*An Intuitive Model of Surface Modification Induced by Cluster Ion Beams*“ stworzyłem nowy model, który w przystępny sposób tłumaczy zjawisko powstawania lub wygaszania morfologii powierzchni podczas bombardowania wiązką klastrową. Przewidywania modelu opierają się na położeniu kąta krytycznego w kątowej zależności redystrybucji masy wywołanej uderzeniem. W publikacji pokazałem, że aby bombardująca wiązka miała wygładzający efekt na powierzchnię, kąt padania musi być mniejszy niż kąt krytyczny. Fakt ten ma bardzo duże znaczenie w technikach profilowania głębokościowego. Dodatkowo pokazałem, że zwiększenie energii kinetycznej pocisku przesunęło położenie kąta krytycznego w kierunku mniejszych wartości.

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## Rozdział 3

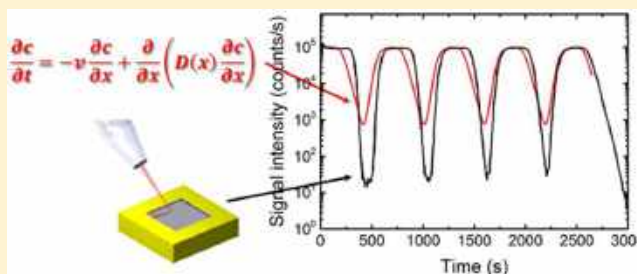
### Przedruki artykułów

# Micro- and Macroscopic Modeling of Sputter Depth Profiling

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## S Supporting Information

**ABSTRACT:** A model for predicting depth profiles due to energetic particle bombardment based on the RMS roughness of the system and the sputtering yield is proposed. The model is an extension of the macroscopic transport model proposed previously [Tuccitto, N.; Zappala, G.; Vitale, S.; Torrisi, A.; Licciardello, A. *J. Phys. Chem. C* **2016**, *120*, 9263–9269]. The model is used to reconstruct the experimental depth profiles of a NiCr heterostructure due to bombardment by C<sub>60</sub>, SF<sub>5</sub>, O<sub>2</sub>, and Ga.



## 1. INTRODUCTION

Efforts have been undertaken toward understanding the factors involved in depth profiling of atomic and molecular solids due to bombardment by energetic projectiles. Typical model systems include embedded delta layers and multilayer heterostructures. The first models introduced the three fundamental factors for depth profiling, that is information depth of sputtered material, ion-beam mixing, and surface roughness.<sup>1,2</sup> These models propose analytic functions for fitting to experimental data and are useful in many applications. The procedure, however, of how to incorporate microscopic information on the atomic or molecular motion, such as comes from atomistic molecular dynamics (MD) simulations, is not clear.

A model has been developed recently to take information from MD simulations and predict the depth profile of a delta layer.<sup>3–6</sup> This model is valuable in providing insight as to how the physics from the MD simulations fits with the concepts of roughness, information depth, and mixing. The computational complexity of this model and the underlying MD simulations, however, make it prohibitive to consider large depths and long times. As a result, modeling depth profiling of systems with 100s of nm depth and inclusion of long time scale processes, such as thermal diffusion, is not tractable. It is also not clear how to connect experimental quantities with the calculated depth profile.

Recently, a continuum transport and reaction model of depth profiling due to energetic ion-beam bombardment or sputtering has been proposed by Tuccitto et al.<sup>7</sup> The physics associated with sputtering, specifically the sputtering yield and the ion-beam damage or displacements, are associated with the macroscopic processes of advection and diffusion, respectively. A reaction term has also been incorporated to include bombardment-induced chemistry. This transport model is capable of correctly reproducing qualitative features of a depth profile. It is not clear, however, how the parameters of

this model map to the microscopic quantities of MD simulations or experimental data. On the other hand, incorporating quantities such as thermal diffusion and modeling large sample depths is straightforward and easy to compute.

We have long been proponent of analytic models that incorporate input from MD simulations, especially for the ion-beam bombardment process of secondary ion mass spectrometry (SIMS). These include the mesoscale energy deposition footprint (MEDF) model<sup>8,9</sup> and the steady-state statistical sputtering model (SS-SSM).<sup>4,5</sup> In the MEDF model, the energy deposition profile from short-time MD simulations of cluster particle bombardment are used to provide input into an analytic model to predict sputtering yields as a function of incident energy. The SS-SSM uses input from repetitive bombardment MD simulations<sup>10</sup> to predict the corresponding depth profile of a delta layer. For C<sub>60</sub> and Au<sub>3</sub> bombardment of a Ag surface, it was found that the best depth profiles resulted when the sputtering yield was high relative to the amount of ion-beam mixing or damage.<sup>5</sup>

In this study, we propose how to use the SS-SSM and underlying MD simulations to determine how to interpret and choose input into the transport model. Specifically we will use the examples of C<sub>60</sub> and Au<sub>3</sub> bombardment of Ag(111)<sup>4,5</sup> and C<sub>60</sub> bombardment of a molecular solid of octane.<sup>6</sup> On the basis of this development, we propose simple relationships of the input quantities to the transport model based on only the experimental quantities of sputtering yield and RMS roughness. The predicted depth profiles from these parametrizations will be compared to the depth profiles predicted by the SS-SSM. Finally, we predict depth profiles for C<sub>60</sub><sup>+</sup>, Ga<sup>+</sup>, SF<sub>5</sub><sup>+</sup>, and O<sub>2</sub><sup>+</sup> depth profiling of a NiCr heterostructure and explain the beam type dependence of the experimental depth profiles.<sup>11–13</sup> The

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ultimate target to be addressed in future studies is explaining the temperature dependence of depth profiling of Irganox delta layers.<sup>14–16</sup> The ability to incorporate the experimental data directly into the transport model makes this model useful in direct interpretation of experimental results.

## 2. MICRO- AND MACROSCOPIC DESCRIPTIONS OF SPUTTER DEPTH PROFILING

The first step is to establish a procedure for using the results of the repetitive bombardment MD simulations and the SS-SSM analysis to understand and quantify the input quantities of the transport model in terms of the basic physics and motion of the bombardment process. On the basis of this analysis and comparison, we formulate an empirical approach based on only experimental quantities for determining the input quantities of the transport model.

**2.1. Transport and Reaction Model.** This model is described in detail in the original reference<sup>7</sup> and is based on the advection–diffusion–reaction equation for mass transfer

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left( D(x) \frac{\partial c}{\partial x} \right) + R(x) \quad (1)$$

The independent variables are  $t$  = time [s] and  $x$  = depth [nm]. The dependent variable is  $c = c(x;t)$  = concentration profile of mass (or number of atoms/molecules). The parameters are  $v$  = velocity the mass is traveling with [nm/s],  $D(x)$  = depth dependent diffusivity [nm<sup>2</sup>/s], and  $R(x)$  = depth dependent reaction term [1/s], a quantity not utilized in this study. The initial condition is  $c_0 = c(x;t=0)$ . A second equation of the same form, with its own set of the parameters, can be added to model the depth profiling of the second component as is needed for the NiCr heterostructure. The initial concentration profile of a delta layer is modeled as a double sigmoid. It corresponds to a layer of mass embedded in the sample at given depth. As the time passes, the mass travels toward the surface of the sample,  $x = 0$ . During this process the profile changes its shape due to the effect of  $D(x)$ . In the original model, the depth profile is determined only by the concentration of the delta layer component at the surface as time is progressed in the numerical integration.<sup>7</sup> Below we will propose a method to include information depth in the transport model based on MD simulation results.

**2.2. Information Available in MD Simulations and the SS-SSM.** The first step is to assess the information available in the MD simulations and the SS-SSM<sup>4–6</sup> analysis to make a connection to the transport model. The critical quantities that arise in a straightforward analysis from the repetitive bombardment MD simulations<sup>10</sup> are the yield expressed in volume per impact and the RMS roughness. The SS-SSM<sup>4–6</sup> provides a formalism for analyzing the results of the MD simulation and also predicts depth profiles of delta layers. The SS-SSM divides the MD system into layers and calculates quantities on a per layer basis. The surface is roughened thus all quantities are relative to the average surface level. The three quantities of relevance are the sputtering yield per layer, displacements of atoms or molecules from one layer to another, and the average occupation of each layer.

The sputtering, displacement, and occupancy distributions as determined in the SS-SSM from the MD simulations are for a roughened surface, whereas the transport model assumes a flat surface. The first step in making these two approaches compatible is to ignore the information from the volume

above the average surface level, peaks in the roughened surface, as there are relatively few particles here. Second, the distributions from the average surface level (50% occupancy) and into the substrate are normalized by the occupancy of each layer. Thus, the distributions now appear as they are from a flat surface. The roughness information remains, however, in the widths of the distributions. In addition, the displacement distributions in the SS-SSM were for movement up and down. These have been converted to movement by one layer, by two layers, and by three layers, where each of these quantities is known as a function of layer position. Finally, the number of atoms per layer that do not move vertically are determined. This step is essential for determination of the value of the ion-beam mixing term. Of note is that for each layer the sum of the number of atoms that do not move, that move one layer, that move two layers, etc., is approximately proportional to the surface area of the master sample used in the MD simulation. Later, we will use the explicit surface area of the master sample for the calculation of time between impacts, and it is important to realize that this information will cancel out.

**2.2.1. Velocity.** The velocity  $v$  that the mass is traveling with is the rate at which the surface recedes and is associated with the sputtering yield,  $Y$ , in nm<sup>3</sup> and experimental fluence,  $F$ , in ions/(nm<sup>2</sup> s) as

$$v = FY \quad (2)$$

**2.2.2. Sampling Depth.** In the original formulation,<sup>7</sup> the depth profile is determined only by the concentration of the delta-layer component as it approaches the surface. In reality, however, also particles located below the surface are being ejected by a single projectile impact. The depth distribution of a number of atoms ejected by a single impact is known as a sampling or information depth. This quantity can be easily determined from the sputtering distributions given by the MD simulations. We normalize this function to a unit area as the total sputtering yield is incorporated in the velocity. The normalized sampling depth,  $S(x)$ , is subsequently used as a weighting factor for the concentration profile,  $c(x)$ , to calculate ejected mass in the predicted depth profile. In addition to containing information about the depth of origin of the sputtered particles, it implicitly contains information about the RMS roughness.

**2.2.3. Ion-Beam Mixing and Diffusion.** The ion-beam mixing and diffusion has the form of

$$D_{\text{total}} = D(x) + D_{\text{diff}} \quad (3)$$

where  $D(x)$  is the depth-dependent ion-beam mixing term. True thermal diffusion is represented by  $D_{\text{diff}}$  and is a constant component that can be temperature dependent.

Conceptually, there is a challenge to tie ion-beam mixing to diffusion. Diffusion is generally considered to be a long time process whereas the ion-beam mixing occurs on a time scale up to tens of picoseconds. Even by examining MD simulations, providing a precise time scale is challenging. We start, however, by implementing the formula used for calculating a diffusion constant in MD simulations. Diffusivity for an infinite one-directional system is described as

$$D(x) = \frac{1}{2} \lim_{t \rightarrow \infty} \frac{\langle \text{disp}(x)^2 \rangle}{t} \quad (4)$$

The sputtering process and associated ion-beam mixing do not exactly fit with the above description, but in order to find a

connection between the macroscopic model for depth profiling and the microscopic motions we assume a similar relation as

$$D(x) = \frac{1}{2} \frac{\langle \text{disp}(x)^2 \rangle}{\Delta t} \quad (5)$$

where  $\Delta t$  is a time interval and thus we proceed from here. To calculate the quantity  $\langle \text{disp}(x)^2 \rangle$ , we use the information contained in the displacement distributions from the SS-SSM analysis as described above modified to account for the flat surface. For each depth we calculate the number of atoms that are displaced by one layer, by two layers, three layers, etc., and the number of atoms that are not displaced. The displacement term is thus a sum of the number of atoms that are displaced one layer times the layer spacing squared plus the number of atoms displaced two layers times twice the layer spacing squared, etc., divided by the total number of atoms. As noted above, the total number of atoms per layer is approximately proportional to the area of the master sample used in the MD simulations. The quantity  $\Delta t$  is assumed to be the time between impacts on the master sample or the reciprocal of the area of the master sample times the fluence  $F$ . The final situation is that we have used the SS-SSM displacement distributions to calculate a  $D(x)$  value. The time factor has an area of the master sample which effectively cancels out the total number of atoms in a layer in the MD simulation, a factor that is not physically relevant. Overall, then we can write  $D(x)$  as

$$D(x) = FD'(x) \quad (6)$$

where  $D'(x)$  has units of  $\text{nm}^4$  per impact. This quantity  $D'(x)$  does not depend on the fluence, the time between impacts, or the size of the master sample. It is a quantity related to an average over single impacts much like the sputtering yield is an average over individual impact events. Now the ion-beam mixing term in the macroscopic transport equation has a microscopic quantity associated with it. At this point we are not prepared to make a precise physical interpretation of the  $D'(x)$  term. What is clear, however, is that  $D'(x)$  only depends upon properties associated with the individual impact events and not any long time diffusion-like behavior. This quantity should depend upon the projectile beam type, the incident kinetic energy, KE, of the projectile beam, and the material properties including displacement energies. Following the convention that sputtering yields<sup>17</sup> are proportional to the ratio of the KE to the cohesive energy,  $U_0$ , we assume the integral of  $D'(x)$  over depth to be proportional to  $\text{KE}/U_0$  when we discuss below the application of the transport model to the experimental NiCr heterostructures.

To summarize, we used the displacement distributions from the MD simulations and the SS-SSM analysis to define a microscopic ion-beam mixing diffusion term,  $D(x)$ . This relation results in the ion-beam mixing term to be a product of the fluence times a term that corresponds a quantity,  $D'(x)$ , related to single impacts.

For convenience, we assume the fluence to be  $1 \text{ ion}/(\text{nm}^2 \text{ s})$  which corresponds to an ion current density of  $6.4 \text{ nA per } (200 \mu\text{m})^2$ . These conditions are in the experimental regime for  $\text{C}_{60}$  cluster sources. In fact, if there is no time-dependent quantity such as diffusion in the transport equation, the fluence does not matter in this model or in the experiment if the depth profile is shown as a function of depth rather than time. For comparisons with experimental data shown below, the apparent fluences are taken from the experimental data.

**2.2.4. Verification of the Transport Model Depth Profiles vs the SS-SSM Depth Profiles.** The first step is to define the  $S(x)$  and  $D'(x)$  quantities from the MD simulations and the SS-SSM quantities, incorporate them into the transport model, and compare the depth profiles. Repetitive bombardment MD simulations have been performed for three systems and the results analyzed by the SS-SSM with the results presented in previous publications.

- 20 keV  $\text{C}_{60}/\text{Ag}(111)$ .<sup>4–6,18</sup> The sputtering yield is  $6.4 \text{ nm}^3$  (or 373 atoms) per impact,<sup>6</sup> and the RMS roughness of the system is  $2.35 \text{ nm}$ .<sup>5</sup>
- 20 keV  $\text{Au}_3/\text{Ag}(111)$ .<sup>5,18</sup> The sputtering yield is  $3.69 \text{ nm}^3$  (or 216 atoms) per impact, and the RMS roughness of the system is  $2.69 \text{ nm}$ .
- 10 keV  $\text{C}_{60}/\text{octane}$ .<sup>6</sup> The total sputtering yield is  $147 \text{ nm}^3$  (or the equivalent of 703 molecules),<sup>6</sup> and the RMS roughness is  $3.3 \text{ nm}$ .

Only the yields and RMS values are given explicitly here as these are the quantities most directly comparable to information that can be extracted in experiments.

As the differential equation solver that we use requires an analytical form of the input distributions sigmoidal functions are fit to the sampling depth distributions,  $S(x)$ , as well as the ion-beam mixing terms,  $D'(x)$ , obtained from the SS-SSM model. The results are shown in Figure 1 with the sigmoid function equation given in the Supporting Information and the parameters given in Table 1.

The sampling distributions  $S(x)$  shown in Figure 1a are normalized to unit area since they are weighting functions used to obtain sputtered signal from concentration profiles. The distributions for the three systems are similar to basically the

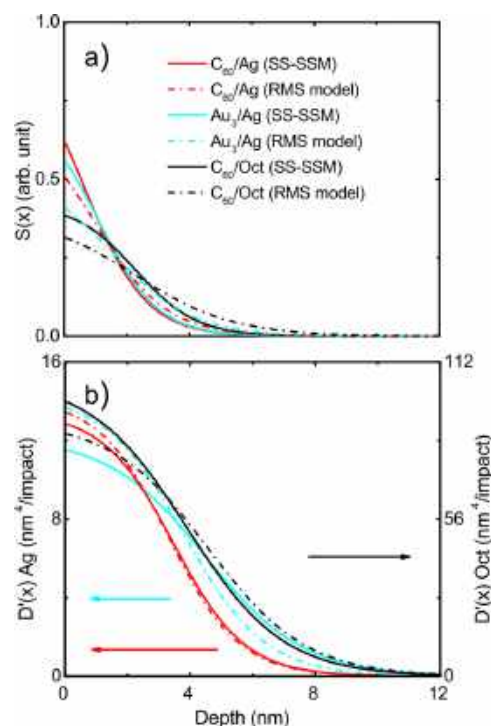


**Figure 1.** Distributions for use in the transport model for the three systems. (a) Sampling depth,  $S(x)$ , from SS-SSM values and the RMS model. (b) Ion-beam mixing,  $D'(x)$ , from SS-SSM values and RMS model; right-hand side scale is for octane, and left-hand side scale is for Ag.

Table 1. Parameters for the Transport Model Based on the MD Results and SS-SSM Analysis

|                                 | velocity (nm/s) | sampling depth, $S(x)$ |              |                 | ion-beam mixing, $D'(x)$            |              |                 |
|---------------------------------|-----------------|------------------------|--------------|-----------------|-------------------------------------|--------------|-----------------|
|                                 |                 | amplitude              | slope (1/nm) | inflection (nm) | amplitude (nm <sup>4</sup> /impact) | slope (1/nm) | inflection (nm) |
| 20 keV C <sub>60</sub> /Ag(111) | 6.4             | 0.94                   | 1.02         | 0.66            | 13.5                                | 0.88         | 3.48            |
| 20 keV Au <sub>3</sub> /Ag(111) | 3.7             | 0.74                   | 1.05         | 1.09            | 12.2                                | 0.64         | 4.50            |
| 10 keV C <sub>60</sub> /octane  | 147             | 0.42                   | 1.03         | 2.28            | 105.8                               | 0.65         | 3.90            |

entire curve at distances less than the twice the RMS roughness. The ion-beam mixing,  $D'(x)$ , functions are shown in Figure 1b. The ion-beam mixing curves are broader than the sampling distributions, consistent with the information from the MD simulations and SS-SSM analysis which shows that the ion-beam mixing occurs at a deeper depth than the sputtering process. The ion-beam mixing distributions are similar in magnitude for C<sub>60</sub> and Au<sub>3</sub> bombardment of Ag and a factor of 7 larger for C<sub>60</sub> bombardment of octane. Explaining the large difference is beyond the scope of this study as we need to develop a better physical or computational picture of  $D'(x)$ . Even though the RMS roughness is not explicitly included in the model, information about the RMS roughness does implicitly appear in the distributions in Figure 1.

The depth profiles calculated with the SS-SSM, which were interpreted previously,<sup>5,6</sup> are shown in Figure 2a. In the

transport model, the delta layer is represented by a double sigmoid as described in the Supporting Information. The depth profiles calculated by the transport model using input from the MD results with SS-SSM analysis are shown in Figure 2b. The SS-SSM distributions do not have an associated time scale; thus, the transport model distributions are shown as a function of depth with the velocity being the conversion factor. In our opinion, there is qualitative agreement between the depth profiles predicted by the transport model and those from the SS-SSM. The worst agreement is for the octane system in which the leading edge of the depth profile from the transport equation is too narrow. In examining the SS-SSM sputtering distribution for this system,<sup>6</sup> it is apparent that a significant amount of material is ejected from above the average surface level, and the assumption stated earlier that we can ignore the peaks of the roughened surface is not valid.

**2.2.5. Development of an Empirical RMS Model.** We feel that we have shown the correspondence between the terms in the transport equation and the microscopic quantities of the MD simulations. Our approach of using information from repetitive bombardment MD simulations provides the quantitative link and the conceptual definition of the impact related ion-beam mixing term,  $D'(x)$ . This approach, however, is not practical for use with experimental data. Consequently, using insights from the previous calibration studies, we developed a simple model that uses the RMS roughness value and the sputtering yield, both quantities that are available from MD simulations or experimental data. This model, called the RMS model for input to the transport equation, is based on following assumptions.

- The inflection point in the  $D'(x)$  distribution is proportional to the RMS value.
- The inflection point in the  $S(x)$  distribution is smaller than  $D'$  inflection point by a constant value,  $d$ , since the analyses of the MD results by the SS-SSM show this to be the case for the model systems.
- The area under the curve of  $D'(x)$  is given, for now, by the area under the curve from the MD results. This assumption is the main area needed for improvement of the RMS model and, in fact, understanding the basic physics underlying  $D'(x)$ .
- For each the  $S(x)$  and  $D'(x)$  sigmoid functions, ignoring the amplitude, we assume that 90% of the amplitude change of the function is between distances of zero and twice the inflection point, a distance denoted “cut”. Since the sigmoid function is antisymmetric around the

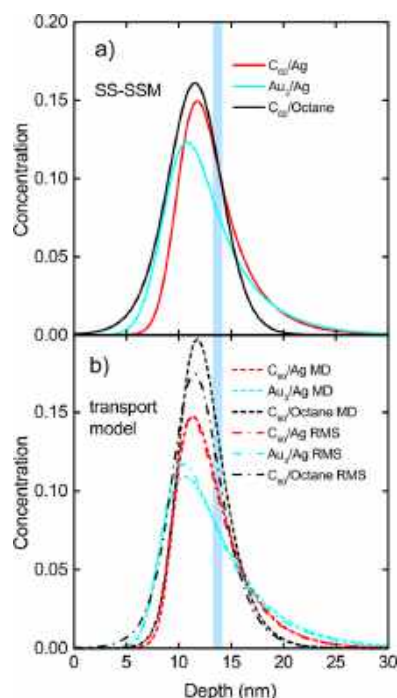


**Figure 2.** Depth profiles for a delta layer, represented by the blue vertical bar, of thickness 1 nm at a depth of 13.2 nm in the solid: (a) SS-SSM; (b) transport model with input from MD results and from the RMS model.

Table 2. Parameters for the Transport Model Based on the RMS Model

|                                 | velocity (nm/s) | sampling depth, $S(x)$ |              |                 | ion-beam mixing, $D'(x)$            |              |                 |
|---------------------------------|-----------------|------------------------|--------------|-----------------|-------------------------------------|--------------|-----------------|
|                                 |                 | amplitude              | slope (1/nm) | inflection (nm) | amplitude (nm <sup>4</sup> /impact) | slope (1/nm) | inflection (nm) |
| 20 keV C <sub>60</sub> /Ag(111) | 6.4             | 0.72                   | 0.89         | 1.01            | 13.46                               | 0.89         | 3.31            |
| 20 keV Au <sub>3</sub> /Ag(111) | 3.7             | 0.54                   | 0.77         | 1.50            | 12.18                               | 0.77         | 3.81            |
| 10 keV C <sub>60</sub> /Octane  | 147             | 0.39                   | 0.64         | 2.28            | 105.8                               | 0.64         | 4.58            |

Table 3. Experimental Conditions

|                                           | RMS<br>(nm) | velocity<br>(nm/s) | Y (nm <sup>3</sup> ) | sampling depth |                 |                    | D'(x)                                  |                 |                    |
|-------------------------------------------|-------------|--------------------|----------------------|----------------|-----------------|--------------------|----------------------------------------|-----------------|--------------------|
|                                           |             |                    |                      | amplitude      | slope<br>(1/nm) | inflection<br>(nm) | amplitude<br>(nm <sup>4</sup> /impact) | slope<br>(1/nm) | inflection<br>(nm) |
| 15 keV C <sub>60</sub> <sup>+</sup> /NiCr | 2.5         | 0.0518             | 2.95                 | 0.628          | 0.835           | 1.23               | 6.78                                   | 0.835           | 3.53               |
| 15 keV Ga <sup>+</sup> /NiCr              | 100         | 0.0122             | 0.174                | 0.007 07       | 0.0209          | 138.7              | 0.2                                    | 0.0209          | 141                |
| 3 keV SF <sub>5</sub> <sup>+</sup> /NiCr  | 10          | 0.201              | 0.174                | 0.082          | 0.209           | 11.8               | 0.181                                  | 0.209           | 14.1               |
| 3 keV O <sub>2</sub> <sup>+</sup> /NiCr   | 62          | 0.441              | 0.087                | 0.011          | 0.0337          | 85.1               | 0.0644                                 | 0.0337          | 87.4               |

inflection point, this means that at a distance of twice the inflection point the value of the function should be 0.05 and the value at zero should be 0.95. This allows us to determine the slope to be

$$\text{slope} = \frac{\ln(1/\text{cut}^{-1})}{\text{inflection point}} \quad (7)$$

We have found that a good agreement between the depth profiles predicted by this simplified RMS model and the depth profiles using MD input can be obtained, if the inflection point for  $D'(x) = 1.4 \cdot \text{RMS}$  and  $d = 3.2$  nm as shown in Figure 2b. The calculated sigmoid function parameters of the RMS model for the three systems are given in Table 2, and the  $S(x)$  and  $D'(x)$  distributions are shown in Figure 1. Regardless of its simplicity, the RMS model reproduces the depth profiles of the SS-SSM method as well as the functions based on the MD results. We have, of course, used information from the MD results to give the area under the  $D'(x)$  curve for the RMS model.

The effect of thermal diffusion on the Ag depth profiles can be easily tested in the transport model by setting the  $D_{\text{diff}}$  parameter. For Ag, self-diffusion has been measured over the temperature ranges of 454–777 K<sup>19</sup> and 903–1208 K,<sup>20</sup> and temperature-dependent diffusion constants have been determined. If these relations are extrapolated to 300 K, the diffusion constant is on the order of  $10^{-18}$  nm<sup>2</sup>/s. This value can be added to the calculation, but this value is 18 orders of magnitude smaller than the ion-beam mixing values; thus, it is obvious that no significant thermal diffusion occurs in Ag. The big point, however, is that both ion-beam mixing and thermal diffusion can be accommodated within the transport model.

### 3. INTERPRETATION OF EXPERIMENTAL DATA

We now take the RMS model one step further and try to reproduce experimental depth profiles of NiCr heterostructures. It will be an important test of model versatility as these depth profiles were obtained with four very different beam conditions. The NiCr heterostructure sample has nine alternating layers of Cr and Ni with the five Cr layers 53 nm thick and the four Ni layers 66 nm thick for a total depth of 529 nm. Two groups have performed depth profiling experiments on this standardized sample. First, Gillen et al. have used 3 keV SF<sub>5</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> beams and measured the Ni<sup>+</sup> and Cr<sup>+</sup> signals.<sup>13</sup> Second, Sun et al. have performed experiments using 15 keV C<sub>60</sub><sup>+</sup> and Ga<sup>+</sup> beams and measured the Ni and Cr signals with multiphoton resonance ionization.<sup>11,12</sup>

The objective of this analysis is to use the available experimental data to predict the depth profiles using the transport model using the RMS model to generate input functions. The three main quantities in the model are the sputtering yield, the displacement quantity  $D'(x)$ , and the fluence. The quantities that appear in the experiment are the

time to depth profile through the 529 nm of material, the RMS roughness, and the sputtering yields for the C<sub>60</sub><sup>+</sup> and Ga<sup>+</sup> beams. The experimental time to depth profile through the sample was used to calculate the average velocity in the model. The obtained values are given in Table 3. In the original publications,<sup>11,12</sup> for C<sub>60</sub><sup>+</sup> and Ga<sup>+</sup> bombardment, the yields were given in atoms per impact, and we converted these to nm<sup>3</sup> by assuming the single crystal atomic density. For Ni and Cr both the atomic densities and yield are within 9% of each other so we used the averaged values for these quantities. The effective fluence is the velocity divided by the yield. This value accounts for the fluence of the beam and also the effect of rastering the beam to produce a depth profile.

The yields for SF<sub>5</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> bombardment were determined by simulation using the experimental values for C<sub>60</sub><sup>+</sup> and Ga<sup>+</sup> as reference points. The calculation of absolute sputtering yields is challenging because none of the interaction potentials are completely accurate and because some physics is missing such as energy loss to electronic effects. Thus, our strategy is to use comparable simulations to estimate relative yields and then determine an estimate of the experimental yields for SF<sub>5</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> bombardment based on the experimental C<sub>60</sub><sup>+</sup> and Ga<sup>+</sup> yields. Previously we determined from MD simulations the yields for C<sub>60</sub> and Ga bombardment of Ag at 15 keV to be 331 and 21 atoms per impact.<sup>21</sup> No potentials exist for bombardment of SF<sub>5</sub> and O<sub>2</sub> on Ag, and we do not want to include too much potential variation so we tried to construct hydrocarbon analogues for these two projectiles. We chose projectiles of neopentane C(CH<sub>3</sub>)<sub>4</sub> and C<sub>2</sub> (with mass of O rather than C). One hundred impacts were calculated for each projectile on the flat surface at an energy of 3 keV and the experimental impact angle of 52°. The calculated yields are  $21.6 \pm 1.5$  and  $10.2 \pm 1.0$  atoms/impact for C(CH<sub>3</sub>)<sub>4</sub> and C<sub>2</sub>, respectively. The neopentane calculated yield is almost the same as the Ga calculated yield, and the C<sub>2</sub> yield is about half the Ga calculated yield on Ag; thus, we scale the experimental yields for Ga<sup>+</sup> on NiCr for SF<sub>5</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> as given in Table 3. The effective fluence is calculated from the experimental average velocity.

The RMS model is used with the experimental RMS values to determine the  $S(x)$  and  $D'(x)$  functions as shown in Figure 3. For the area under the  $D'(x)$  curve we feel that the appropriate calculation should be for the metal substrate, and since  $D'(x)$  for both the C<sub>60</sub> and Au<sub>3</sub> projectiles have similar areas, we chose the 20 keV Au<sub>3</sub>/Ag system, which has a value of 55.8 nm<sup>5</sup>. This value was scaled for each set of beam conditions by  $\text{KE}/U_0$ , as it is commonly used to scale sputtering yields.<sup>22</sup> We assume that it is also a logical scaling factor for displacements. The value of  $U_0$  for Ag is 2.93 eV,<sup>23</sup> and the average value for the NiCr system is 4.27 eV.<sup>23</sup> The four experimental conditions break into two groups depending on the RMS value. The RMS values for the C<sub>60</sub><sup>+</sup> and SF<sub>5</sub><sup>+</sup> bombardment are 2.5 and 10 nm, respectively. For these two systems the axes at the left and bottom of Figure 3 should be

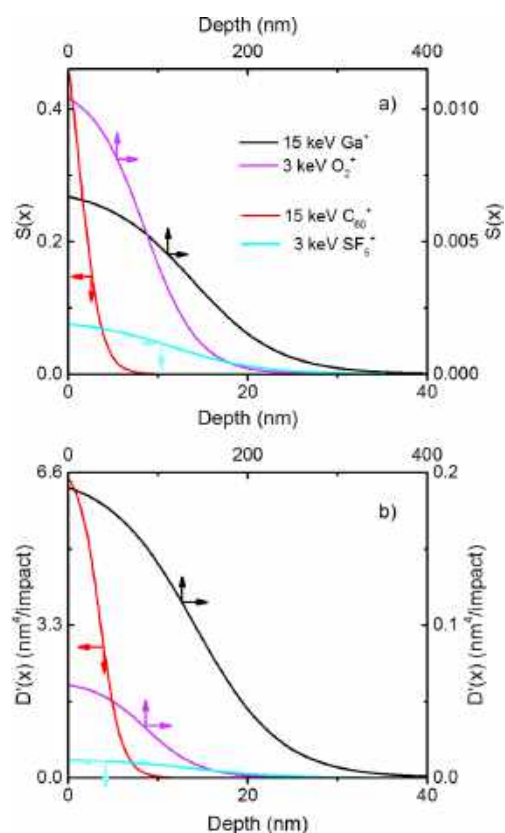


**Figure 3.**  $S(x)$  and  $D'(x)$  functions for the NiCr system for the four beam conditions using the RMS model.

used. The  $S(x)$  and  $D'(x)$  functions are relatively short-ranged and intense. In contrast, the RMS values for  $O_2^+$  and  $Ga^+$  have larger RMS values of 62 and 100 nm, respectively. The right and top axes should be used for their  $S(x)$  and  $D'(x)$  functions. These functions are longer-ranged and less intense than the ones for  $C_{60}^+$  and  $SF_5^+$ . Of note is that the NiCr layers are 53 and 66 nm wide, distances larger than the  $C_{60}^+$  and  $SF_5^+$  functions, smaller than the  $Ga^+$  functions, and comparable to the  $O_2^+$  functions.

The predicted depth profiles are shown in Figure 4 overlaid on the experimental data that was digitized from the original literature. The double sigmoid used to describe the NiCr heterostructure is described in the Supporting Information. We have maintained the plot representation, linear vs log scale, of the experimental publications. The intensities of the individual Ni and Cr signals have a multitude of experimental factors so we used two normalization factors per plot. Overall, we are pleased with the agreement between the transport model depth profiles using the RMS model for predicting the  $S(x)$  and  $D'(x)$  functions with the experimental data. The RMS roughness values for  $C_{60}^+$  and  $SF_5^+$  bombardment are less than the heterostructure layers, and consequently the depth profiles show discrete layers. For the  $O_2^+$  and  $Ga^+$  bombardment there is an induction time to develop the large RMS roughness values, a factor not included in the transport model. Even with this omission, we feel that the predicted depth profiles qualitatively reproduce the experimental distributions. We did try not using  $KE/U_0$  to scale the  $D'(x)$  area. The resulting depth profiles were slightly broader but not qualitatively different.

There is one additional piece of information available in the experimental study on the  $C_{60}^+$  bombardment of NiCr;<sup>11</sup>

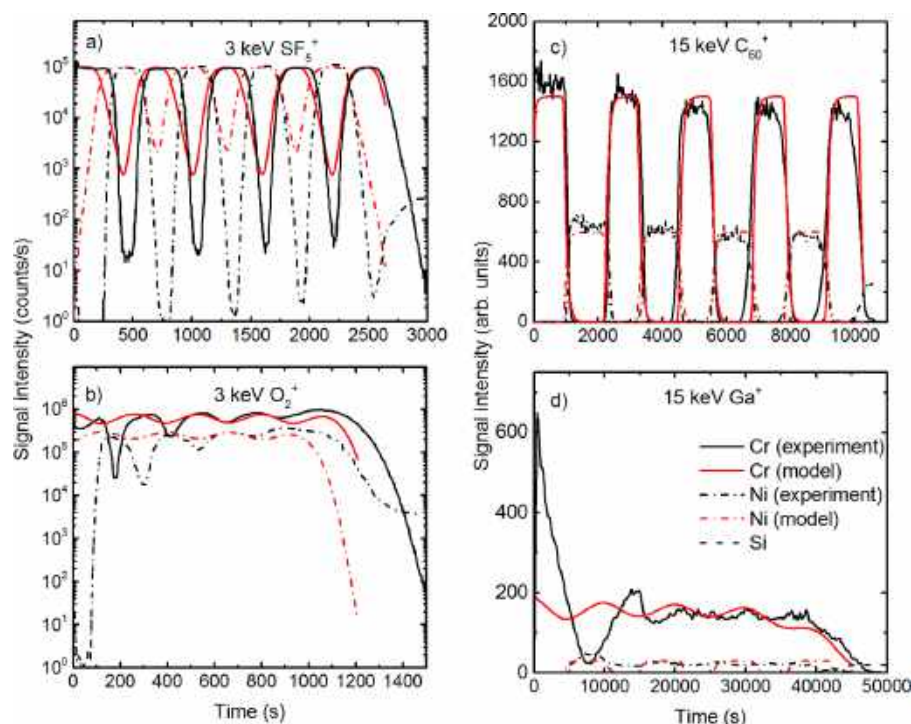


**Figure 4.** Dependence of signals of ions (a, b) and neutral atoms (c, d) on the sputter time for a nine-layer Ni:Cr multilayer stack bombarded by (a) 3 keV  $SF_5^+$ , (b) 3 keV  $O_2^+$ , (c) 15 keV  $C_{60}^+$ , and (d) 15 keV  $Ga^+$ . Black curves depict experimental signal of Cr (solid line) and Ni (dash-dotted line) atoms, while red curves depict analogous data obtained from the RMS model. The dashed black line depicts experimental intensity of the substrate Si signal which was not modeled.

namely, the intensity of the NiCr dimer is measured as a function of time. The emission of these dimers should only occur where both Ni and Cr are present in the sample, that is, at the interfaces between the layers. The experimental data clearly show that the widths of the NiCr peaks increase as the material is depth profiled. This observation is also slightly visible in the experimental depth profile shown in Figure 4c. The transport model does not show the same broadening, and in fact, it cannot since the  $S(x)$  and  $D'(x)$  functions become vanishingly small at about one-half the layer width. This discrepancy implies to us that some experimental condition may not be fully controlled or understood. One possibility could be, for instance, nonuniform material removal, which would result in a formation of a crater with a bottom that becomes less parallel to the sample surface with time.

#### 4. CONCLUSIONS

Using results from molecular dynamics simulations and the steady-state statistical sputtering model for predicting depth profiles due to energetic particle bombardment, we have defined the quantities in a macroscopic model for predicting depth profiles based on the transport equation. Specifically, we developed a microscopic definition for the ion-beam mixing or diffusion term, a quantity that is associated with the amount of displacements in the individual impact event. In addition, we proposed a protocol to incorporate sampling or information depth calculated from individual impacts, a term that was not present in the original model. The transport model for depth profiling was calibrated for three test cases for which there are associated repetitive bombardment MD simulations and predicted depth profiles from the SS-SSM. Using the functions developed for these calibration studies, we developed a simple RMS model that predicts the functions for the transport model from just the RMS roughness value and the sputtering yield. We show that we can reproduce the depth profiles of a NiCr heterostructure for four beam conditions that range from RMS values of 2.5 to 100 nm. In addition, we interpret the observed broadening of the depth profile for  $C_{60}$  bombardment, the system with the smallest RMS value of 2.5 nm, to be due to some unknown experimental condition. The main open issue is how to define theoretically the impact related ion-beam mixing term and develop a protocol for calculating it.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b09228.

Procedure used to solve eq 1; definition of sigmoid functions used in our study (PDF)

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##### Notes

The authors declare no competing financial interest.

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# Simple model of surface roughness for binary collision sputtering simulations



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## ABSTRACT

It has been shown that surface roughness can strongly influence the sputtering yield – especially at glancing incidence angles where the inclusion of surface roughness leads to an increase in sputtering yields. In this work, we propose a simple one-parameter model (the “density gradient model”) which imitates surface roughness effects. In the model, the target’s atomic density is assumed to vary linearly between the actual material density and zero. The layer width is the sole model parameter. The model has been implemented in the binary collision simulator IMSIL and has been evaluated against various geometric surface models for 5 keV Ga ions impinging an amorphous Si target. To aid the construction of a realistic rough surface topography, we have performed MD simulations of sequential 5 keV Ga impacts on an initially crystalline Si target. We show that our new model effectively reproduces the sputtering yield, with only minor variations in the energy and angular distributions of sputtered particles. The success of the density gradient model is attributed to a reduction of the reflection coefficient – leading to increased sputtering yields, similar in effect to surface roughness.

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## 1. Introduction

It is well known that ion bombardment roughens the target surface [1], which in turn may influence the sputtering yield [2]. In a recent study [3] we demonstrated that the simulation of sputtering yields for grazing incident ions requires the consideration of surface roughness. Grazing incidence conditions are typically found during transmission electron microscopy (TEM) sample preparation, one of the most important applications of focused ion beams (FIB) [4,5]. Glancing incidence angles may also occur during FIB milling of holes [6] or during irradiation of nanowires, for instance, when the nanowires bend towards the beam [7]. Recently, several groups have developed Monte Carlo binary collision (BC) codes that are capable of simulating ion bombardment of 2D and 3D micro- and nanostructures [8–14]. They all lack models of surface roughness, prohibiting meaningful simulation of glancing angle effects.

BC simulation studies of the effect of surface roughness on sputtering have mostly used geometrically modified flat surfaces, employing square waves [2], sinusoidal waves [3], or by applying fractal surface models [15,16]. All these models would be difficult

to implement in 2D and 3D simulations, since the simulation needs to store a rough surface geometry interspersed with any mesoscale topographies of interest.

Yamamura et al. [2] have shown that reducing the target density in a surface layer has a similar effect as a geometrically defined rough surface. However, they used a monoatomic surface layer only, which limited the degree of roughness that could be introduced. In the present work, we generalize Yamamura’s idea by using a surface layer with a density that decreases linearly towards the surface, which we henceforth call density gradient model. The sole parameter of this model is the thickness of the layer, which may be larger than monoatomic. This removes ambiguity from the model as compared to, e.g., the sinusoidal model where fits to the experimental data are available across multiple pairings of wavelengths and amplitudes [3]. Equally important, the density gradient model is easily implemented in 2D and 3D BC simulations.

To validate the model, we compare sputtering yields and energy and angular distributions of sputtered atoms with the predictions of three geometrically defined models with wave vectors parallel to the projection of the ions’ incidence direction to the surface. To aid the construction of a realistic rough surface, we have also performed molecular dynamics (MD) simulations of sequential Ga impacts on a Si surface.

This study is carried out for 5 keV Ga ions impinging on Si. The simulations are compared to experimental data obtained at FEI

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Company [17]. A lower ion energy is used than in our previous study [3] mainly to facilitate the MD simulations.

## 2. Simulation specifics

### 2.1. MD modeling

MD modeling was carried out at Jagiellonian University using a modified version of LAMMPS [18]. The simulation cell was  $120 \text{ Å} \times 120 \text{ Å} \times 80 \text{ Å}$  initially filled with single-crystalline (100)-Si with a  $(2 \times 1)$  reconstructed surface. The number of Si atoms in this cell was 57112. Periodic boundary conditions were used in the lateral directions. Stochastic and rigid layers, 7 Å and 3 Å thick, respectively, were used at the bottom to simulate the thermal bath that kept the sample at the required temperature and to keep the shape of the sample. The simulations were run at 0 K temperature. The target was sequentially bombarded with 5 keV Ga ions at polar angles of  $89^\circ$  and  $85^\circ$  and an azimuthal angle of  $35^\circ$  with respect to the cell edge which is a [010] direction. The latter was chosen as to minimize possible artifacts of the periodic boundary conditions due to the passage of the ions over regions they have previously interacted with while slowly glancing off the surface. Each impact was simulated for 2 ps. The resulting structure was used as initial condition for the subsequent impact after removal of all sputtered atoms and any excess kinetic energy from the system. The latter was achieved by an energy quenching procedure that involved application of gentle viscous damping forces to the entire sample for 0.2 ps. A Tersoff-3 potential [19] was used for Si-Si interactions, and the ZBL potential [20] splined with a Lennard-Jones (LJ) potential for Ga-Si interactions.

### 2.2. BC modeling

Monte Carlo simulations using the BC approximation were carried out at TU Wien using the simulator IMSIL [21,22]. As in our earlier work [3] we use the ZBL interatomic potential [20], the Oen–Robinson model for electronic stopping [23] with a cutoff energy of 10 eV, and a planar surface potential with a surface binding energy between Si and Si of 4.7 eV. Since the refraction of the incident ions at the surface potential is significant under the conditions studied, the choice of the surface binding energy between Ga and Si is also critical. We use a value of 2.82 eV [24]. All of the BC simulations were carried out using the static mode of IMSIL, wherein the target starts in an amorphous state as pure silicon, and its modification by the implanted gallium is not taken into account over the course of the simulation. 25,000 impacts were carried out for sputter yield calculations and 5 million impacts for determining the energy and angular distributions of sputtered atoms.

2D geometries are specified in IMSIL by polygons which are converted to a signed distance function defined on a Cartesian grid covering the simulation domain [13]. IMSIL was adapted for this research through the addition of a periodic geometry mode, which allowed to set the lateral size of the simulation domain equal to one wavelength. The vertical size was chosen 300 Å plus the roughness amplitude, which led to a negligible forward sputtering yield of  $2 \times 10^{-4}$ , thus indicating sufficient thickness to simulate an infinitely thick target. In order to exclude any significant discretization errors, we used 2000 segments for the polygons and 1 million cells for the internal grid.

Three geometric surface models were used: Cosine, triangular, and double cosine (Fig. 1). The double cosine function is defined by the superposition of two cosine functions with wavelengths differing by a factor of three:

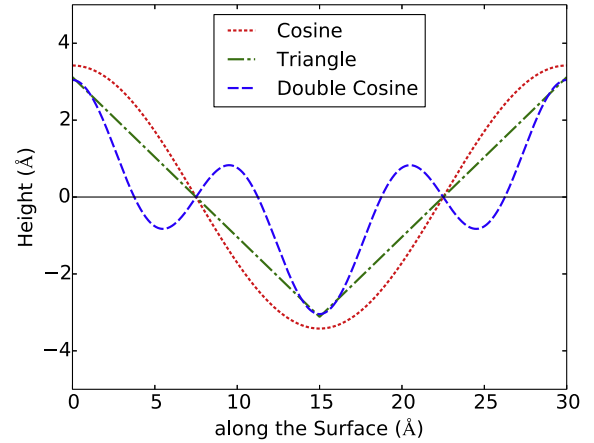


**Fig. 1.** Geometric roughness models used in this study, shown for a wavelength of 30 Å: Cosine, triangular, and double cosine. All surface models are shown with best-fit parameters.

$$z(x) = \frac{A}{2} \cos \frac{2\pi}{\lambda} x + \cos \frac{6\pi}{\lambda} x, \quad (1)$$

where  $A$  is the amplitude and  $\lambda$  is the period. The choice of the wavelength  $\lambda$  is not very critical and will be estimated from the results of the MD simulations. The amplitude  $A$  will be determined by fitting to experimental sputtering yield data.

The density gradient model is implemented by creating collision partners at the end of the free flight paths with probabilities

$$p = \begin{cases} 1 & \text{for } d \leq -w \\ d/w & \text{for } 0 < d < w \\ 0 & \text{for } d \geq 0, \end{cases} \quad (2)$$

where  $d$  denotes the signed distance from the surface (negative values outside the target) and  $w$  is the width of the density gradient layer. Effectively this means that the density of target atoms decreases linearly towards the surface within the layer  $0 < d < w$ , as illustrated in Fig. 2a. The parameter  $w$  will be determined by fitting to the experimental sputtering yield data. Note that in the limit of zero wavelengths the geometric surface models correspond to reduced-density layers. These densities are shown in Fig. 2b and are compared with the density gradient model.

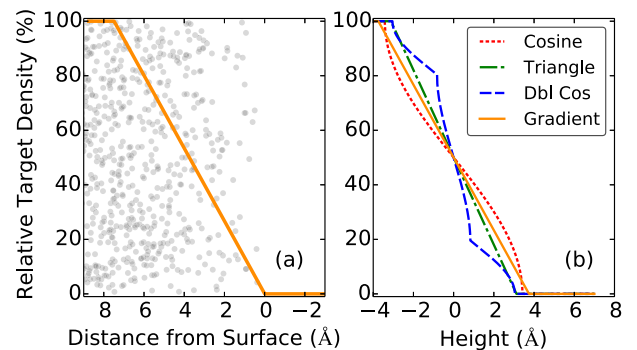


**Fig. 2.** (a) Schematic drawing of the target density in the density gradient model. Filled circles represent atoms. (b) Comparison of the density with equivalent density profiles of the geometric roughness models. The height axis in (b) has been shifted with respect to (a) so its origin is at the center of each roughness layer. All surface models are shown with best-fit parameters.

### 3. Results

MD simulations were performed for an incidence angle of  $89^\circ$  with different binding energies of the LJ potential. The best fit to the experimental sputter yield of 1.7 was obtained with a binding energy of 0.9 eV. In these simulations, the sputtering yield was averaged between the 1100th impact, when the sputtering yield had stabilized, and the 2191st (last) impact. With the same binding energy, impacts at an incidence angle of  $85^\circ$  were simulated resulting in a sputtering yield of 6.49, which compares favorably with the experimental value of 6.66, thus giving confidence in the simulations. The RMS roughness amplitudes of the surface after the last impact are 2.8 Å and 3.1 Å for incidence angles of  $89^\circ$  and  $85^\circ$ , respectively.

Inspection of the surface at the end of the simulation reveals intertrough/intercrest distances of approximately 20–50 Å (Fig. 3). We therefore chose a wavelength of  $\lambda = 30$  Å for our geometric roughness models. BC simulations were then performed with all models, and least squares fitting was used to determine the best fit of the amplitudes  $A$  to the experimental sputtering yields at incidence angles of  $86.6^\circ$ ,  $88.1^\circ$ , and  $89^\circ$ , resulting in  $A = 3.42$  Å, 3.12 Å, and 3.04 Å for the cosine, triangle, and double cosine model, respectively. In the same way the best-fit layer width  $w = 7.49$  Å of the density gradient model was obtained. The surface models with these optimized parameters are represented in Figs. 1 and 2. Sputtering yields obtained with these models are shown in Fig. 4a and b, and are compared with the experimental data. Good fits are observed for all roughness models. Interestingly, the density gradient model features the best fit (see Fig. 4b). In contrast, large deviations between simulation results and experimental data are observed when a flat surface is assumed in BC simulations of incidence angles larger than  $\sim 82^\circ$ . Comparing this to our earlier study of 30 keV Ga ions impinging on Si [3], where flat surface simulations have been found to deviate from the experimental data at angles larger than  $\sim 86^\circ$ , it may be concluded that the range of conditions at which sputtering yields

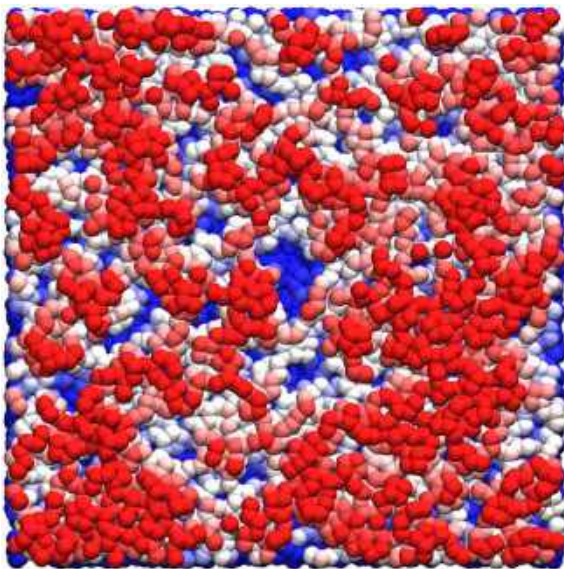


**Fig. 3.** Top view of the silicon sample after 2100 sequential hits by 5 keV Ga ions simulated by MD for a polar angle of  $89^\circ$  and an azimuthal angle of  $35^\circ$ . Atoms are colored according to their  $z$  coordinate; red: the position of the topmost atoms, white: 3 Å below the top level, and blue: 6 Å below the top level. The edge length of the cell shown is 120 Å. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

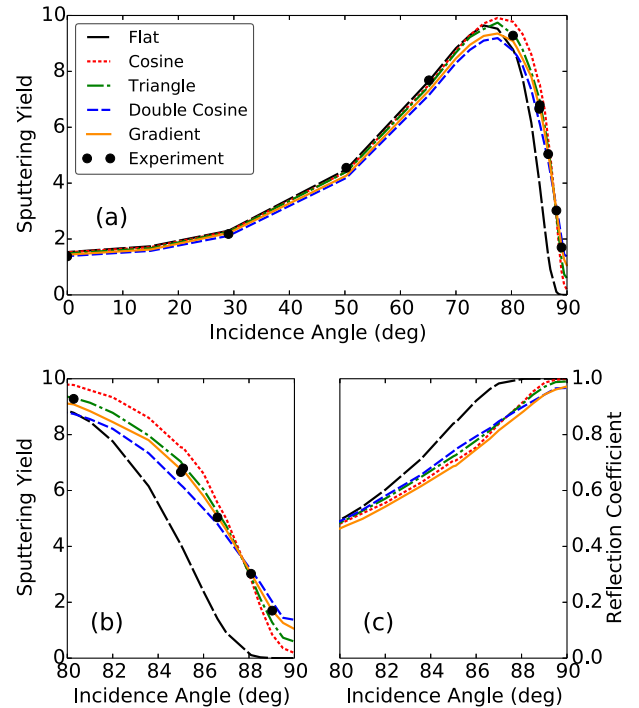


**Fig. 4.** (a,b) Sputtering yields as a function of incidence angle: Experimental data [17] (filled circles), simulation results for a flat surface (long-dashed line) and for the various roughness models with the amplitude fitted to the last three experimental data points, (b) is a magnification of the range between  $80^\circ$  and  $90^\circ$ , (c) shows the reflection coefficients obtained with all models.

are affected by surface roughness, increases with decreasing ion energy.

The reflection coefficients (the fraction of the incident ions that are reflected or backscattered) in these simulations are shown as a function of incidence angle in Fig. 4c. The results indicate that all models that include surface roughness increase the sputtering yield by means of reducing the reflectivity of the target. The relation between sputtering yield and reflection coefficient is easily understood, as reflected ions interact weaker with the target and therefore produce fewer recoils than ions that are scattered into the material.

While it is reassuring that the density gradient model fits the experimental sputtering yield data over the whole range of incidence angles with a single value of the layer width, higher order yield statistics such as the energy and angular distribution of the sputtered atoms are also important, especially when the simulation data is used as an input to topography simulations [17,26,27]. Modeling of surface roughness clearly plays a role in the resulting energy and angular distributions as shown in Fig. 5a and b, respectively. For this comparison, energy and angular distributions have been simulated for an incidence angle of  $87.7^\circ$ , the approximate crossover point of the sputtering yield curves obtained with the four roughness models (see Fig. 4b). Near-perfect agreement of the energy distributions is observed between all roughness models, while the energy distribution of atoms sputtered from the flat surface (black long-dashed line) is significantly different. For the angular distribution the agreement between the roughness models is less marked, but all four roughness models yield a more pronounced first-knock-on peak than the flat surface. This peak in the angular distribution is attributed to high-energy ejected target atoms that undergo relatively few collisions before leaving the target and thus retain more energy and a greater fingerprint of the incoming ion trajectory. The larger role of primary recoils in sputtering from a rough surface can also be induced from

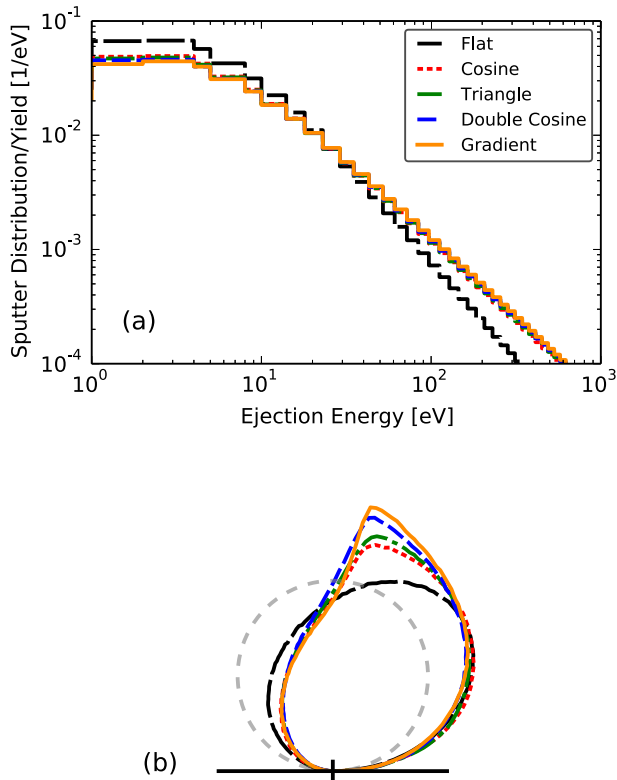


**Fig. 5.** (a) Energy distributions and (b) angular distributions of sputtered particles obtained by BC simulations at an incidence angle of  $87.7^\circ$ : Flat surface (long-dashed line) compared to the four roughness models. The gray dashed circle in (b) indicates a cosine distribution, which is predicted by theory [25] for well developed cascades.

the energy distribution which is weaker than  $E^{-2}$ , since a dependence as  $E^{-2}$  is expected when the collision cascades are well developed [25].

Despite the favorable results presented so far, there is one discrepancy: The RMS amplitudes obtained from the MD simulations are larger than those of the geometric roughness models fitted to the experimental data. To shed light on a possible explanation, we have fitted the amplitudes of our three geometric roughness models as a function of the wavelength. The results for the ampli-

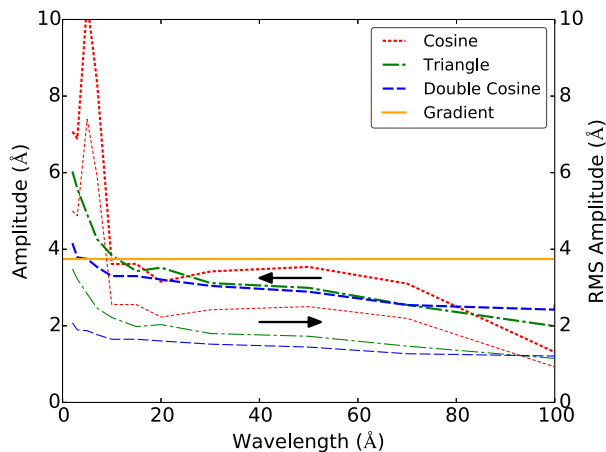


**Fig. 6.** Best fits of roughness profile amplitudes to the experimental data as a function of assumed wavelength. While the upper three, thicker lines show the amplitude  $A$ , the lower three, thinner lines represent the respective RMS values. Half of the best-fit layer thickness  $w$  of the density gradient model is shown for comparison (horizontal line labelled “gradient”).

tudes are presented in Fig. 6 (upper curves) together with the corresponding RMS values (thinner broken lines in the lower part of the figure). It can be seen that the amplitudes rise towards small wavelengths. This can tentatively be explained by the increasing role of redeposition: With decreasing wavelength the aspect ratio of the topography increases, which increases the amount of redeposition. Redeposited atoms are not sputtered, so to fit the model to the experimental sputtering yield, the roughness amplitude has to be increased. When using a roughness model with a wavelength  $\lambda > 10$  Å in the BC simulations, short-wavelength components that are present in the MD simulations are suppressed, therefore redeposition is underestimated, and smaller amplitudes are sufficient to fit the experimental data. It should be noted, however, that other factors may play a role such as the planar surface potential model used in the BC simulations that becomes questionable on a rough surface.

We note that all wavelengths except for extremely small ones ( $\sim 1$  Å) give sputtering yields that are in good agreement with the experimental data over the whole range of incidence energies (not shown).

#### 4. Conclusions

We have demonstrated that the newly proposed “density gradient” model can be used to fit BC simulations to experimental data on sputtering yields as a function of incidence angle. We have also shown that a variety of roughness models is capable of describing the data reasonably with the density gradient model providing the best fit in the particular case studied. That one and the same roughness model can describe sputtering conditions for all incidence angles, is not self-evident – different surface roughness could develop as a result of different incidence angles. Our MD simulations show that for 5 keV Ga bombardment of Si the RMS roughness amplitude is only slightly different for incidence angles of  $85^\circ$  and  $89^\circ$ . We have not investigated surface roughness for more-perpendicular ion impact. However, moderate beam-induced surface roughness as investigated in this work, affects sputtering yields only weakly at most incidence angles ( $< 82^\circ$  for 5 keV Ga incident on Si). So even a discrepancy of the roughness model with the actual target topography at these less-oblique incidence angles would not inhibit successful simulation of sputtering effects.

We have also shown that all roughness models investigated lead to almost identical energy distributions of the sputtered atoms and to similar angular distributions and reflection coefficients. It may be concluded that the main effect of a surface roughness model for sputtering simulations must be a reduction in the reflection coefficient, while the actual shape of the assumed surface is of less importance as long as the correct sputtering yield is fitted. This explains why a physically questionable model – densities approaching zero as in our density gradient model are not possible in condensed matter – may be so successful.

The new density gradient model is computationally efficient and easy to implement in BC codes. This is true even for 2D and 3D topographies, provided a signed distance function field is available such as in our IMSIL simulator. It is hoped that the new roughness model enables a greater degree of realism in BC sputtering simulations with very little computational overhead.

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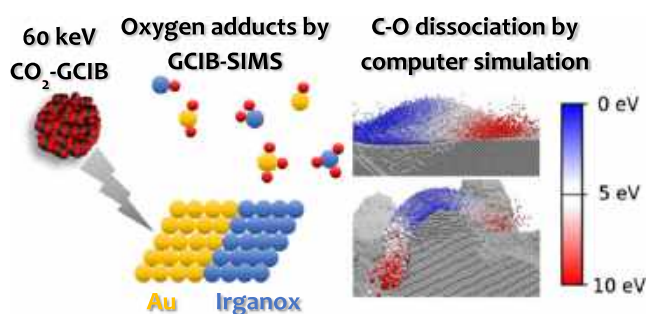
## RESEARCH ARTICLE

# C-O Bond Dissociation and Induced Chemical Ionization Using High Energy $(\text{CO}_2)_n^+$ Gas Cluster Ion Beam

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**Abstract.** A gas cluster ion beam (GCIB) source, consisting of  $\text{CO}_2$  clusters and operating with kinetic energies of up to 60 keV, has been developed for the high resolution and high sensitivity imaging of intact biomolecules. The  $\text{CO}_2$  molecule is an excellent molecule to employ in a GCIB source due to its relative stability and improved focusing capabilities, especially when compared to the conventionally employed Ar cluster source. Here we re-

port on experiments aimed to examine the behavior of  $\text{CO}_2$  clusters as they impact a surface under a variety of conditions. Clusters of  $(\text{CO}_2)_n^+$  ( $n = 2000\text{--}10,000$ ) with varying sizes and kinetic energies were employed to interrogate both an organic and inorganic surface. The results show that C-O bond dissociation did not occur when the energy per molecule is less than 5 eV/n, but that oxygen adducts were seen in increasing intensity as the energy is above 5 eV/n, particularly, drastic enhancement up to 100 times of oxygen adducts was observed on Au surface. For Irganox 1010, an organic surface, oxygen containing adducts were observed with moderate signal enhancement. Molecular dynamics computer simulations were employed to test the hypothesis that the C-O bond is broken at high values of eV/n. These calculations show that C-O bond dissociation occurs at eV/n values less than the C-O bond energy (8.3 eV) by interaction with surface topological features. In general, the experiments suggest that the projectiles containing oxygen can enhance the ionization efficiency of surface molecules via chemically induced processes, and that  $\text{CO}_2$  can be an effective cluster ion source for SIMS experiments.

**Keywords:** Gas cluster ion beam, C-O bond dissociation, Carbon dioxide cluster, Irganox 1010, Au film, Molecular dynamics computer simulations

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## Introduction

Gas cluster ion beam (GCIB) sources have gained popularity in conjunction with secondary ion mass spectrometry (SIMS) experiments. These beams provide an effective means of eroding an organic material without damage accumulation,

resulting in improved molecular depth profiling behavior. Moreover, when employed as a SIMS source, the GCIB yields mass spectra that exhibit improved detection of larger intact molecular ions and reduced formation of molecular fragment ions relative to atomic ion and  $\text{C}_{60}$  clusters conventionally employed [1–4]. The most commonly employed GCIB consists of clusters composed of Ar, generally in the size range of  $n = 100$  to 10,000 atoms. At a typical acceleration energy of 20 keV, each Ar atom carries between 2 and 200 eV/n. This eV/n value spans the range of energies associated with chemical bonds and is the primary reason that less fragmentation is observed during desorption, particularly for the larger clusters.

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An advantage of the GCIB design is that the composition of the cluster can be varied at will. For example, it has been possible to tune the chemistry of the GCIB to enhance ionization probability, and hence, expand the range of applications amenable to study. We have employed the concept of a mixed cluster whereby a hydrogen-containing small molecule is doped into the Ar cluster to create an environment suitable for protonation of desorbed molecules [5]. This approach has been particularly successful when using HCl as a dopant, especially when H<sub>2</sub>O is present either in the vacuum or on the sample surface. The water presumably enhances the formation of H<sub>3</sub>O<sup>+</sup> and the formation of [M + H]<sup>+</sup>, where M is the molecule of interest. In a related effort, large water clusters have been generated directly, and have demonstrated ion yield enhancements of greater than a factor of 10 [6–8]. Moreover, the HCl-doped Ar cluster beam can overcome salt suppression by promoting the protonated molecule ion, mitigating the pronounced matrix effect in biological samples [7].

In an effort to search for the ideal gas candidate for the cluster, we explored the possibility of employing clusters of CO<sub>2</sub> as the GCIB. In earlier work, we demonstrated that this cluster is more stable than Ar clusters and hence is produced using lower pressures in the expansion region of the GCIB source [9]. Moreover, this stability results in better focusing properties than Ar clusters. For example, using a 20-keV beam, Ar clusters could be focused to a 20-μm spot, while a similar CO<sub>2</sub> beam could be focused to a 7-μm spot. This result is obviously critical for molecule-specific imaging experiments where it has been a goal to reach submicron spatial resolution, a value important for imaging of biological cells. And finally, both molecular dynamics computer simulations and experiments suggested that the behavior of CO<sub>2</sub> was very close to that of Ar when energy per molecule < 5 eV/n, where the CO<sub>2</sub> molecule acts as a pseudo-atom of mass 44 amu [9]. To improve the spatial resolution of GCIB sources for bioimaging applications, an ion gun has been constructed with an acceleration voltage of 60 keV, allowing submicron spot sizes to be achieved. However, this expanded energy range opens the possibility that CO<sub>2</sub> molecules will be dissociated during ion impact. Akizuki et al. have reported that SiO<sub>2</sub> film forms on silicon surface upon the CO<sub>2</sub> cluster beam irradiation with minimum energy per molecule of 40 eV/n, resulting from the high density energy deposition within localized surface area [10]. Here we show from experiment and computer simulations that for energy per molecule above 5 eV/n dissociation is observed as evidenced by ejected molecular ions that have incorporated oxygen atoms. We present a systematic study over the kinetic energy range of 20 to 60 keV, and for cluster sizes of 2000 to 10,000 CO<sub>2</sub> molecules to examine the magnitude of the effect. As a consequence of this new chemistry, the intensity of molecular ions containing oxygen can be enhanced by more than a factor of 10 with organic molecules and more drastically on metal surfaces. In general, we show that this ion source offers new opportunities for GCIB SIMS.

## Experimental

### Sample Preparation

The Irganox 1010 thin film was purchased from the National Physical Laboratory (NPL, Huntington, UK). The film was deposited onto finely polished silicon wafers (1.0 × 1.0 × 0.5 mm<sup>3</sup>). The thickness of the film was monitored during the deposition process at NPL by a quartz crystal microbalance calibrated by spectroscopic ellipsometry. Specifically, the sample measured in this work had a thickness of 49.5 nm.

A gold film was purchased from Electron Microscopy Sciences (Hatfield, USA) with a thickness of 18 μm. The film was pre-sputtered using a 20-keV Ar<sub>1000</sub><sup>+</sup> cluster beam with a current of 100 pA for 30 min to remove the organic contaminants on the surface.

### SIMS Characterization

The initial motivation for this work stems from an observation of intense gold oxide ions from a Au surface under bombardment by (CO<sub>2</sub>)<sub>n</sub><sup>+</sup>. Due to the limited supply of oxygen in the vacuum chamber where the sample is analyzed, it was speculated that O is produced by dissociation of CO<sub>2</sub> molecules. This study is aimed toward elucidating the conditions where C-O bonds break and if the oxidization occurs on organic surfaces as well.

The gas cluster ion beam utilized here (GCIB SM from Ionoptika, UK) is shown schematically in Figure 1. The system is designed to operate at kinetic energies of up to ~60 keV,

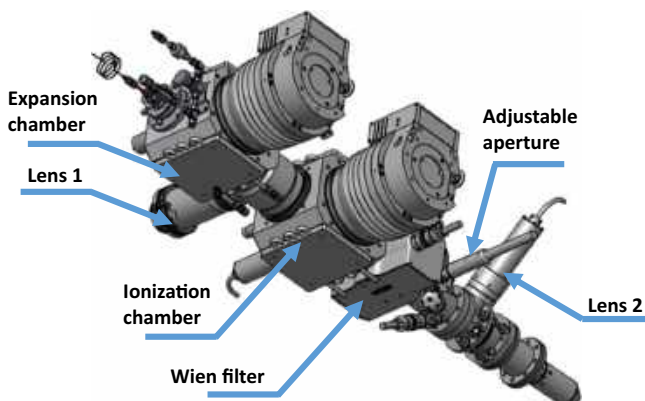


**Figure 1.** Schematic of GCIB SM. The GCIB SM is a gas cluster ion beam source developed by Ionoptika (Chandler's Ford, UK), for molecular imaging SIMS. It operates at a maximum acceleration potential of 70 kV, using a two lens system to form a spot size of 1 μm. Running CO<sub>2</sub> gas, the system is capable of operating with cluster sizes of < 30,000. Cluster generation occurs as high pressure input gas passes through a de Laval nozzle, condensing into clusters at the exit due to rapid expansion and cooling of the gas. The neutral gas beam is then ionized by electron bombardment, before being focused through the column. A Wien filter allows for mass filtering, and a narrower cluster size distribution. Time of flight measurements enable precise tuning of the clusters size

with a cluster size of up to 30,000 molecules. The GCIB SM was installed on a buncher-TOF SIMS instrument, J105 3D Chemical Imager (Ionoptika, UK) [11] and is incident upon the sample with an angle of 45°.

The spectra from fresh Irganox and Au surfaces were acquired using (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> with varying cluster sizes and energies. The kinetic energy of the clusters has a range of 2.5–30 eV/n, determined by the availability of the cluster from the GCIB SM. Specifically, (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> clusters consisting of 2000, 4000, 6000, 8000, and 10,000 molecules with an energy range of 20–60 keV were used. The cluster size was selected using a Wien filter. A spread of  $\sim \pm 5$   $\mu$ s (FWHM) ToF was measured, which, for instance, corresponds to a spread  $\pm 370$  CO<sub>2</sub> molecules for 50 keV (CO<sub>2</sub>)<sub>2000</sub><sup>+</sup> and  $\pm 830$  for 50 keV (CO<sub>2</sub>)<sub>10000</sub><sup>+</sup> cluster projectiles.

On the Irganox film, the spectra were acquired over area of  $50 \times 50 \mu\text{m}^2$  using 10 pA of each cluster ion beam with  $32 \times 32$  pixels and 100 shots per pixel. The ion dose for each spectrum is  $2.5 \times 10^{13}$  ions·cm<sup>-2</sup>. Five parallel measurements on a fresh Irganox 1010 film surface were conducted. On the gold surface, 10 parallel measurements were conducted on the same spot, but only the last five spectra were used for data processing to avoid surface contamination by organic adventitious sources of organic molecules.

Control experiments were performed using 50 keV (Ar)<sub>n</sub><sup>+</sup> with a cluster size of 2000, 4000, 6000, 8000, and 10,000 with the same condition as corresponding (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> clusters on both the Irganox 1010 and the Au film.

### Data Processing

The software Ionoptika Image Analyser (Version: 1.0.8.14) was used to read the intensity of selected ions, [M + 2O]<sup>-</sup> at  $m/z$  1207.77 ( $\Delta m/z$  0.6) for Irganox 1010 and  $m/z$  228.96 ( $\Delta m/z$  0.2) for Au. The average intensity and the standard deviation of selected ions were plotted against energy per molecule of the cluster ions beams.

### Computer Simulation

A detailed description of the molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere [12]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among the particles are described by a blend of pairwise additive and many-body potential energy functions. The interaction among cluster projectile molecules consisting of C and O atoms is described by the ReaxFF-Ig [13] potential splined with a ZBL potential [14] to properly describe high-energy collisions. For interaction among gold atoms, the EAM potential [15] is used while the interaction between gold atoms and cluster projectile atoms is described by a ZBL potential. The calculations are performed with a LAMMPS code [16] that was modified for a more efficient modeling of sputtering phenomena.

The experiments were performed on an organic substrate (Irganox) and a metal (gold) with the measured quantities

being attachment of O atoms to the ejected molecule or atom. The more straightforward of the samples to model is Au because the only source of O in the ejected species is the incident cluster beam. Thus, the dissociation of the CO<sub>2</sub> molecules that occurs early in the collision cascade can be used as a signal that Au-O adducts can be formed. Two types of Au samples were studied, a flat Au(100) surface and an Au sample with already developed morphology which was created in a previous study [17]. In the case of flat Au(100), a hemisphere with a diameter of  $\sim 40$  nm, consisting of  $\sim 1$  million atoms, was cut out of perfect gold crystal. For the roughened surface, a cylinder with a diameter of  $\sim 60$  nm and height of 25 nm, consisting of  $\sim 2.4$  million atoms, was chosen. In both cases, rigid and stochastic regions with a thickness of 0.7 and 2.0 nm, respectively, were used around the sample. These boundary conditions simulate the thermal bath that keeps the sample at the required temperature and helps inhibit the pressure wave reflection from the system boundaries [18]. These samples were bombarded by 50 keV (CO)<sub>n</sub> cluster projectiles consisting of 4000, 6000, 8000, and 10,000 molecules at 45° impact angle to reproduce experimental conditions. For the roughened surface, two types of impacts were chosen, one that aimed at a hill or protrusion into the vacuum and one that aimed at a depression or hole position. The simulations are calculated for a 0-K target temperature. Each impact event is evaluated to 8 ps, which is sufficiently long to determine the number of CO<sub>2</sub> molecules that dissociate.

## Results and Discussions

### Investigation of Oxygen Adducts from Organic and Inorganic Surfaces Under Bombardment of (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> Beams

During bombardment by the (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> cluster ion beam, oxygen adducts [M + nO]<sup>-</sup> were observed to be emitted from the surface of Irganox 1010 and Au, as shown in Figure S1. Several oxide ions are seen from Irganox 1010, described as [M<sub>Irganox</sub>-H + nO]<sup>-</sup>  $n = 1\sim 4$ . Correspondingly,  $m/z$  values at  $m/z = 1191.77$ , 1207.77, 1223.76, and 1239.76 are observed. The intensity of the oxygen adducts decreases slightly with the addition of O atoms. On the Au surface, [M<sub>Au</sub> + nO]<sup>-</sup>  $n = 1\sim 3$  are the most intense ions, with  $m/z$  values of 212.96, 228.96, and 244.95. Meanwhile, oxygen adducts of gold clusters are observed with composition of [2M<sub>Au</sub> + nO]<sup>-</sup> and [3M<sub>Au</sub> + nO]<sup>-</sup>  $n = 1\sim 3$ , with intensities that are lower when compared to [M<sub>Au</sub> + nO]<sup>-</sup>. Only the bi-oxygen adducts, [M<sub>Irganox</sub>-H + 2O]<sup>-</sup> and [M<sub>Au</sub> + 2O]<sup>-</sup> are discussed as they are representative of the other oxide products.

### The Study on the Formation of Oxygen Adducts at Varying Kinetic Energy of (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> Beams

To understand the formation of oxygen adducts, a systematic study was performed using (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> beams with

varying cluster size and energy. The ion intensities of  $[M_{\text{Irganox}}\text{-H} + 2\text{O}]^-$  and  $[M_{\text{Au}} + 2\text{O}]^-$  are plotted versus the kinetic energy per molecule, eV/n, in Figure 2a, c, respectively. It is clear that oxygen adducts occur beyond a threshold value  $\sim 5$  eV/n. Above the threshold, the intensity of the oxygen adducts increases along with the increase of the energy per molecule. In general, for a given energy per molecule value, the beam with the higher kinetic energy yields higher oxygen adduct intensities than the beam with lower kinetic energy at the same energy per molecule. For example, at energy per molecule of 10 eV/n, the intensity of  $[M_{\text{Irganox}}\text{-H} + 2\text{O}]^-$  from Irganox 1010 is 30% higher using 60 keV  $(\text{CO}_2)_{6000}^+$  than using 40 keV  $(\text{CO}_2)_{4000}^+$ , and 63% higher compared with 20 keV  $(\text{CO}_2)_{2000}^+$  as shown in Figure 2. A similar trend of  $[M_{\text{Au}} + 2\text{O}]^-$  from the Au surface is observed in term of the intensity changes of oxygen adducts with varying eV/n of the analyzing beams, except that there is more dramatic enhancement of oxygen adducts at higher kinetic energy and eV/n. These results certainly suggest that oxygen originates from the  $(\text{CO}_2)_n^+$  cluster itself. Above 3 eV/n according to our observations, the C-O bonds dissociate during impact on the sample surface. The energy carried by each CO<sub>2</sub> molecule allows the free O atoms to interact with the sample surface instead of escaping, yielding the various oxygen adducts. The ratio of C-O bond

dissociation increases along with the increasing kinetic energy and energy per molecule of the beams, resulting in the higher intensity of oxygen adducts. The very low intensity of oxygen adducts on the Au surface using 20 keV  $(\text{CO}_2)_n^+$  beams could result from the lower sputter rate of metal atoms. At higher kinetic energy, 30, 40, and 50 keV, the sputtering yield increases and more free O atoms promote the formation of Au oxide. This concerted action leads to the enhancement of the Au oxygen adducts at higher kinetic energy.

To rule out the possibility of other sources of free O atoms, the control measurements were carried out using  $(\text{Ar})_n^+$  beams at the same cluster size. Here, only the measurements using 50 keV  $(\text{Ar})_n^+$  beams are plotted as in Figure 2b, d to simplify the presentation. It is clear that only 16–30% of oxygen adducts,  $[M_{\text{Irganox}}\text{-H} + 2\text{O}]^-$ , are observed on the Irganox 1010 surface using 50 keV  $\text{Ar}_n^+$  compared with corresponding  $(\text{CO}_2)_n^+$  beams when energy per molecule is over 8 eV/n as shown in Figure 2b. The source of the O atoms for these oxide products could be fragmented from the Irganox 1010 molecule during bombardment. While on the Au surface, the oxygen adducts,  $[M_{\text{Au}} + 2\text{O}]^-$ , are barely detectable using 50 keV  $\text{Ar}_n^+$  beams as shown in Figure 2d. The oxygen adducts of Au are drastically increased by up to 850-fold using 50 keV  $(\text{CO}_2)_n^+$  beams. It is evident that  $(\text{CO}_2)_n^+$  beams with

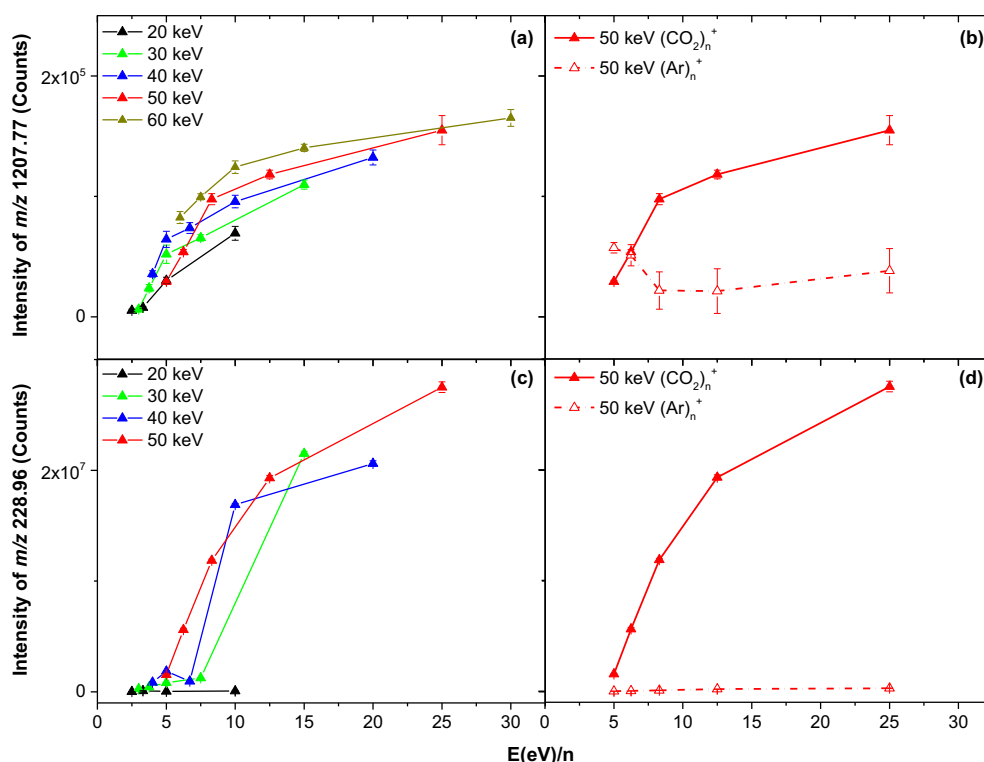


**Figure 2.** Ion intensities as a function of kinetic energy per molecule, eV/n for different total energies of CO<sub>2</sub> or Ar cluster. (a) Signal of  $m/z$  1207.77, assigned as  $[M_{\text{Irganox}}\text{-H} + 2\text{O}]^-$  from Irganox 1010 using 20–60 keV  $(\text{CO}_2)_n^+$  cluster at energy per molecule of 2.5–30 eV/n. (b) Comparison of signal of  $m/z$  1207.77 from Irganox 1010 using 50 keV  $(\text{CO}_2)_n^+$  and  $\text{Ar}_n^+$  at energy per molecule of 5–25 eV/n. (c) Signal of  $m/z$  228.96, assigned as  $[M_{\text{Au}} + 2\text{O}]^-$  from Au film using 20–50 keV  $(\text{CO}_2)_n^+$  cluster at energy per molecule of 2.5–25 eV/n. (d) Comparison of signal of  $m/z$  228.96 from Au film using 50 keV  $(\text{CO}_2)_n^+$  and  $\text{Ar}_n^+$  at energy per molecule of 5–25 eV/n

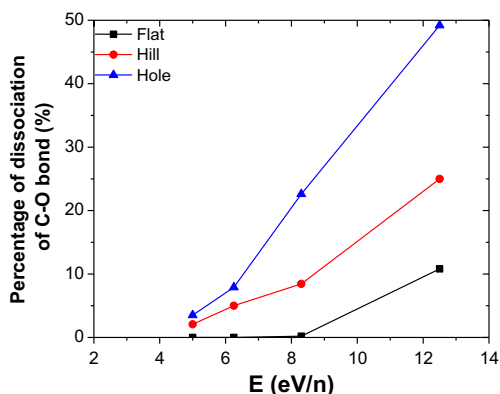


**Figure 3.** Percentage of dissociated CO<sub>2</sub> molecules for 50 keV (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> impact on different configurations of Au surface

higher energy per molecule favor the oxygen adducts, leading to the enhanced chemical ionization by providing an oxygen atom source through the dissociation of C-O bonds in the cluster beam itself.

### Computer Simulation of C-O Bonds Dissociation at Energy per Molecule below 5 eV/n

The percentages of CO<sub>2</sub> molecules that dissociate in the simulations as a function of energy per molecule are shown in Figure 3 for impacts on the flat Au surface, the hill position, and the hole position. Examining first the flat surface results (black line and points), there is no dissociation below eV/n ~ 8 eV, consistent with the CO bond energy in CO<sub>2</sub> of ~8.3 eV. The results for the roughened surface (red and blue lines and points) indicate that the CO<sub>2</sub> molecule dissociates at incident energies as low as 5 eV/n. The side views of the 50 keV (CO<sub>2</sub>)<sub>10000</sub><sup>+</sup> cluster-surface impact event at the flat and roughened surface are shown in Figure 4 for three times at the beginning of the impact event for the flat surface and a hill configuration. For these impact events, the initial kinetic energy per molecule is 5 eV/n. Small balls depict intact molecules, while large balls represent molecules that have undergone dissociation. The impact at the bottom of the valley is not shown but leads to the same conclusions. The color of the

species is based on the current center of mass kinetic energy where white is the original value of 5 eV, blue molecules have less energy, and red molecules have more kinetic energy.

The initial sequence of events is similar for the flat and roughened surfaces. The cluster projectile flattens during the impact, which leads to a buildup of pressure inside the projectile. The pressure is subsequently relieved by material ejection in a lateral direction. As indicated by the red color, many molecules during the decompression phase are accelerated to a kinetic energy higher than the initial value. The fate of accelerated molecules is, however, different on the flat and roughened surfaces. On the flat surface, most of these molecules slide along the surface and are reflected into the vacuum intact. For the roughened surface, however, some of accelerated (red) molecules collide with the nearby irregular surface. Now the kinetic energy per molecule can be as high as 10 eV, sufficient to cause dissociation on the second collision. We would expect the same process to occur on a roughened organic substrate such as Irganox.

The effect of the buildup in pressure and subsequent increase in the kinetic energy of a molecule during the impact event should be greater the higher the total incident energy for a given initial energy per molecule value. This effect is seen in the experimental data shown in Figure 2c. There are no [M<sub>Au</sub> + 2O]<sup>−</sup> ions observed for a total energy of 20 keV up to energy per molecule of 10 eV/n. On the other hand, for a total energy of 50 keV, the [M<sub>Au</sub> + 2O]<sup>−</sup> ions are observed at less than energy per molecule of 5 eV/n.

## Conclusion and Outlook

A systematic study was performed to investigate the dissociation of C-O bonds in a CO<sub>2</sub> GCIB upon impact with a sample surface, consisting of an Irganox 1010 thin film and a Au film. The clusters with varying eV/n at different kinetic energy were employed to interrogate the sample surface. The dissociation of C-O bonds and the observation of oxygen adducts occurs above ~5 eV/n for both samples. The moderate increase ~2 times of oxidation was observed on organic Irganox 1010 film along with the energy per molecule and kinetic energy of the

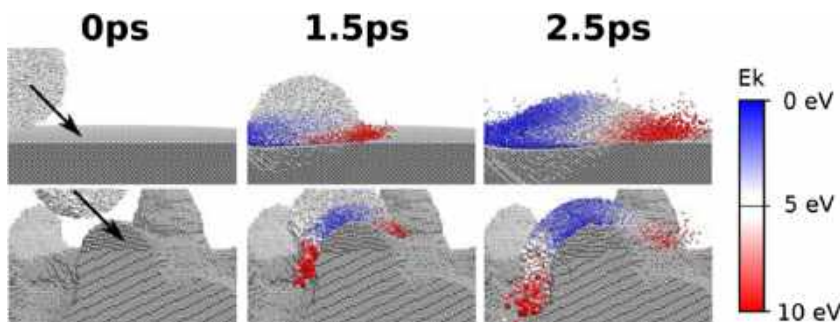


**Figure 4.** Time lapse images of distribution of energy per molecule in 50 keV (CO<sub>2</sub>)<sub>10,000</sub> cluster during the impact on the flat (top panels) and roughened (bottom panels) Au(100) surface. The small balls represent intact CO<sub>2</sub> molecules. The larger balls represent dissociated molecules. The color scale is the center of mass kinetic energy of each particle. The initial kinetic energy is energy per molecule of 5 eV/n, denoted by the white color

beam, and the enhancement tends to reach a plateau when energy per molecule reaches 25 eV/n. The same trend was observed on Au films but with more drastic enhancement up to 14-fold compared the beams at 5 and 20 eV/n with kinetic energy of 60 keV; moreover, the trend points to further increases if the beam energy could be increased beyond 60 keV.

The unexpectedly observed dissociation of (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> below 8 eV/n is shown via computer simulation to arise from surface topography. The results demonstrate that on a rough surface, CO<sub>2</sub> molecules may be compressed during interaction with surface features, yielding higher kinetic energies during the decompression phase. Our findings provide new insight into the cluster-sample interaction, revealing a new chemical ionization pathway that could lead to enhanced sensitivity. Moreover, operating in a high kinetic energy regime opens the possibility of finding additional gas candidates that may more effectively exploit the chemical ionization mechanism.

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**Crater function moments: Role of implanted noble gas atoms**Gerhard Hobler,<sup>1,\*</sup> Dawid Maciążek,<sup>2</sup> and Zbigniew Postawa<sup>2</sup><sup>1</sup>*Institute of Solid-State Electronics, TU Wien, Floragasse 7, A-1040 Wien, Austria*<sup>2</sup>*Institute of Physics, Jagiellonian University, ul. Łojasiewicza 11, 30348 Kraków, Poland*

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Spontaneous pattern formation by energetic ion beams is usually explained in terms of surface-curvature dependent sputtering and atom redistribution in the target. Recently, the effect of ion implantation on surface stability has been studied for nonvolatile ion species, but for the case of noble gas ion beams it has always been assumed that the implanted atoms can be neglected. In this work, we show by molecular dynamics (MD) and Monte Carlo (MC) simulations that this assumption is not valid in a wide range of implant conditions. Sequential-impact MD simulations are performed for 1-keV Ar, 2-keV Kr, and 2-keV Xe bombardments of Si, starting with a pure single-crystalline Si target and running impacts until sputtering equilibrium has been reached. The simulations demonstrate the importance of the implanted ions for crater-function estimates. The atomic volumes of Ar, Kr, and Xe in Si are found to be a factor of two larger than in the solid state. To extend the study to a wider range of energies, MC simulations are performed. We find that the role of the implanted ions increases with the ion energy although the increase is attenuated for the heavier ions. The analysis uses the crater function formalism specialized to the case of sputtering equilibrium.

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The crater function formalism [1–3] has recently established itself as an important technique in the theory of ion-beam induced spontaneous pattern formation. Earlier approaches used Sigmund’s theory of sputtering [4] together with a surface smoothing mechanism to derive equations of motion for the surface height function [5–8], some including simplified models of atom redistribution due to momentum transfer to target atoms [9–13]. Other work explains pattern formation in terms of mechanical stress [14–18]. In contrast, in the crater function formalism, the coefficients of the equation of motion are calculated in terms of the moments of the so-called crater function. The crater function is defined as the average response of the surface to a single ion impact [19] and may be obtained by molecular dynamics (MD) [19–22] or binary collision Monte Carlo (MC) simulations [23–26]. In this way, the crater function formalism allows to include the results of numerical simulations in the theory of spontaneous pattern formation.

In most previous work, using the crater function formalism, only sputtering and atom redistribution have been taken into account. The effect of the implanted ions on pattern formation has been investigated only recently [27,28]. It has been found that ion implantation has a destabilizing effect on the surface along the projected beam direction, if the incidence angle exceeds a critical value, while it always has a stabilizing effect in transverse direction. The impact of the implant contributions is expected to be particularly significant when erosion and redistribution are moderate such as for energetic light ions, and when the surface binding energy is high [28].

It is commonly assumed that the effect of the implanted ions on pattern formation is negligible, if the implanted atom species is a noble gas (NG). This is motivated by the fact that NG atoms have a tendency to leave the target [29], so the retained fluence is lower than for nonvolatile ions. Radiation induced transport of NG atoms towards the surface is well established experimentally [30] and has been named “rapid relocation” [31,32] in the absence of a clear understanding of the mechanism on an atomistic level. MC simulations cannot explain rapid relocation [33], thus it seems to be a nonballistic effect.

The rationale for neglecting implanted NG atoms in pattern formation, however, is flawed. First, the effect strongly depends on the system studied. For instance, while after 1-keV Ar bombardment of SiO<sub>2</sub> virtually no Ar is present in the oxide [32], for 5-keV Ne bombardment of ta-C [28] the experimentally found areal density of Ne agrees with that predicted by MC simulations. Second, the NG ions do not disappear instantaneously when they come to rest, but require additional ion bombardment to be transported (“rapidly relocated”) towards the surface. It will be shown that the separation of implantation and removal of the NG atoms leads to a contribution to the crater function.

The purpose of this work is to demonstrate that the implanted NG ions indeed have an important effect on the crater function moments. As a target we choose Si, which is a commonly studied material. Selected low-energy ion bombardments are investigated by MD simulations. MC simulations are used to study the effect in a wider range of impact energies. In the absence of a model for rapid relocation, MC simulations cannot predict the contribution of NG atom redistribution within the target. However, we will show that the net effect of the volumes added by the implanted ions and removed by their erosion is well predicted by MC simulations.

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Our analysis will be based on the assumption of sputtering equilibrium. We therefore present the crater function formalism specialized to sputtering equilibrium in Sec. II. Details of the MD and MC methods employed are given in Sec. III. In Sec. IV, the MD and MC results are presented. Finally, in Sec. V we discuss the limitations of our approach and argue that they do not affect our qualitative conclusions.

## II. CRATER FUNCTION FORMALISM

We start with a summary of the crater function formalism in order to define the nomenclature (Secs. II A and II B). Assumptions that are either normally made or are introduced by us, will be discussed in Sec. II C. Their consequences for the calculation of the crater function moments will be presented in Secs. II D and II E.

### A. The crater function

In the crater function formalism, the equation of motion of the surface is written in terms of the moments of the crater function  $F(x, y)$ , where  $x$  is parallel to the projection of the beam direction to the originally flat surface,  $y$  is the surface coordinate perpendicular to  $x$ , and  $x = y = 0$  corresponds to the impact point. The crater function is the average change in height due to the impact of a single ion. Different signs have been used for the crater function in previous work. When only erosion is considered, it is natural to define  $F(x, y)$  as the negative change in surface height [2,28] so  $F(x, y)$  is always positive. Here, we consider implantation and erosion on an equal footing. Therefore we prefer to adhere to the original convention introduced by Kalyanasundram *et al.* [19], which has also been used by Norris *et al.* [1,3], where erosion leads to negative and implantation to positive contributions to the crater function.

### B. Crater function moments and surface stability

The  $i$ th moment with respect to  $x$  is defined by

$$M^{(i)} = \iint_{-\infty}^{\infty} x^i F(x, y) dx dy. \quad (1)$$

The crater function is composed of contributions from different atom species  $X$  and different mechanisms (erosion, redistribution, and implantation), so we can write

$$F(x, y) = \sum_X F_X(x, y) \quad (2)$$

with

$$F_X(x, y) = F_{X,\text{eros}}(x, y) + F_{X,\text{redist}}(x, y) + F_{X,\text{impl}}(x, y). \quad (3)$$

The same partitioning applies to the moments:

$$M^{(i)} = \sum_X M_X^{(i)} \quad (4)$$

with

$$M_X^{(i)} = M_{X,\text{eros}}^{(i)} + M_{X,\text{redist}}^{(i)} + M_{X,\text{impl}}^{(i)}. \quad (5)$$

Some of the contributions vanish by definition; for the zeroth moment, the contribution of atom redistribution is zero

if one assumes that the atomic volume does not change during relocation:

$$M_{X,\text{redist}}^{(0)} = 0. \quad (6)$$

Moreover, the target atom species  $X \neq \text{NG}$ , of course, have no implant contributions:

$$M_{X \neq \text{NG}, \text{impl}}^{(i)} = 0. \quad (7)$$

In the work, introducing the extended crater function formalism [2], the moments defined in Eq. (1) were written  $M_X^{(i)}$  to distinguish them from moments with respect to  $y$  or curvature. However, in the final result, neither the moments with respect to  $y$  nor the moments with respect to curvature of order higher than zero appear. Zeroth-order moments are physically the same, independent of which quantity is considered variable. We have therefore dropped the index “ $x$ ” in order to avoid confusion with  $X$ , which we use to denote atom species.

According to Harrison and Bradley, surface stability is determined by the curvature coefficients  $C_{11}$  and  $C_{22}$  given by [2]

$$C_{11} = \underbrace{\frac{\partial}{\partial \theta}(M^{(1)} \cos \theta)}_{S_{11}} + \underbrace{\frac{\partial}{\partial K_{11}}(M^{(0)} \cos \theta)}_{T_{11}} \quad (8)$$

and

$$C_{22} = \underbrace{\cot \theta (M^{(1)} \cos \theta)}_{S_{22}} + \underbrace{\frac{\partial}{\partial K_{22}}(M^{(0)} \cos \theta)}_{T_{22}}, \quad (9)$$

where  $\theta$  denotes the incidence angle with respect to the surface normal and  $K_{11}$ ,  $K_{22}$  the surface curvatures in  $x$  and  $y$  direction, respectively. The derivatives with respect to the curvatures are evaluated at zero curvature. Compared to Ref. [2], all terms appear with the opposite sign here due to the different sign conventions for the crater function. However, the meaning of  $C_{11}$  and  $C_{22}$  is the same as in Ref. [2]; instabilities occur when  $C_{11}$  and/or  $C_{22}$  is negative. Apart from the signs, the magnitudes of  $C_{11}$  and  $C_{22}$  are also of interest since the growth rate and velocity of the patterns in the linear regime depend on them [5]. As will be shown,  $M^{(0)}$  is largely independent of the implanted ions in the cases studied, so the effect of the implanted ions on the stability of the surface is via  $S_{11}$  and  $S_{22}$  only [compare Eqs. (8) and (9)].

### C. Assumptions

We will use the following assumptions as appropriate. (1) Each atom species  $X$  has a fixed atomic volume  $\Omega_X$  that is known or can be determined and does not change during ion bombardment. (2) Sputtering equilibrium has been established, which means that the average rates of addition and removal of the ion species are equal. (3) The implanted ions do not affect the spatial characteristics of the collision cascades. (4) The spatial distribution of NG ejection with respect to the ion's impact point is unaffected by rapid relocation.

Assumption 1 has first been made by Norris *et al.* [1] to arrive at a simplified algorithm for determining the moments from MD simulations (see Sec. II D). This algorithm is also the only known way to determine the moments from MC

simulations [23]. It is, however, not self-evident, in particular for NG atoms: when NG atoms are implanted, they are likely to initially end up in an interstitial position, while they usually form bubbles upon further bombardment [34]. The NG atoms do not necessarily have the same volume in these configurations, and the atomic volume is also not known *a priori*. Section IV B will address this in some detail.

Assumption 2 seems safe: sputtering equilibrium is reached for sputter depths on the order of the ions' projected range [35], while pattern formation usually requires higher fluences.

Assumption 3 can be valid only approximately: the different mass and volume of the implanted ions changes the stopping power of the target and therefore the spatial characteristics of the collision cascades. The effect is weaker the smaller the mass difference and the ion concentration. For the cases studied in this work (Ar, Kr, Xe in Si) we find from our MD simulations that assumption 3 is well fulfilled. Beyond these cases, we expect the effect of the implanted ions to increase with increasing implant energy, at lower implant angles, and when the rapid relocation effect is weaker, as all these conditions increase the implanted ion concentrations.

The rationale for assumption 4 is the following: the implanted NG atoms do not disappear immediately; otherwise, no NG concentration would be measured in the target. Instead, a thin near-surface region depleted from NG atoms is observed [31,32]. It is therefore reasonable to assume that the ejected NG atoms originate near this layer. Since the layer is thin, the properties of the collision cascade at these positions are similar as at the surface, and the spatial distribution of the ejected atoms is similar as in conventional sputtering.

#### D. Calculation and interpretation of the moments

With assumption 1, the crater functions may be approximated by sums of  $\delta$  functions [1,3]

$$F(\mathbf{r}) = \sum_X \Omega_X \left\langle \sum_{i=1}^{n_X^F} \delta(\mathbf{r} - \mathbf{r}_{Xi}^F) - \sum_{i=1}^{n_X^I} \delta(\mathbf{r} - \mathbf{r}_{Xi}^I) \right\rangle, \quad (10)$$

where  $\Omega_X$  is the atomic volume of atom species  $X$  (NG or Si, in our case),  $\mathbf{r}_{Xi}^F = (x_{Xi}^F, y_{Xi}^F)$  denote the final positions of the  $n_X^F$  atoms of species  $X$  after the impact,  $\mathbf{r}_{Xi}^I = (x_{Xi}^I, y_{Xi}^I)$  the initial positions of the  $n_X^I$  atoms of species  $X$  before the impact, and  $\mathbf{r} = (x, y)$  the position where the crater function is evaluated. The atoms considered in Eq. (10) include only atoms in the target. This means,  $n_X^F$  includes the implanted ion if it ends up in the target, and the redistributed atoms.  $n_X^I$  includes the eroded and redistributed atoms. The angle brackets denote the average over a sufficient number of impacts.

Inserting Eq. (10) into Eq. (1), one obtains

$$M^{(0)} = \sum_X \Omega_X \langle n_X^F - n_X^I \rangle \quad (11)$$

$$M^{(1)} = \sum_X \Omega_X \left\langle \sum_{i=1}^{n_X^F} x_{Xi}^F - \sum_{i=1}^{n_X^I} x_{Xi}^I \right\rangle \quad (12)$$

The crater function as well as the moments may be decomposed into the contributions by the different atom species and physical mechanisms in an obvious way.

The contributions of implantation and erosion to the moments have simple physical meaning:  $\langle n_{\text{NG}}^F \rangle_{\text{impl}}$  is one minus the reflection coefficient  $r_{\text{NG}}$ , thus

$$M_{\text{NG,impl}}^{(0)} = \Omega_{\text{NG}}(1 - r_{\text{NG}}), \quad (13)$$

while  $M_{X \neq \text{NG,impl}}^{(0)} = 0$ , see Eq. (7).  $\langle n_X^I \rangle_{\text{eros}}$  is the partial sputtering yield  $Y_X$ , thus

$$M_{X,\text{eros}}^{(0)} = -\Omega_X Y_X. \quad (14)$$

Next, we observe that the contribution of ion implantation to the crater function is always positive, i.e.,  $F_{\text{NG,impl}}(x, y) \geq 0$  for all  $x$  and  $y$ .  $F_{\text{NG,impl}}(x, y)/M_{\text{NG,impl}}^{(0)}$  may therefore be interpreted as the probability density that the end point of an ion trajectory has coordinates  $(x, y)$ . It follows that

$$\bar{x}_{\text{NG,impl}} = M_{\text{NG,impl}}^{(1)} / M_{\text{NG,impl}}^{(0)} \quad (15)$$

is the mean  $x$  coordinate of the ion trajectory end points. Similarly,  $F_{X,\text{eros}}(x, y) \leq 0$  for all  $x$  and  $y$ , and  $F_{X,\text{eros}}(x, y)/M_{X,\text{eros}}^{(0)}$ , which is always positive, defines the probability density that the origin of a sputtered atom of type  $X$  has coordinates  $(x, y)$ . Therefore

$$\bar{x}_{X,\text{eros}} = M_{X,\text{eros}}^{(1)} / M_{X,\text{eros}}^{(0)} \quad (16)$$

is the mean  $x$  coordinate of the origins of sputtered  $X$  atoms. Henceforth, we will call  $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{X,\text{eros}}$  the mean projected implant and erosion distance, respectively, where distance is meant to be defined with respect to the impact point. Note that  $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{X,\text{eros}}$  are determined solely by the geometry of the collision cascades, while  $M_{\text{NG,eros}}^{(0)}$  and  $M_{\text{NG,eros}}^{(1)}$  are proportional to the near-surface concentrations of the NG atoms.

#### E. The moments in sputtering equilibrium

Assumption 2 means that the average number of implanted atoms per incident ion, which is one minus the reflection coefficient, equals the partial sputtering yield of the ion species:

$$1 - r_{\text{NG}} = Y_{\text{NG}}. \quad (17)$$

From Eqs. (13) and (14) follows

$$M_{\text{NG,eros}}^{(0)} = -M_{\text{NG,impl}}^{(0)}, \quad (18)$$

and because of Eqs. (5) and (6) the contribution of the implant species (NG) to the zeroth moment vanishes:

$$M_{\text{NG}}^{(0)} = 0. \quad (19)$$

The total zeroth moment is therefore given by

$$M^{(0)} = \sum_{X \neq \text{NG}} M_X^{(0)} = \sum_{X \neq \text{NG}} M_{X,\text{eros}}^{(0)}, \quad (20)$$

where in the last step Eqs. (6) and (7) have been used. Thus  $M^{(0)}$  is simply minus the sum of the partial sputtering yields of the target atoms times the respective atomic volumes.

Introducing  $M_{\text{NG,impl}}^{(1)}$  and  $M_{\text{NG,eros}}^{(1)}$  from Eqs. (15) and (16), respectively, in Eq. (5) and using Eq. (18), the contribution of the implanted ions to the first moment can be written:

$$M_{\text{NG}}^{(1)} = (\bar{x}_{\text{NG,impl}} - \bar{x}_{\text{NG,eros}}) M_{\text{NG,impl}}^{(0)} + M_{\text{NG,redist}}^{(1)}. \quad (21)$$

For the redistributed atoms, the number of initial and final positions within the target are equal ( $n_{X,\text{redist}}$ ), and the contribution of redistribution of atom species  $X$  in Eq. (12) can be written:

$$M_{X,\text{redist}}^{(1)} = \Omega_X \left\langle \sum_{i=1}^{n_{X,\text{redist}}} (x_{Xi}^F - x_{Xi}^I) \right\rangle. \quad (22)$$

The sum is over all  $x$  components of the displacement vectors of the redistributed atoms. Because of momentum conservation, the average displacement must be in the direction of the incident ion. Therefore the sum is positive, and so is  $M_{X,\text{redist}}^{(1)}$ . Specializing to  $X = \text{NG}$ ,

$$M_{\text{NG},\text{redist}}^{(1)} > 0 \quad (23)$$

follows, and from Eq. (21),

$$M_{\text{NG}}^{(1)} > (\bar{x}_{\text{NG,impl}} - \bar{x}_{\text{NG,eros}}) M_{\text{NG,impl}}^{(0)}. \quad (24)$$

Equation (24) specifies a lower limit to the contribution of the implanted NG atoms to the first moment. The importance of the assumption of sputtering equilibrium lies in the fact that all quantities on the right-hand side of Eq. (24) are independent of the implanted ion concentration, if this is the case for the geometry of the collision cascade (assumption 3) and the spatial distribution of NG ejection (assumption 4). This means that we now may use static MC simulations with a target containing a small constant concentration of NG atoms to determine at least a lower limit to the contribution of the implanted NG atoms to the first moment, even in the absence of a rapid relocation model. The only missing term in the NG contribution to the first moment, Eq. (21), then is  $M_{\text{NG,redist}}^{(1)}$ , which is proportional to the NG content. If, in addition, the contributions of the target atoms to the moments are independent of the NG content, then we may also estimate the other moment contributions using static MC simulations.

Note that an imbalance of the implant and erosion related contributions to the first moment, and thus a nonvanishing right-hand side of Eq. (24), implies that implantation and erosion are separate effects that have different spatial distributions. Our MD results presented in Sec. IV C validate this picture.

### III. SIMULATION METHODS

#### A. Molecular dynamics simulations

MD simulations were carried out at Jagiellonian University using LAMMPS [36]. The simulation cell had a surface area of  $28a \times 20a (\approx 152\text{\AA} \times 109\text{\AA})$ , where  $a = 5.431\text{\AA}$  is the lattice constant of Si, and the sample thickness was adjusted as to accommodate most of the collision cascades. The cell was initially filled with single-crystalline (100)-Si with a  $(2 \times 1)$  reconstructed surface. Periodic boundary conditions were used in the lateral directions. Stochastic and rigid layers, 7 Å and 3 Å thick, respectively, were used at the bottom to simulate the thermal bath that kept the sample at the required temperature and to keep the shape of the sample. The simulations were run at 0 K temperature. The target was sequentially bombarded with 2-keV Kr ions at polar angles of 40°, 50°, 60°, 70°, 80°, and 85° and an azimuthal angle of 0° with respect to the cell edge, which is a [010] direction. In addition, one simulation was carried out each for 1-keV Ar and 2-keV Xe impacts

at an incidence angle of 60°. Each impact was simulated for 2 ps. The resulting structure was used as initial condition for the subsequent impact after removal of all sputtered atoms and any excess kinetic energy from the system. The latter was achieved by an energy quenching procedure that involved application of gentle viscous forces to the entire sample for 5 ps. A Tersoff-3 potential [37] was used for Si-Si interactions, and the ZBL potential [38] for all other interactions (Kr-Kr, Ar-Ar, Xe-Xe, Kr-Si, Ar-Si, Xe-Si). Since the ZBL potential is known to overestimate the interaction at large interatomic separations, we also performed a simulation with the Söle potential for the Kr-Si and Kr-Kr interaction [39,40], which has been fitted to *ab initio* calculations. The Kr-Kr Söle potential is close to the well established HFD-B2 potential [41] in the eV energy range.

The sequential impact simulations take several weeks to run on a few dozens of CPUs for each incidence angle. It is quite obvious that such simulations currently cannot be performed for much higher impact energies, e.g., 200 keV, at reasonable expense. According to SRIM [42], the projected range  $R_p$  of Kr ions increases by a factor of 23 when going from 2 to 200 keV. To estimate the simulation time required for the MD simulation of a 200-keV Kr impact we assume that the cell size has to be scaled proportional to  $R_p$  in each dimension. This means that the number of atoms in the simulation and thus, roughly, the simulation time per impact increases as  $R_p^3$ , i.e., by a factor of  $23^3 \approx 1.2 \times 10^4$ . In addition, the number of impacts required to reach sputtering equilibrium increases by about the same factor: to reach a certain fluence, the number of impacts scales with  $R_p^2$  corresponding to the change in surface area. To reach sputtering equilibrium, a depth of  $\sim R_p$  has to be sputtered [35]. Since the sputtering yield is only weakly dependent on the energy in the keV energy range [43], the fluence required to reach sputter equilibrium scales as  $R_p$ , and the number of impacts as  $R_p^3$ . This motivates the use of MC simulations to investigate a wider range of impact energies.

#### B. Monte Carlo simulations

The sequential MD impact simulations correspond to a “dynamic mode” in MC parlance in that the changes to the target induced by one impact are taken into account in the next impact. Dynamic simulations are also performed with MC for the comparison of the retained fluence (Sec. IV A). For the MC simulations we use the IMSIL code [44,45]. The dynamic mode has been added to IMSIL some time ago based on the algorithm implemented in TRIDYN [46]. In this approach, the substrate is subdivided into slabs, whose thicknesses are adjusted periodically as to relax the atom densities to their equilibrium values. In our simulations, we used an initial slab thickness of 1 Å and perform target relaxation after every 100 impacts, corresponding to a fluence increment of  $10^{12} \text{ cm}^{-2}$ . For reasons explained in Sec. II E, the MC simulations for the moments calculations are performed in static mode with a Si target containing a constant NG concentration of 2%.

In the MC simulations, atoms interacted via the Ziegler-Biersack-Littmark (ZBL) potential [38]. Electronic stopping was calculated using a mixed Lindhard/Oen-Robinson model [47,48] with Si parameters given in Ref. [49] and similar parameters for the NG. At low energies, electronic stopping plays only a minor role, since the Lindhard (nonlocal)

part is small at low energies [49], and the apsis of collision used in the Oen-Robinson model is always large. To obtain realistic sputtering yields, a planar potential barrier [50,51] corresponding to a surface binding energy of  $E_s = 4.7$  eV is assumed for Si atoms and of  $E_s = 0.25$  eV for the NG atoms. The former is chosen independent of the NG concentration contrary to the default model of IMSIL, as in reality we expect the near-surface region to deplete from the NG [32]. The surface binding energy for the NG atoms was chosen so that reduction towards smaller values did not change sputtering yields and  $E_s \leq E_d$  (see below) was fulfilled. Unnecessarily low values of  $E_s$  should be avoided, since for the sake of a consistent model, trajectories are simulated down to a cutoff energy  $E_f$  equal to the minimum surface binding energy of all atoms, which leads to large simulation times if  $E_s$  is small. For the displacement energy  $E_d$  [38,52], a value of 0.25 eV was used in order to fit the first redistributive moments of MC to those of the MD simulations as much as possible without having to accept excessive simulation times. The use of a very low value of  $E_d$  is in line with earlier MC simulations within the crater function formalism [23].

### C. Calculation of moments and derivatives

Since the crater functions are defined as the average response to a single ion, the moments have to be averaged over a number of impacts. In the MD simulations, we use 750 impacts for averaging, corresponding to a fluence increment of about  $5 \times 10^{14} \text{ cm}^{-2}$ . The 750 impacts are either chosen after the first 375 impacts (“low fluence”) or as the last 750 impacts of a simulation (“steady state”). In the MC simulations, averaging is done over all impacts (usually 100 000) since there is no transient in the simulation.

As stated in Sec. II A, the origin of the coordinate system is defined by the impact point. Determination of the impact point in the MD simulations is complicated by the fact that surface roughness develops during bombardment (the typical RMS amplitude in our MD simulations is  $\sim 2\text{--}3$  Å). In MD, we define the surface by moving a probe atom with radius 2.1 Å over the sample and taking the coordinates of the sample atom that is touched by the probe as the surface position. The impact point is taken as the intersection of the incoming ion direction with the average surface position. In the MC simulations, we define the surface position at the plane that divides the half spaces where target atoms are randomly generated or not.

We note that the definition of the impact point is relevant to the values of the first moment contributions by implantation and erosion ( $M_{\text{NG,impl}}^{(1)}$  and  $M_{\text{X,eros}}^{(1)}$ , respectively), but it is irrelevant to the sum of the two NG contributions ( $M_{\text{NG,impl}}^{(1)} + M_{\text{NG,eros}}^{(1)}$ ) in sputtering equilibrium, see Eq. (24). When comparing the individual contributions, however, e.g., between MD and MC, it is important to use consistent definitions.

The derivative with respect to the incidence angle  $\theta$  occurring in the first term of Eq. (8) is calculated by fitting parabolas through three adjacent  $\theta$  values, which is second-order accurate in  $\Delta\theta$  [70]. Derivatives of the sputtering yield with respect to curvature are calculated by simulating sputtering from cylinders of radius  $R = 5a$ , where  $a$  is the mean depth of energy deposition at normal incidence, and taking the derivative equal

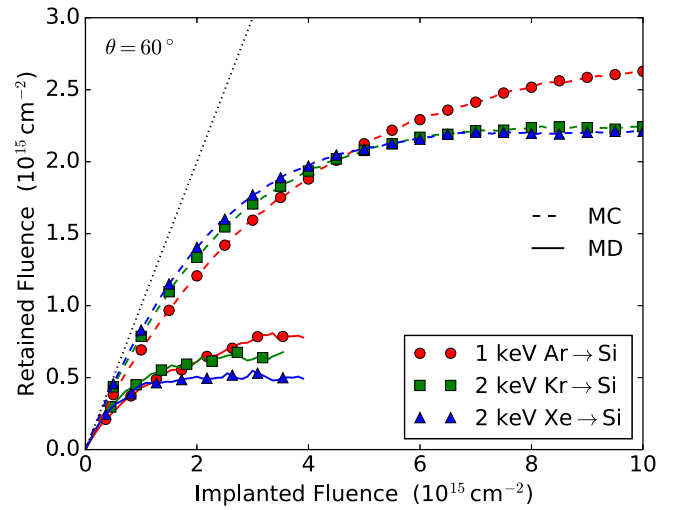


FIG. 1. Retained NG fluence as a function of implanted fluence for 1-keV Ar, 2-keV Kr, and 2-keV Xe bombardment of Si at an incidence angle of  $60^\circ$  as obtained with MD (solid lines) and MC simulations (dashed lines). Note the significantly higher steady-state retained fluence in the MC simulations than in MD.

to  $-R$  times the difference in sputtering yield between cylinder and flat target [53].

It is difficult to do this with MD, since the dependence of the sputtering yield on the curvature becomes nonlinear for relatively little changes in the yield [71]. So, in order to approximate the derivative with respect to curvature by a difference quotient, small changes have to be evaluated, which require statistics that is expensive to obtain with MD. We will therefore use MC results for the terms  $T_{11}$  and  $T_{22}$  when reporting results for  $C_{11}$  and  $C_{22}$ .

## IV. RESULTS

### A. Retained fluence

Figure 1 shows the retained NG fluence as a function of implanted fluence for 1 keV Ar, 2 keV Kr, and 2 keV Xe bombardment of Si at an incidence angle of  $60^\circ$ . While all curves start at the origin with a slope close to unity (dotted line), indicating that little reflection occurs at this angle, they saturate at different levels: the MC steady-state values are more than a factor of three larger than the MD values. This can be assigned to the rapid relocation effect discussed in Ref. [31], which is not included in the MC simulations.

Figure 2 shows the Ar concentration depth profiles after 1 keV Ar bombardment of Si as predicted by MC and MD, compared to experimental data obtained by medium energy ion scattering (MEIS) [54]. Obviously, the MD simulations describe a large fraction of the rapid relocation effect. To check whether the remaining difference is due to insufficient simulation times, we annealed one sample at 600 K for 10 ns, and found a reduction in the retained NG fluence of only  $\sim 10\%$  (this was done for 2-keV Kr at an incidence angle of  $60^\circ$ ). This modification seems low enough to be neglected in our study. It also might be a real effect due to the elevated temperature.

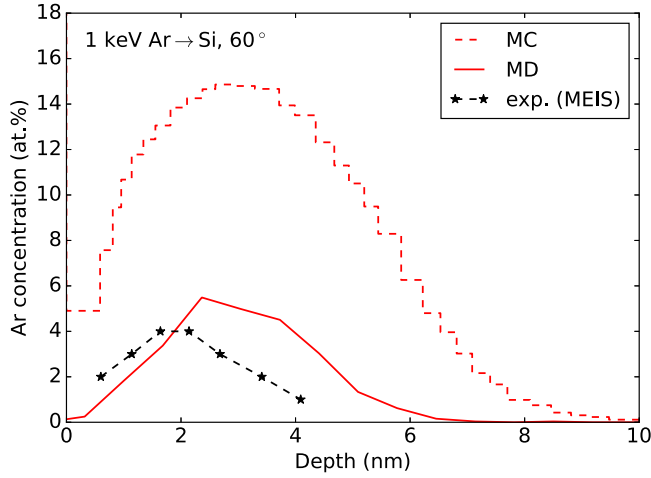


FIG. 2. Steady-state Ar concentration profiles after 1-keV Ar bombardment of Si as obtained with MD (solid line), MC (dashed line), and MEIS [54] (dashed line with symbols).

### B. Atomic volume of the implanted species

According to Eqs. (10) to (12) the effect of the implanted ions on the crater function and its moments is proportional to their atomic volume. As a first guess, it might be plausible to use the densities in the liquid or solid phase [55]. However, bubbles are known to form during NG implantation, and the atomic density in the bubbles is uncertain. We have therefore determined the atomic density of the NG atoms by assuming a fixed value of  $\Omega_{\text{Si}} = 20.4 \text{ \AA}^3$  for the atomic volume of amorphous Si [56] and fitting the NG atomic volume  $\Omega_{\text{NG}}$  to the densities observed in the MD simulations. This is done by counting the NG and Si atoms ( $n_{\text{NG}}$  and  $n_{\text{Si}}$ , respectively) in a layer of thickness  $4a \approx 21.7 \text{ \AA}$  at a depth of 1–4 nm below the surface. The known volume  $V$  of the slab must equal

$$V = n_{\text{NG}}\Omega_{\text{NG}} + n_{\text{Si}}\Omega_{\text{Si}}. \quad (25)$$

Plotting  $n_{\text{Si}}$  versus  $n_{\text{NG}}$  after each impact provides a point cloud to which Eq. (25) can be fitted by adjusting the only unknown  $\Omega_{\text{NG}}$ . Since we are only interested in the steady state values, only the last 750 impacts are used for the fit.

In Fig. 3(a), the  $n_{\text{Si}}(n_{\text{NG}})$  data are shown for 1-keV Ar, 2-keV Kr, and 2-keV Xe bombardment of Si at  $60^\circ$ . Each data set starts with  $n_{\text{NG}} = 0$ ,  $n_{\text{Si}} = 17920$ , the situation before the first impact, and evolves towards the right. The first few impacts lead to a reduction in target density (strong decrease in  $n_{\text{Si}}$  with only moderate increase in  $n_{\text{NG}}$ ), which is subsequently reversed. Closer inspection of the data shows that relaxation of the initial dilution occurs after 50–100 impacts (50 for Ar and 100 for Xe), corresponding to fluences around  $5 \times 10^{13} \text{ cm}^{-2}$ . This fluence is on the order of the amorphization threshold. The initial density reduction can be explained by the fact that target atoms are ejected from the near-surface region, where we measure the density, to either the vacuum or deeper parts of the target [57]. The subsequent increase of the target density is due to relaxation during amorphization. The last 750 data points in each set lead to the mean values and standard deviations of the atomic volumes given in the inset. The standard deviations might be slight underestimates caused by the limited impact

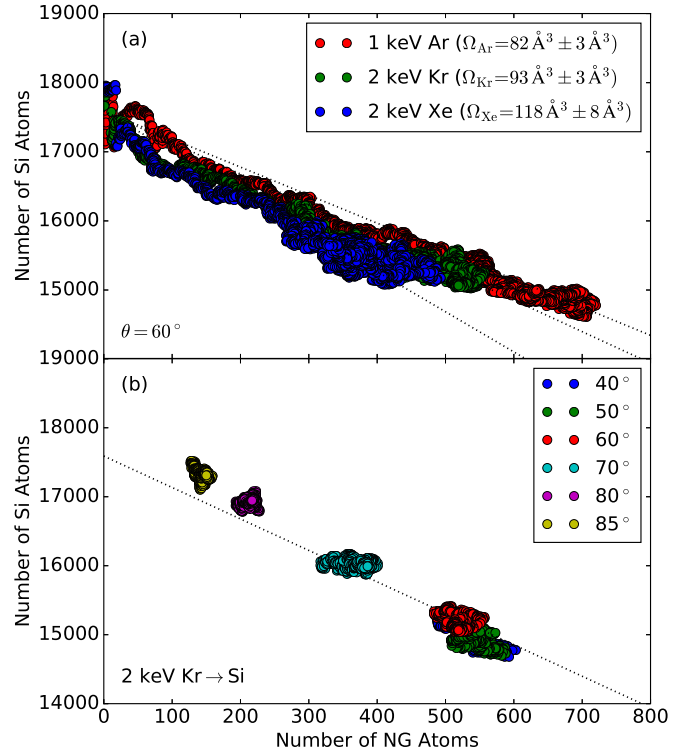


FIG. 3. Number of Si atoms vs number of NG atoms in a constant volume  $V$  (a) after each impact for 1-keV Ar, 2-keV Kr, and 2-keV Xe bombardment of Si at an incidence angle of  $60^\circ$ , and (b) after each of the last 750 impacts of 2-keV Kr at various incidence angles. The dotted lines are fits of the NG atomic volume to the last 750 impacts at  $60^\circ$  assuming the atomic volume of Si to equal the experimental value of  $\Omega_{\text{Si}} = 20.4 \text{ \AA}^3$  [56].

intervals used for averaging. Choosing different 750-impact intervals after the first  $\sim 5 \times 10^{14} \text{ cm}^{-2}$  (not shown), the atomic volumes are stable to within  $\sim 10\%$ .

Equation (25) with  $\Omega_{\text{Kr}}$  fitted to the  $60^\circ$  data is shown in Fig. 3(b) together with the MD data for incidence angles between  $40^\circ$  and  $85^\circ$  (last 750 impacts). For incidence angles up to  $70^\circ$  the fit is excellent. For larger angles ( $80^\circ$  and  $85^\circ$ ), the MD data lie above the fit, which means that the material is denser than described by the fit. A possible explanation is that at the lower incidence angles bubbles form which have a somewhat lower density than small NG clusters and interstitial NG atoms. Bubbles are less likely to emerge at large incidence angles where the sputtering yield is high and the reflection coefficient is considerable.

The results for the atomic volumes  $\Omega_{\text{NG}}$  are plotted in Fig. 4 together with published experimental data of solid state atomic volumes [55]. Our data exceed the solid state data by about a factor of two. To exclude an artifact of the ZBL interatomic potential, we have repeated the Kr simulation with the S  le potentials. These potentials are weaker at large interatomic separations, so one would expect to obtain a smaller atomic volume. This is not the case within the statistical error, see the red symbol in Fig. 4. We conclude that the error introduced by the ZBL potential, if any, is quite moderate.

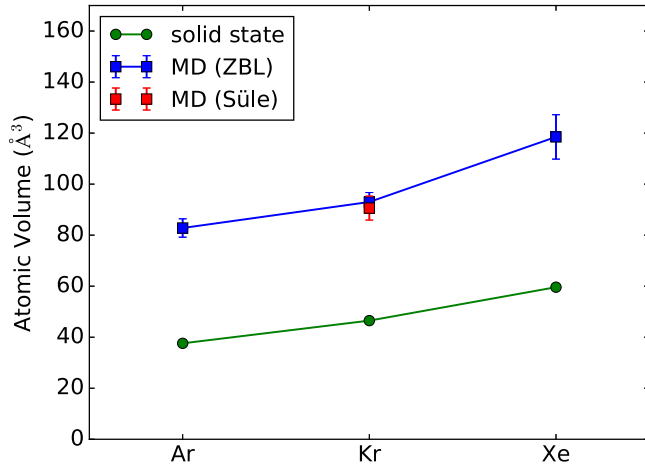


FIG. 4. Atomic volumes of Ar, Kr, and Xe as obtained by our MD simulations (squares with error bars) and experimental values in the solid state (green circles, [55]). In the MD simulations the NG-NG and NG-Si interatomic potentials have been chosen according to ZBL [38] (blue symbols and line) and Süle *et al.* [40] (red symbol). The lines are drawn to guide the eye.

The 600-K annealing described in Sec. IV A decreased the atomic volume by  $\sim 10\%$  (not shown). We conclude that the atomic volumes are well determined in our MD simulations.

### C. Effect of the implanted ions on the crater function moments: MD results

MD results for the contributions of implantation and erosion to the zeroth moment  $M^{(0)}$  are shown in Fig. 5(a) as a function of incidence angle for 2-keV Kr bombardment of Si. As mentioned in Sec. II, atom redistribution does not contribute to the zeroth moment. Both “low-fluence” (dashed lines) and “steady-state” results (solid lines) as defined in Sec. III C are shown. Notably, the contributions of Si erosion and Kr implantation have hardly any fluence dependence, while the contribution of Kr erosion only gradually builds up as the Kr ions are implanted. In the high-fluence case, the erosive contribution of Kr is approximately the negative of its implant contribution, indicating that steady state has indeed been reached to a good degree.

Given these results, it is not surprising that the total zeroth moment in steady state [blue line labeled “total” in Fig. 5(b)] agrees well with the values of Si erosion alone (green curve labeled “Si only”). The remaining small difference is probably due to the fact that sputtering equilibrium has not completely been reached. The added Si and implant contribution (red curve labeled “Si + Kr implant”) is not a good approximation of the total zeroth moment in steady state.

As for the zeroth moment  $M^{(0)}$ , the contributions of Si erosion and Kr implantation to the first moment  $M^{(1)}$  hardly depend on the fluence, see Fig. 6(a). The same holds true for the contribution by Si redistribution. Kr redistribution plays only a minor role, while the effect of Kr erosion on  $M^{(1)}$  depends on fluence as expected: the influence of Kr erosion develops only gradually as Kr ions are implanted. However, in contrast to its contribution to  $M^{(0)}$ , the effect of Kr erosion is not completely compensated for in steady state by the effect of implantation.

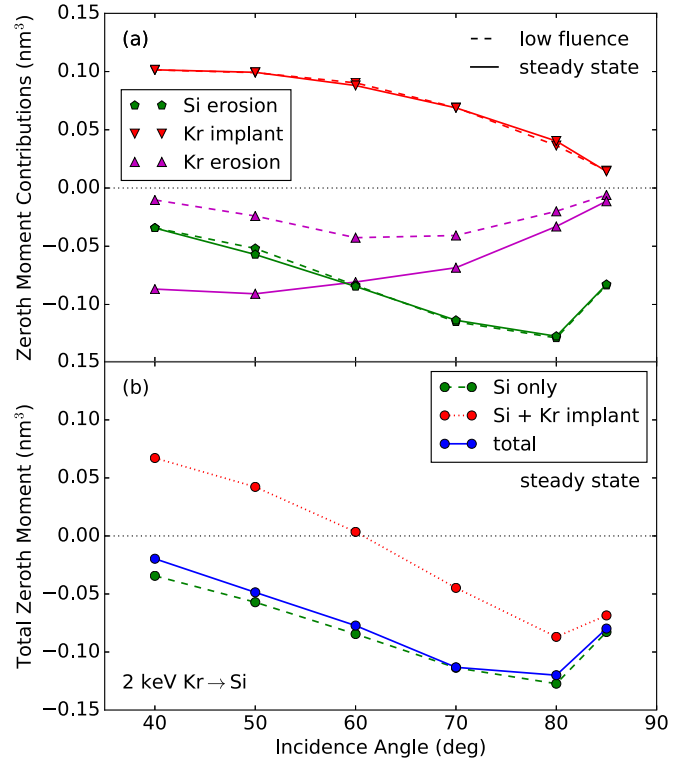


FIG. 5. MD results for the zeroth moment  $M^{(0)}$  of the crater function of Si bombarded with 2 keV Kr vs incidence angle. (a) Contributions by implantation and erosion comparing low fluence and steady state; (b) sum of contributions in steady state. The difference between the blue solid line and the green dashed line in panel (b) should vanish in sputtering equilibrium.

According to Eq. (21), this would be the case if the mean projected implant distance  $\bar{x}_{\text{Kr,impl}}$  equaled the mean projected erosion distance  $\bar{x}_{\text{Kr,eros}}$ . Rather,  $M_{\text{Kr,impl}}^{(1)} > |M_{\text{Kr,eros}}^{(1)}|$  can be read from Fig. 6(a), and therefore  $\bar{x}_{\text{Kr,impl}} > \bar{x}_{\text{Kr,eros}}$  validating, at least qualitatively, assumption 4.

As a consequence, the first moment in steady state does not agree well with the contributions of Si alone [solid blue and dashed green line, respectively, in Fig. 6(b)]. This is an important conclusion: the contribution of the implanted NG ions to the first moment is significant, on the order of 50% of the Si contribution in the present case.

Adding the Kr implant contribution to the Si contribution overestimates the total first moment  $M^{(1)}$  [dotted red line in Fig. 6(b)]. Further adding the negative contribution of Kr erosion, thus neglecting only the redistributive contribution of the NG atoms, gives a lower limit to the total first moment  $M^{(1)}$  (magenta line with triangles), see Eq. (24). For large angles it is a good approximation of  $M^{(1)}$ , while the deviation increases with decreasing incidence angle. In any case, it is a better approximation to  $M^{(1)}$  than neglecting the Kr contributions altogether (dashed green line).

In Fig. 6(c), the curvature coefficient  $S_{11}$  is plotted as calculated from the data given in Fig. 6(b). As for  $M^{(1)}$ , the contribution of Kr to  $S_{11}$  is significant. Considering only the implant and erosive contributions (magenta line with triangles) is a reasonable approximation to the total values, although the deviation increases with decreasing incidence angle.

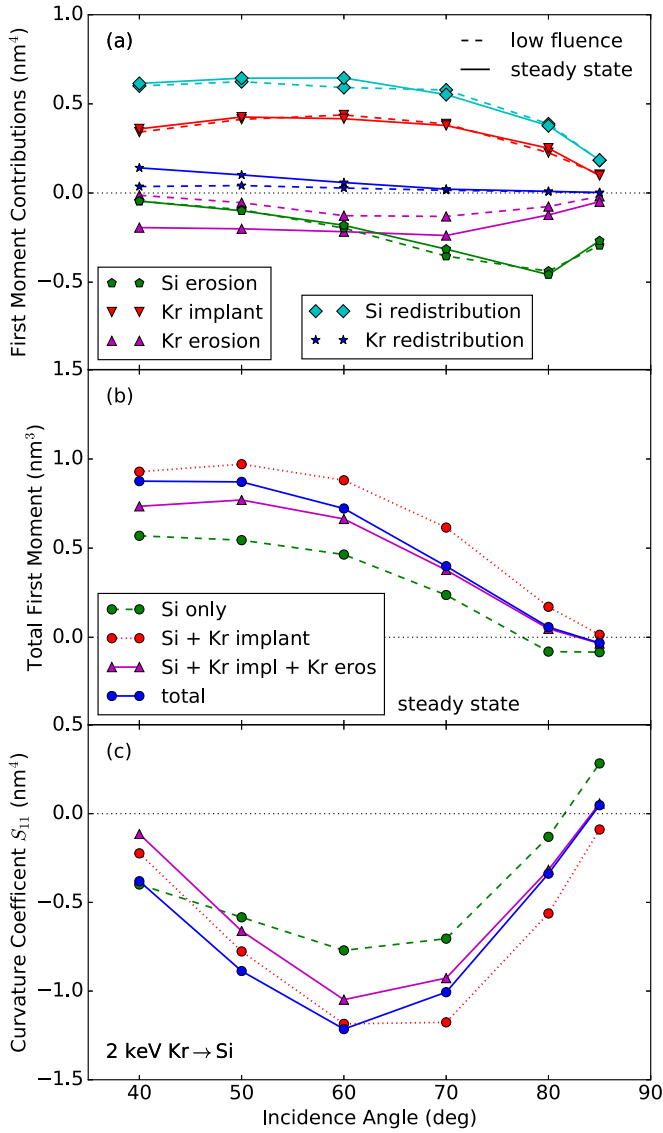


FIG. 6. MD results for the first moment  $M^{(1)}$  of the crater function [(a) and (b)] and for the curvature coefficient  $S_{11}$  as defined in Sec. II (c) for Si bombarded with 2 keV Kr as a function of incidence angle. (a) Contributions by implantation, erosion, and redistribution; [(b) and (c)] sum of all contributions. For the meaning of the line styles see Fig. 5. In addition, results neglecting only the Kr erosive contribution [Eq. (24)] are shown by the magenta lines with triangles. The differences between the solid blue line and the dashed green line in (b) and (c) indicate the role of the implanted Kr ions.

Similar results for both the zeroth and first moment are also obtained for Ar and Xe ions, see Fig. 7. In all cases, the contribution of the implanted ions is significant, and the lower limit according to Eq. (24) is the best approximation to the full calculation.

Figure 8 shows three versions of the curvature coefficients  $C_{11}$  and  $C_{22}$  for the Kr case: according to the original crater function formalism considering only flat targets and Si atoms [1,21], according to the extended crater function formalism considering in addition the effect of surface curvature [2], and considering in addition the contributions of the Kr atoms as proposed in this work. As is obvious from

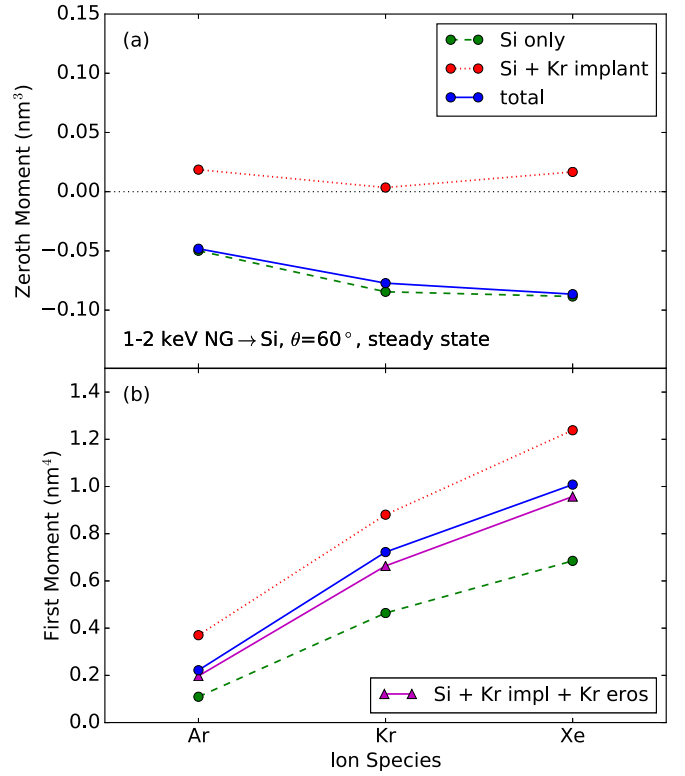


FIG. 7. Analogous to Figs. 5(b) and 6(b), but as a function of ion species for an incidence angle of 60°. For the meaning of the line styles see Fig. 6.

the plot, all contributions are significant. For  $C_{11}$ , the effect of surface curvature (the difference between the red dashed line and the green dotted line) partly compensates for the effect of the Kr atoms (difference between blue solid line and red dashed line), while for  $C_{22}$  both contributions work in the same direction.

#### D. MC versus MD results

As discussed in Sec. III A, the computational expense of MD simulations increases dramatically with increasing impact energy. To investigate the energy dependence of the role of the implanted ions, we have therefore performed MC simulations as described in Sec. III B. We recall that it is not possible to reliably predict the NG concentration in the target using MC simulations. As a consequence, there is uncertainty for the redistributive and erosive NG contributions to the first moment. The redistributive contribution has turned out to be small in the cases studied [Figs. 6(a) and 7(b)] and will therefore be neglected. The erosive contribution can be approximated assuming sputtering equilibrium and that the mean erosion distance does not depend on the details of the NG profile in the target. We use a Si target with a constant Kr concentration of 2% for our calculations.

In Fig. 9, MD and MC results of the contributions to the first moment according to Eq. (24) are compared (magenta triangles connected by solid and dashed lines, respectively), showing good agreement. Towards lower incidence angles this approximation increasingly underestimates the total Kr contribution [blue circles, Fig. 9(a)] as the Kr redistributive contribution

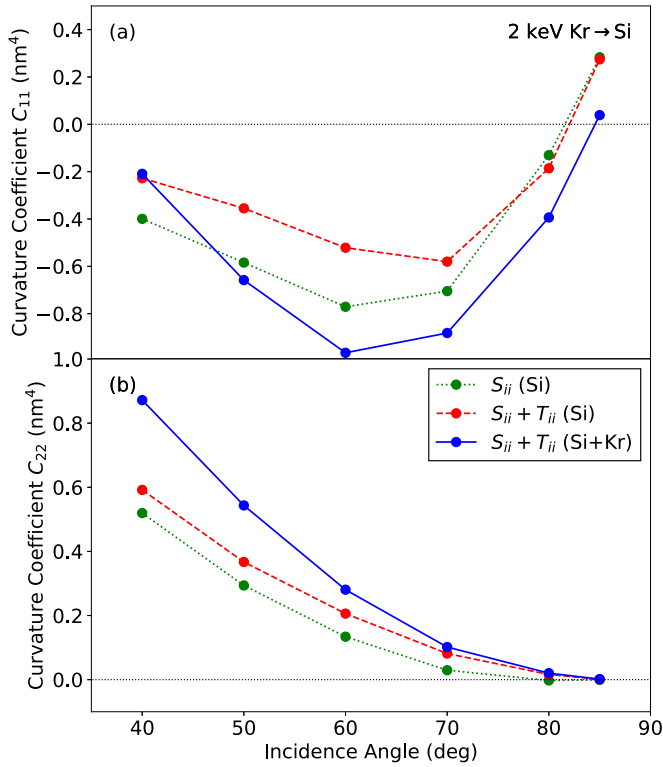


FIG. 8. MD results for the curvature coefficients (a)  $C_{11}$  and (b)  $C_{22}$  for 2-keV Kr bombardment of Si considering only flat targets and Si atoms [ $S_{ii}$  (Si), green dotted lines], considering in addition the effect of surface curvature [ $S_{ii} + T_{ii}$  (Si), red dashed lines], and considering all contributions including those of the NG atoms as proposed in this work [ $S_{ii} + T_{ii}$  (Si+Kr), blue solid lines]. Note that the first zero of  $C_{11}$  would occur at  $\theta < 40^\circ$  if data points at smaller incidence angles were added.

increases [compare also Fig. 6(b)]. For comparison, the Si redistributive contributions are also shown. The MD and MC results are similar, but again somewhat diverge towards smaller incidence angles. Figure 9(b) shows similar agreement for the lighter Ar and the heavier Xe ions. The ion mass dependence of the Si redistributive contribution is somewhat underestimated by MC, which may be explained by a spike effect [58] not included in the MC simulations.

The two critical quantities in Eq. (24) are the mean projected distances of the implant positions  $\bar{x}_{\text{NG,impl}}$  and the erosion points  $\bar{x}_{\text{NG,eros}}$  from the impact point. The distributions of these distances for 60° Kr impacts at 2 keV are plotted in Fig. 10(a). Good agreement between the MD and MC results is observed. Very clearly, the average implant distance is larger than the average erosion distance, i.e., implantation takes place considerably further away from the impact point than sputtering. This is plausible as nuclear energy is preferably deposited in a narrow region close to the impact point (see Fig. 15 of Ref. [59]). According to Eq. (21),  $\bar{x}_{\text{NG,impl}} > \bar{x}_{\text{NG,eros}} > 0$  means that the added contributions of NG erosion and implantation are positive but smaller than the contribution by implantation alone.

The agreement between the MD results, which include the rapid relocation effect, and the MC results, which do not, is remarkable also because it confirms the picture proposed in as-

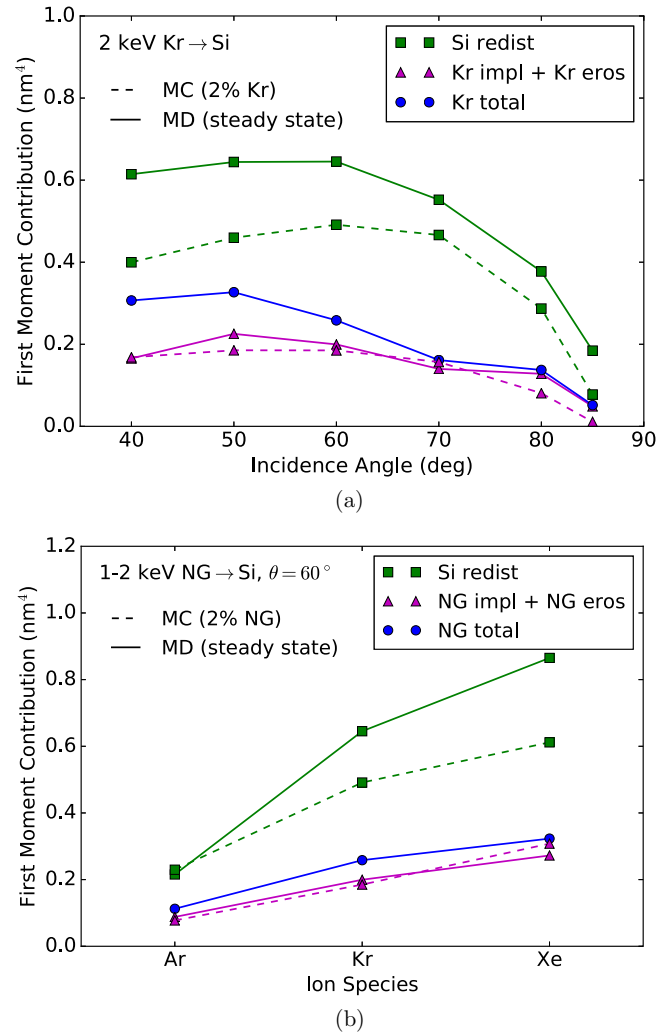


FIG. 9. Contributions of the NG (blue circles) and Si (green squares) to the first moment  $M^{(1)}$  as obtained by MD (solid lines) and MC simulations (dashed lines). In addition, the implant plus erosive contributions of Kr are shown by the magenta triangles. (a) 2-keV Kr as a function of incidence angle; (b) for an incidence angle of 60° as a function of ion species (1-keV Ar, 2-keV Kr, and 2-keV Xe).

sumption 4 of Sec. II C: while the NG atoms are driven towards the surface by rapid relocation, their eventual sputtering has similar spatial properties as in the absence of rapid relocation.

In Fig. 10(b), these quantities are compared as a function of incidence angle. Excellent agreement is found for angles up to 60°, while MC and MD results moderately diverge at larger angles. However, all that matters to the added effect of implantation and erosion is the difference between  $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{\text{NG,eros}}$ , which agrees well between MC and MD also for the larger angles. This also explains why the added contributions of Kr implantation and Kr erosion to the first moment (magenta lines in Fig. 9) agree well between MD and MC. The MD results in Fig. 10(b) also show that the mean projected implant and erosion distances hardly depend on the fluence, compare the solid and dotted lines. This confirms that  $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{\text{NG,eros}}$  are robust quantities that may be calculated without exact knowledge of the NG concentration in the target.

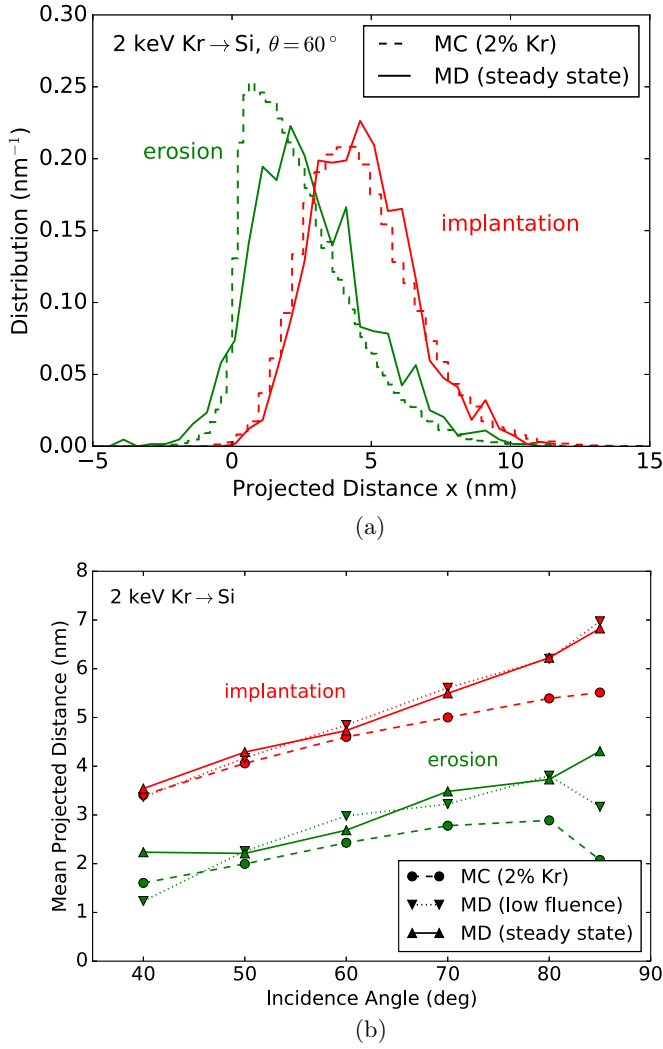


FIG. 10. (a) Distribution of the projected distance from the impact point ( $=x$  coordinate) for 2-keV Kr bombardment of Si at an incidence angle of  $60^\circ$ ; (b) mean projected distance from the impact point as a function of incidence angle for 2 keV Kr bombardment of Si. Red lines: implanted ions; green lines: sputtered Kr atoms. Solid lines: MD in steady state; dashed lines: MC; dotted lines: MD at low fluence. In (a), the MD results have been averaged over the last 1500 ion impacts.

### E. MC results for a wider range of impact conditions

The ion species and energy dependence of  $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{\text{NG,eros}}$  as calculated by our MC simulations for an incidence angle of  $60^\circ$  is shown in Fig. 11. Note that always  $\bar{x}_{\text{NG,impl}} > \bar{x}_{\text{NG,eros}}$ . According to Eq. (24) this means that the added contributions of NG implantation and erosion on the first moment are always positive. Both quantities increase with energy, and this is also true of their ratio  $\bar{x}_{\text{NG,impl}}/\bar{x}_{\text{NG,eros}}$ . While  $\bar{x}_{\text{NG,impl}}/\bar{x}_{\text{NG,eros}}$  is only 1.33, 1.57, and 1.88 at 200 eV for Ar, Kr, and Xe ions, respectively, it exceeds a factor of three at 200 keV.

The importance of the implanted ions to the crater function must of course be related to the contributions of the target atoms. In Fig. 12, we therefore compare the curvature coefficients  $C_{11}$  and  $C_{22}$  with and without consideration of

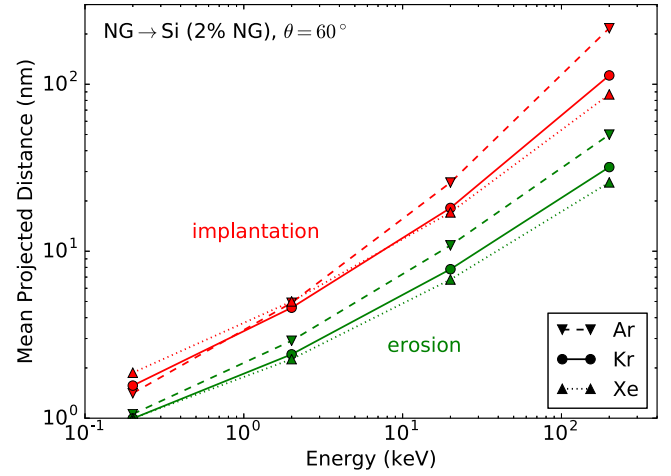


FIG. 11. MC results for the mean projected distances from the impact point for the implanted ions ( $\bar{x}_{\text{NG,impl}}$ , red lines and symbols) and for the sputtered atoms ( $\bar{x}_{\text{NG,eros}}$ , green lines and symbols) as a function of impact energy. Data for the three ion species Ar, Kr, and Xe at an incidence angle of  $60^\circ$  are shown.

the NG atoms (solid and dashed lines, respectively), where the contribution of the NG atoms has been estimated using Eq. (24). Data are given as a function of incidence angle for three ion species (Ar, Kr, and Xe) and four energies (0.2, 2, 20, and 200 keV). The effect of the implanted NG ions is significant in all cases, increases with impact energy although the increase is attenuated for the heavier ions. In all cases the ions have a destabilizing effect on the surface with respect to parallel mode ripples (contribution to  $C_{11} < 0$ ) for incidence angles larger than  $40^\circ$ – $50^\circ$  up to at least  $85^\circ$ . They do not change the lower critical angle for parallel mode ripple formation [zero of  $C_{11}(\theta)$ ] significantly, but move the upper critical angle to higher values. On the other hand, the ions always have a stabilizing effect on the surface with respect to perpendicular mode ripples (contribution to  $C_{22} > 0$ ). These results are qualitatively the same as for self-implantation [27,28].

## V. DISCUSSION AND CONCLUSION

From the results presented in the previous section, we conclude that the implanted NG ions in general play an important role in determining crater function moments. The rationale may be summarized as follows: (i) the average projected distance of the implanted ions from the impact point, measured along the surface, is larger than the corresponding average distance of the sputtered atoms. This leads to incomplete compensation of the effects of ion implantation and erosion on the first moment. (ii) Redistribution of the implanted ions due to subsequent impacts is always away from the impact point and therefore can only add to (rather than compensate for) the effect of ion implantation. (iii) The average atomic volumes of the NG atoms have been found in our MD simulations to be approximately twice those of the NG atoms in the solid state. This means that their effect on the crater function moments is twice that one would obtain with the solid state volumes.

There are some uncertainties in the simulations; however, they do not compromise our conclusion. First, MD may only

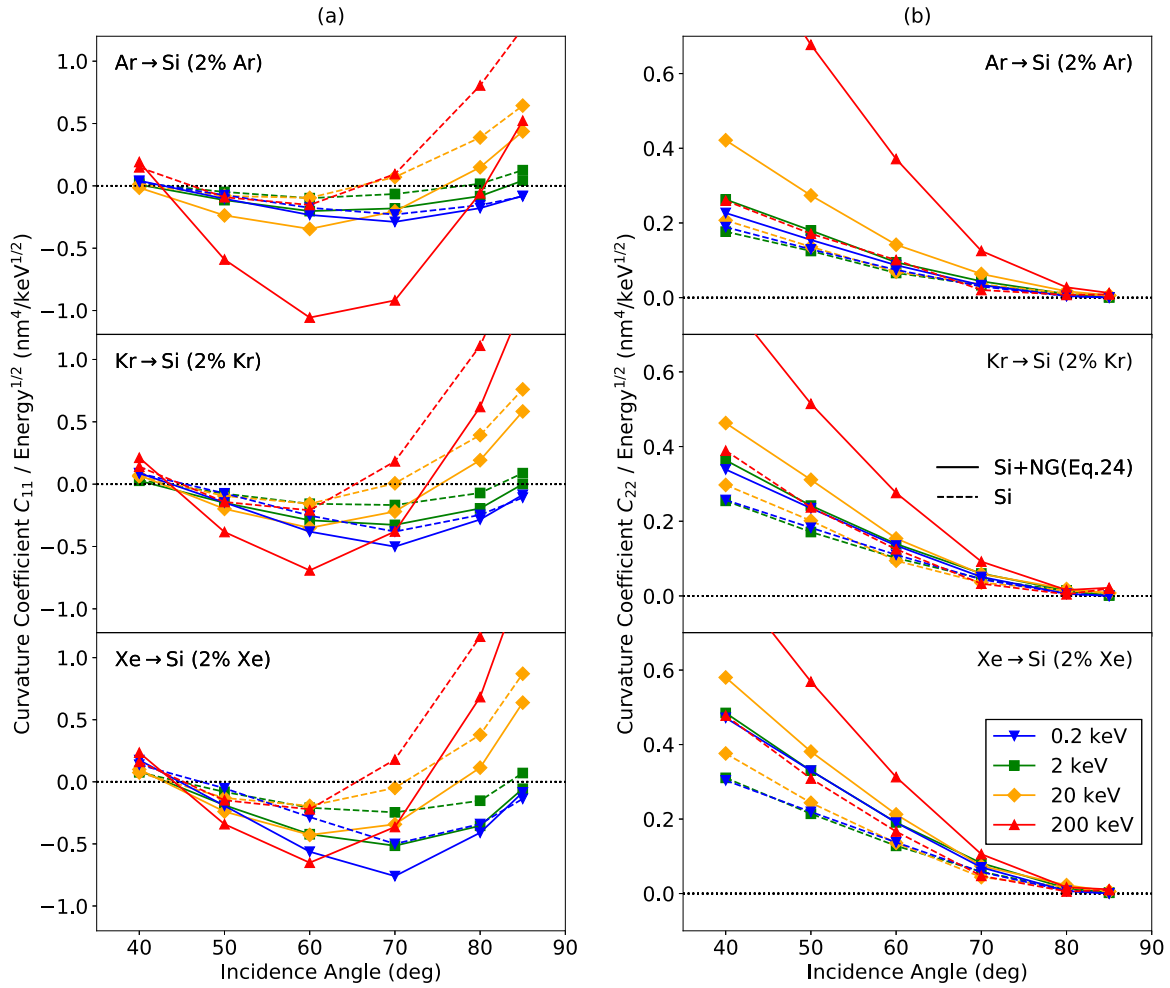


FIG. 12. MC results for the curvature coefficients (a)  $C_{11}$  and (b)  $C_{22}$ , comparing simulations with and without consideration of the effect of the implanted NG ions (solid and dashed lines, respectively). Data are shown for Si bombarded with Ar, Kr, and Xe at energies of 0.2, 2, 20, and 200 keV as a function of incidence angle. The results have been scaled with the square root of the impact energy to better represent them in the plots.

describe effects that occur on the timescale of the collision cascades. Thermally activated processes that mainly operate between the collision cascades are not included. While a systematic understanding of the effect of temperature on pattern formation is still lacking [60], there are indications that temperature does have an effect, even not too far from room temperature [61–65]. Also, thermally activated NG diffusion could explain the differences between the Ar concentration profiles obtained by MD and experimentally, see Fig. 2, although our annealing simulation did not provide enough evidence for a thermal effect. Anyway, thermal effects do not influence the range of the implanted ions and thus the implant contribution to the first crater function moment. Moreover, NG redistribution would be reduced, if the NG concentrations in the target were decreased by thermal diffusion, but our argument is not based on the redistributive NG contribution, which is small in our MD simulations and has been neglected in the MC simulations.

Second, MC simulations have their inaccuracies due to the binary collision approximation. As a result, the ion mass dependence of redistribution is underestimated by MC, see the Si redistribution results in Fig. 9(b). This is reminiscent of the ion mass dependence of damage formation in crystalline

Si, which is explained by the increasing relevance of thermal spikes with increasing ion mass [58]. However, the effect is moderate and is not expected to increase with ion energy: higher impact energies add high-energy portions to the ion trajectories, which are well described in the binary collision approximation.

Another consequence of the binary collision approximation is its failure to describe the rapid relocation effect that leads to an overestimation of the retained NG fluence, see Fig. 2. The retained fluence is expected to increase with ion energy [31]. Therefore one may expect an increasing contribution of NG redistribution to the first crater function moment with increasing energy. This would further enhance the importance of the implanted NG atoms beyond the analysis given in Sec. IV E. The argument is not so straightforward, however, since the other contributions to the first moment also increase with energy. The issue could be clarified by using a rapid relocation model [33] in the MC simulations that is fitted to experimental data on the retained fluence where such data is available. Again, NG redistribution would only add to the effects of implantation and erosion, so it would only increase the importance of the implanted ions.

As mentioned in Sec. II C, our MC simulations are based on the assumption that it is not necessary to know the exact concentration of the implanted NG atom (or that the actual concentration is close to the assumed one). This assumption is not perfectly valid. For instance, the sputtering yield increases by 25% from a pure Si target to steady state for 140-keV or 270-keV Xe bombardments [66]. This is explained by a reduction in ion and recoil range by the implanted heavy Xe atoms. This also means that the mean projected implant and erosion distances ( $\bar{x}_{\text{NG,impl}}$  and  $\bar{x}_{\text{NG,eros}}$ ) both shrink, which would not invalidate our analysis. It should also be taken into account that the ion species and energy in this study [66] represent extreme cases in view of the present study, and that this experiment was done at normal incidence, while we are more interested in oblique incidence where NG gas retention is reduced.

Before finishing, a few words on how our calculated curvature coefficients compare to experiments seem appropriate. From a qualitative point of view, all levels of sophistication of the crater function formalism [considering planar surfaces only [1], including the effect of curvature [2], and including the effect of the implanted NG atoms (this work)] agree with experiments performed under impurity-free conditions [60], in that they predict parallel mode ripple formation ( $C_{11} < 0$ ) for incidence angles above a critical angle around  $45^\circ$  up to another critical angle at grazing incidence. On closer examination, several discrepancies manifest themselves. For instance, the very careful experiments on 2-keV Kr bombardment of Si by Engler *et al.* [67] yielded a lower critical angle of  $58^\circ$ , significantly larger than  $45^\circ$ . For Ar ions, it has been found that no ripples occur for ion energies of 3 to 10 keV [26] in contrast to the predictions of the crater function formalisms. Finally, perpendicular mode ripples have been measured for 10-keV Xe bombardment at an incidence angle of  $80^\circ$  [68], while our MC results do not predict perpendicular mode ripple formation ( $C_{22} < 0$ ) at any of the investigated conditions. Unfortunately, we cannot report resolution of these discrepancies due to consideration of the effect of the implanted ions. On the other hand, the crater function formalism is intuitive, and MD and MC simulations are well-established techniques. We therefore believe that the cause of the discrepancy lies outside the crater function formalism, possibly in

stress effects operating in the amorphous layer on a scale not covered by MD simulations [15–18].

Finally, we wish to comment on a recent study of pattern formation by 1-MeV Au in Ti and its alloy TiAlV [69]. Applying our MC analysis to these conditions, we arrive at exactly the same conclusions as the authors of Ref. [69]. The relative importance of the implanted ions is close to negligible (results not shown). Au is about 50% heavier than Xe, which might be the cause why the implanted ions can be neglected in spite of the high impact energy. This also indicates that our conclusion about the importance of the implanted NG ions might not apply to Rn, the only NG heavier than Xe, which is even heavier than Au.

Au, of course, is not a NG, and Au implanted at this high energy is substantially incorporated in the target as demonstrated in Ref. [69] by RBS measurements. Such conditions should be analyzed by dynamic MC simulations, which would predict the implanted ion depth profile. In these simulations the redistributive contribution of the implanted ions to the first moment would be significant. This contribution could be determined with confidence, since depth profiles of nonvolatile ions are well predicted by MC simulations; the “rapid relocation” effect is a phenomenon associated with NG atoms only.

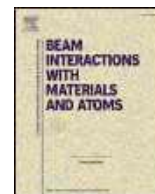
Our main finding in this work is that due to the difference between the mean projected implant and erosion distances ( $\bar{x}_{\text{NG,impl}} - \bar{x}_{\text{NG,eros}}$ ) the implanted NG ions usually play a role comparable to those of sputtering and atom redistribution as evaluated by crater functions. This is the case even though NG atoms are rapidly removed from the target so that their concentration is low at any time. While there are still open questions in the modeling of ion-target interaction that must be solved to make quantitative predictions, the fact that  $\bar{x}_{\text{NG,impl}} - \bar{x}_{\text{NG,eros}}$  agrees well between MD and MC simulations (Fig. 10) is strong support for this conclusion to be true not only at the conditions investigated by MD but also at higher energies.

## ACKNOWLEDGMENTS

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# Ion bombardment induced atom redistribution in amorphous targets: MD versus BCA

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## ABSTRACT

Atom redistribution is an important mechanism of ion bombardment induced spontaneous pattern formation in amorphous or amorphized targets. It may be characterized by either molecular dynamics (MD) simulations or by Monte Carlo (MC) simulations based on the binary collision approximation (BCA). In this work we analyze problems of the BCA approach in predicting atom redistribution by comparing MC and MD simulations of recoil events in amorphized Si. We find that the MC results critically depend on the displacement energy used, on the choice of the free flight paths and maximum impact parameters, and on the construction of the trajectories. Moreover, the net atom redistribution as determined by MD is significantly larger for recoils starting near the surface than for bulk recoils. The effect is not reproduced by the MC simulations.

## 1. Introduction

Spontaneous pattern formation by energetic ion beams has received significant impetus in recent years from progress in the understanding of its mechanisms [1–12]. An important contribution to the field is the so-called crater function formalism [2,7,12], which derives the coefficients of the equation of surface motion from the moments of a crater function. These moments can be calculated by molecular dynamics (MD) simulations or by Monte Carlo (MC) simulations based on the binary collision approximation (BCA).

The crater function moments have contributions from sputtering [13], atom redistribution within the target [14], and ion implantation [10,12]. Often, the effect of atom redistribution dominates or at least is an important contribution. It enters the formalism through its contribution to the first crater function moment

$$M_x^{(1)} = \Omega_{\text{Si}} \sum_{i=1}^n \Delta x_i. \quad (1)$$

Here, a Si target has been assumed and the contribution of relocated implanted ions has been neglected.  $\Omega_{\text{Si}}$  denotes the atomic volume of Si,  $n$  the number of Si atoms redistributed within the target, and  $\Delta x_i$  their displacement component in the direction of the projection of the ion beam to the surface ( $x$  axis). The redistributive contribution to the first moment thus describes the net displacement of the target atoms in  $x$  direction.

The purpose of this paper is to analyze problems of the BCA approach in determining the sum of the displacements appearing in Eq. (1). Shortcomings of the BCA compared to MD with respect to atom redistribution have been pointed out before [15,16]. On the other hand, MC simulations using the BCA have successfully been used in combination with the crater function formalism [17,18]. The discrepancy is likely due to different parameters and implementations of the MC codes. In the present work we focus our attention on the roles of displacement energy, free flight path selection, and trajectory construction.

## 2. Methodology

We assess the quality of BCA implementations by comparison of MC and MD simulations of atom redistribution resulting from recoils starting with given energy  $E$ , direction with respect to the surface, and depth  $z$  below the surface (Fig. 1). For MD the choice of the initial atom configuration is critical. At fluences sufficient to produce patterns, Si is amorphized. A not well relaxed sample may lead to unrealistic displacements [4,16]. One approach therefore is to exercise particular care when relaxing the initial atom configuration [16]. We have alternatively used sequential ion impacts on an initially virgin target until a steady state has been reached [12]. We use the target from Ref. [12] which has been produced by 2 keV Kr impacts with an incidence angle of 60° on a Si cell with  $x \times y \times z$  dimensions approximately equal to

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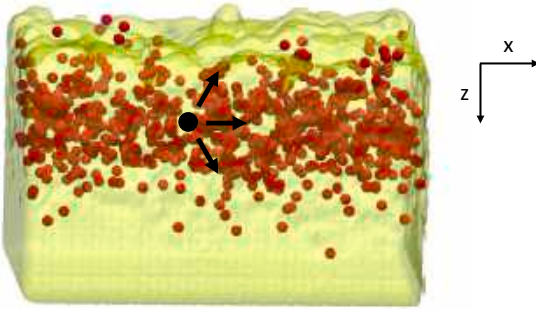


**Fig. 1.** Visual representation of the master sample used in the simulations of the recoil events. Si atoms are represented as a yellow transparent isosurface, Kr atoms as red spheres. A chosen primary recoil is represented by the black sphere.

150 Å × 100 Å × 100 Å, compare Fig. 1. The target contains a few percent of Kr atoms with a profile decaying towards the surface and the bulk. We assume their influence on the redistribution of Si atoms to be negligible. The target also exhibits surface roughness developed during the sequential impacts.

Simulations of the primary recoil events with energies between 5 eV and 100 eV are performed for three orientations of the velocity vector (Fig. 1), parallel to the  $x$  axis, at 60° pointing towards the surface, and at 60° pointing into the sample. For any given energy and orientation, 300 simulations are carried out where atoms with initial velocity are chosen randomly from a region 60 Å thick starting from the surface. Each simulation starts with a perfect copy of the master sample at 0 K temperature and is run for 1 ps. The applied boundary conditions and interatomic potentials are the same as in Ref. [12].

For the MC simulations we use the IMSIL code [19]. Unless otherwise noted we use the same models and parameters as in Ref. [12]. Unlike in [12], we neglect electronic stopping in order to allow a more consistent comparison with the MD results. In addition, we introduce variations into the BCA model as follows: First, in [12] the maximum impact parameter is chosen such that no collisions with energy transfer exceeding the displacement energy  $E_d$  are missed. This requires very large impact parameters  $p_{\max}$  on the order of 3–4 Å at low recoil and displacement energies. The value of  $p_{\max}$  is calculated from the minimum energy transfer and ion energy as proposed in [20]. The free flight path  $L$  is chosen according to

$$\pi p_{\max}^2 L = \Omega_{\text{Si}} \quad (2)$$

in order to use the correct atomic density [21]. In contrast, often simply a constant free flight path of  $L = \Omega_{\text{Si}}^{1/3}$  is used together with Eq. (2) [16,22]. For Si this leads to a fixed maximum impact parameter of  $p_{\max} = 1.53$  Å, which we consider as an option in our simulations.

Second, ion and recoil trajectories may be constructed in different ways. The most accurate treatment of a binary collision calculates the intersection point of the asymptotes using the “time integral”  $\tau$  [23,24]. In Fig. 2 this point is denoted 1', and its distance from the foot of the impact parameter on the incoming asymptote is denoted  $x_1$ . Putting the ion at this point after a collision is the standard treatment in IMSIL, which we therefore label as “IMSIL default”. Note that the initially chosen free flight path  $L$  is the distance between the ion (1) and the foot of the impact parameter on the incoming asymptote. The actual free flight path is reduced by  $x_1$  to  $ffp = L - x_1$  as shown in Fig. 2a.

At low energies,  $x_1$  may be quite large [24], and at the same time the free flight paths  $L$  are small due to the energy transfer criterion. Therefore the actual free flight paths  $ffp$  may become negative, meaning that the ion is moved in the opposite direction of its momentum (cf. Fig. 2b). To avoid this unphysical situation, the free flight paths  $ffp$  were limited to non-negative values in Ref. [12]. We denote this model as “ $ffp > 0$ ”. It comes at the expense of unphysically shifting the outgoing asymptote in the forward direction.

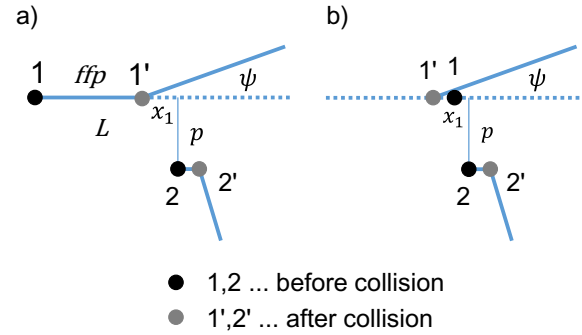


**Fig. 2.** Asymptotes of the ion (1) and recoil (2) trajectories. The ion is assumed to initially move to the right. In the standard model, after the collision, ion and recoil are placed into the intersection points of incoming and outgoing asymptotes. This normally leads to positive actual free flight paths  $ffp$  for a given chosen free flight path  $L$  (panel a), but can also lead to movement in the direction opposite to the initial ion momentum at low energies (panel b).

As a third option, the turning point of the ion trajectory may be assumed at the foot of the impact parameter on the incoming asymptote ( $x_1 = 0$ , which we will refer to as “no  $\tau$ ” or “TRIM”) as is done in most MC codes for amorphous targets. This avoids the discrepancy between actual and chosen free flight path ( $ffp$  vs.  $L$ ), again at the expense of constructing a wrong outgoing asymptote. The latter may seem as the lesser of the two evils. However, consider the case when the ion trajectory ends and the impact parameter  $p$  and the distance  $x_1$  are large. Then the model which puts the ion at the intersection of the asymptotes terminates the trajectory considerably before the target atom (2), which is qualitatively correct. In contrast, the “no  $\tau$ ” model puts the ion close to atom 2, which is unphysical.

### 3. Results and discussion

#### 3.1. Bulk simulations

In our recoil simulations we first only consider recoils starting at depths between 30 Å and 60 Å in order to exclude surface effects. A first set of results for recoils starting parallel to the surface is summarized in Fig. 3. In all panels the first moment according to Eq. (1) is shown as a function of the recoil energy. Results obtained with different BCA models (dashed lines) are compared to the MD results (black dots with error bars connected by black lines). Different displacement energies  $E_d$  are indicated by different colors. In the top row the energy dependent model for the maximum impact parameter is used which guarantees that no energy transfers above  $E_d$  are missed. With the default IMSIL model (left column) the MC simulations cannot be fitted to the MD data by varying the displacement energy; the best result is obtained with  $E_d = 5$  eV. Oddly, the first moment can become negative for small displacement energies ( $E_d = 1$  eV and  $E_d = 0.25$  eV), i.e., the sum of the atom displacements is opposite to the direction of the initial recoil momentum, which is clearly unphysical. This does not happen when the actual free flight paths are restricted to non-negative values as described in Section 2 (middle column). Then a displacement energy of 5 eV yields an excellent fit to the MD data. With the TRIM model (right column) the problem of negative moments does not occur either, but an optimum fit is now obtained with a displacement energy near 15 eV. With the TRIM model the longest free flight paths are chosen among the three models, which is compensated for by a smaller number of recoils resulting from a larger displacement energy. In the bottom row of Fig. 3, the corresponding MC results using a fixed maximum impact parameter of 1.53 Å are shown. Now the MD data are well fitted with displacement energies near 15 eV.

Fig. 4 shows the displacement  $\Delta x_1$  of the primary recoil in addition to the sum of all displacements for the three models with the best fit of

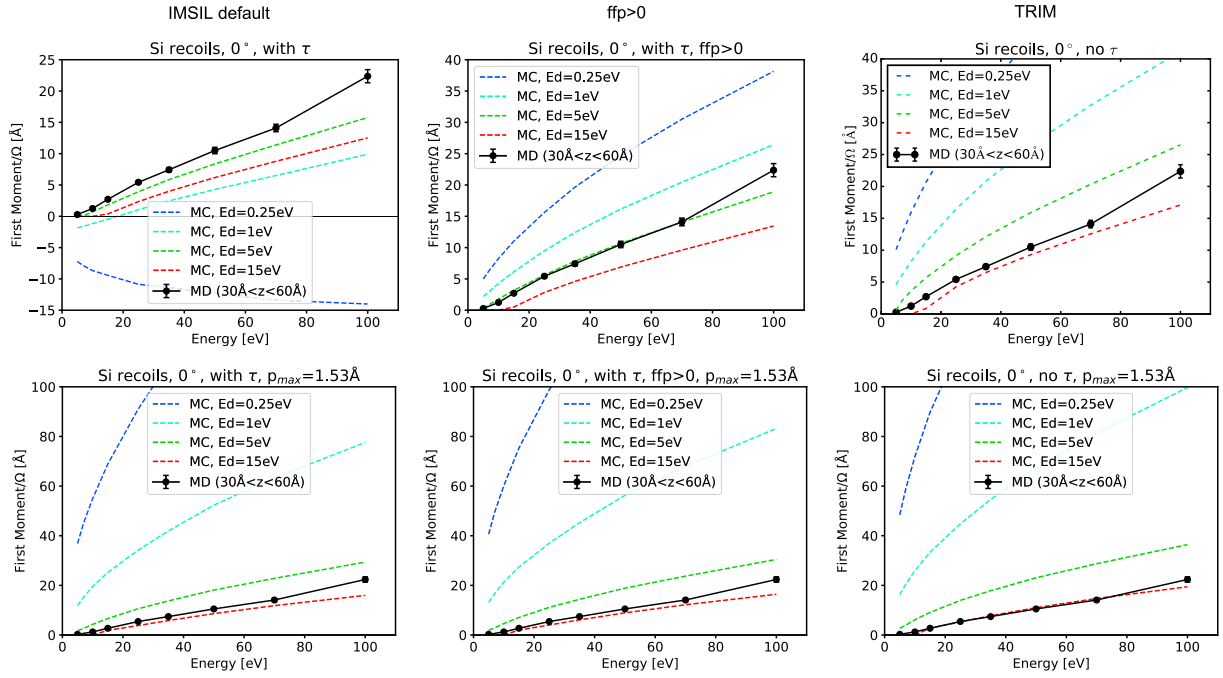


**Fig. 3.** First moment as a function of the recoil energy using various BCA models. Top row: using the energy dependent maximum impact parameter; bottom row: using a fixed maximum impact parameter of 1.53 Å. Columns 1–3: different trajectory construction models, see Section 2. The MD results represented by the black symbols with error bars, connected by lines, are the same in all panels. Recoils are started parallel to the surface.

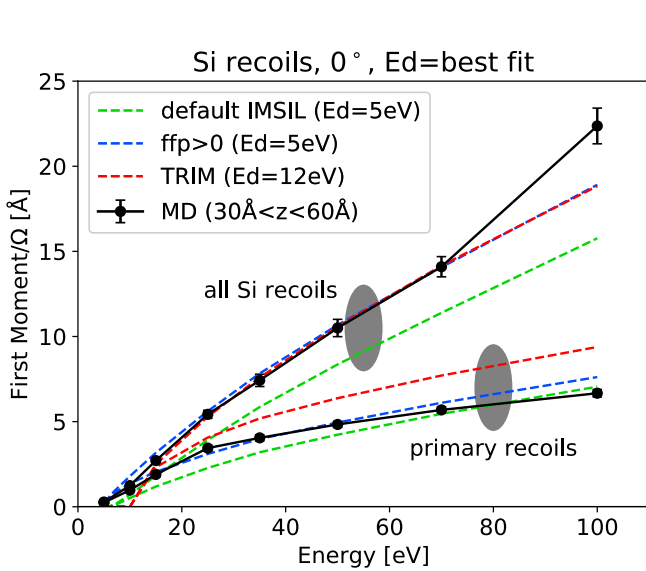


**Fig. 4.** First moment as a function of recoil energy. Symbols and lines have the same meaning as in Fig. 3. The displacement energy with the best fit to the MD data and the energy dependent maximum impact parameter model have been chosen for the MC simulations. In addition to the first moment the contribution of the primary recoil, i.e., the displacement of the primary recoil parallel to the surface, is shown.

the displacement energy. While both the  $ffp > 0$  model and the TRIM model are in excellent agreement with the MD data taking all recoils into account, the TRIM model overestimates the displacement of the primary recoil. Since the displacement of the primary recoil is one term in the sum defining the first moment, Eq. (1), this is compensated for by fewer terms in the sum, which is accomplished by the higher displacement energy. Thus, the TRIM model partitions the first moment unphysically into contributions of the primary recoils and those of higher-order recoils. The  $ffp > 0$  model therefore appears to be preferable.

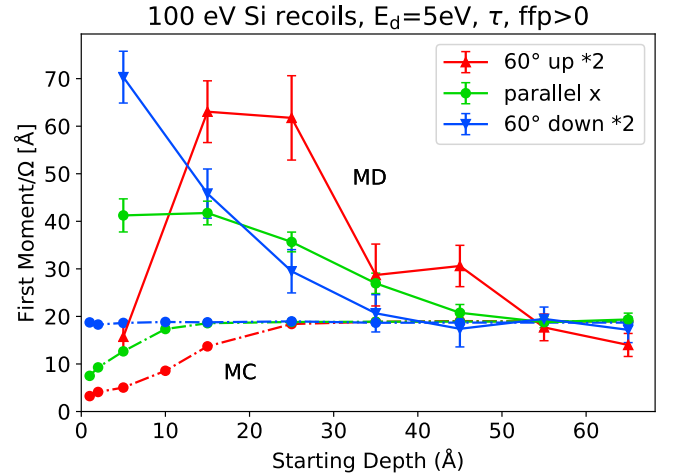


**Fig. 5.** First moment as a function of primary recoil depth  $z$  for 100 eV recoils starting parallel to the surface or at 60° with respect to the  $x$  axis towards or away from the surface. MD results collect data from  $[z-5 \text{ Å}, z+5 \text{ Å}]$ . MC simulations have used the  $ffp > 0$  model. The results for the inclined initial recoil directions have been multiplied with two.

### 3.2. The effect of the surface

First moments resolved with respect to the starting depth of the primary recoils are shown in Fig. 5 for a recoil energy of 100 eV. Focussing first on recoils starting parallel to the surface (green lines), one observes a significant increase in the first moment towards the surface in case of the MD results, while the first moment calculated by MC decreases towards the surface. The decrease in the MC results is easily explained: Some recoils escape into the vacuum and cannot produce higher-order recoils there, thus reducing the number of terms in Eq. (1). The increase in the MD results indicates a reduced resistance of the surface atoms against relocation. As the effect is quite substantial, this reduced resistance likely extends to considerable depth, indicating collective motion of atoms in a near-surface layer of the target.

Fig. 5 also contains simulation results for recoils starting at  $60^\circ$  with respect to the  $x$  axis either towards the surface (red lines) or towards the bulk (blue lines). At large enough depths, under isotropic conditions the calculated first moments should be  $\cos 60^\circ = 1/2$  of the results for the initial direction parallel to the surface. The results for the inclined initial directions have therefore been multiplied with a factor of two. The good agreement of the results for the three initial conditions deeper in the sample indicates the absence of (artificial) anisotropies.

The first moments calculated by MD for primary recoils directed towards the surface (red lines) show a strong increase as a function of decreasing initial depth, until close to the surface where they are strongly lowered. A pronounced decrease towards the surface is also observed in the MC results. The larger decrease in both the MD and MC results, compared to when the primary recoils start parallel to the surface, is due to the fact that recoils have a larger probability of escaping into the vacuum when the primary recoil is directed towards the surface. The strong increase in the MD result at intermediate depths indicates that the collective motion is facilitated when a larger part of the recoil cascade is near the surface.

When the primary recoils are directed towards the bulk (blue lines), there is virtually no influence of the primary recoil depth on the first moment in the MC results, indicating that very few recoils escape into the vacuum even when the primary recoil starts at the surface. This is confirmed, e.g., by a MC sputtering yield of  $Y = 0.1$  for primary recoils starting at a depth of  $2 \text{ \AA}$  with a component into the bulk, compared to  $Y = 1.05$  for the same primary recoils starting parallel to the surface. The MD results show a substantial increase towards the surface with a maximum at the surface that exceeds even the maximum for the recoils directed towards the surface.

#### 4. Conclusions

We have shown that atom redistribution as calculated by MC simulations strongly depends on the implementation of the BCA, i.e., on the displacement energy, the choice of the free flight path and the maximum impact parameter, and the construction of the trajectories. To the knowledge of the authors, in all previous work targeted at predicting spontaneous pattern formation using MC simulations, these details have not completely been specified. This means that none of these publications is reproducible.

For recoils starting deep in the bulk, we have obtained best results by limiting the free flight paths to non-negative values and choosing a displacement energy of  $E_d = 5 \text{ eV}$ . This value is considerably higher than the value used in our impact simulations [12]. For the impact simulations, the choice of  $E_d = 5 \text{ eV}$  results in considerably underestimated contributions to the first moment. The reason is the surface effect described in Section 3.2: The target atoms are much more mobile near the surface, probably due to some collective motion. Modeling this surface effect is an important challenge, if realistic MC simulations are aspired.

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simulations were performed at the PLGrid computer facilities.

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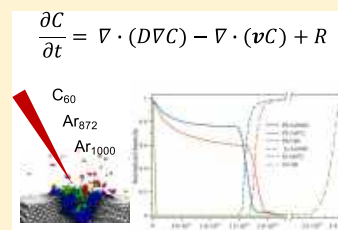
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## MD-Based Transport and Reaction Model for the Simulation of SIMS Depth Profiles of Molecular Targets

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## Supporting Information

**ABSTRACT:** We present a novel theoretical approach allowing us to model erosion and chemical alteration of organic samples during depth profiling analysis by secondary-ion mass spectrometry with cluster projectile ion beams. This approach is able to take into account all of the cumulative phenomena occurring during such analysis, including ion-beam-induced reactions and atomic/molecular mixing by means of the numerical solution of an advection–diffusion–reaction (ADR) differential equation. The results from the single-impact molecular dynamics computer simulations are used as a source for the input parameters into the ADR model. Such an approach is fast and allows turning the phenomenological model into a more quantitative tool capable of calculating molecular secondary-ion mass spectrometry depth profiles. The model is used to describe phenomena taking place during depth profiling of polystyrene samples by 20 keV C<sub>60</sub>, Ar<sub>872</sub>, and Ar<sub>1000</sub> projectiles. It is shown that theoretical findings are in good agreement with the experimental results. The model is also used to determine the overall efficiency of nitrogen monoxide molecules in eliminating the radicals responsible for polystyrene cross-linking induced by analyzing ion beams.



## INTRODUCTION

In recent years, secondary-ion mass spectrometry (SIMS), a well-established technique for the characterization of solid surfaces and thin films of both inorganic and organic materials,<sup>1,2</sup> has undergone a drastic evolution, related to the introduction of polyatomic primary ion beams,<sup>3</sup> which boosted new perspectives in the analysis of organic materials and polymers. A big effort has been made to model the impact of primary cluster ions on the organic target by means of molecular dynamics (MD) simulations.<sup>4–9</sup> These simulations are used to model the phenomena involved in an individual cluster-target impact that typically occurs over a time scale of the order of a few tens of picoseconds.<sup>10</sup> In some aspects, MD simulations can be considered as the theoretical counterpart of static-SIMS experiments. In contrast, the theoretical modeling of the physicochemical phenomena occurring during dynamic-SIMS (D-SIMS) depth profiling of organic and polymer targets under cluster ion beams is less developed.

In modeling D-SIMS experiments, time scales much larger than those involved in MD simulations must be considered to take into account slower and cumulative phenomena. Such phenomena, including ion-beam-induced reactions and atomic/molecular mixing, can substantially modify the nature of the target. Wucher et al.<sup>11,12</sup> were the first to develop a model (statistical sputtering model, SSM) aimed to correlate the information obtained from molecular dynamics simulations to depth profiles. Additional models based on the SSM concept appeared later.<sup>4,5</sup> However, all of these approaches were computationally intensive. Recently, we simulated D-SIMS experiments by means of the numerical solution of an advection–diffusion–reaction differential equation.<sup>13</sup> Such a

transport–reaction (TR) model takes into account the effects of ion-beam-induced mixing and reactivity, which occur during the depth profiling experiments. This model is able to simulate a complete D-SIMS experiment without requiring large computational capabilities. The values for the model input parameters can be estimated either from experimental data, as in our previous work, or from the output of computational simulations. Recently, it has been shown that the results of MD simulations can be used successfully for determining these parameters in the case of nonreactive inorganic samples.<sup>14</sup> In this paper, we present the integration of MD simulations results into the transport–reaction model for depth profiling of polymer films, also in the case when ion-beam-induced chemical damage cannot be neglected. The MD simulation outputs are used as input parameters into the model. This allowed us to turn the previously reported phenomenological transport–reaction (TR) model into a quantitative model for the prediction of molecular D-SIMS depth profiles by the MD results. Henceforth, we call this model MD-TR.

## EXPERIMENTAL METHODS

The molecular dynamics (MD) computer simulations are used to model cluster bombardment of polystyrene, silicon, and diamond surfaces by 20 keV C<sub>60</sub> at a 45° impact angle. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among carbon atoms in the system are described by the ReaxFF-Ig force

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field,<sup>15</sup> which allows for the creation and breaking of covalent bonds. This potential is splined at short distances with a ZBL potential<sup>16</sup> to describe high-energy collisions accurately. The forces among Si–Si are described by the Tersoff-3 potential.<sup>17</sup> The interactions between Ar atoms in the projectile and between the projectile atoms and all other atoms in the systems are represented by the Lennard-Jones potential splined at short distances with the KrC potential,<sup>18</sup> which is better than ZBL to describe energetic collisions of noble gas atoms. Energetics of bond breaking, essential for our studies (C–H or C–C bond cleavage), was calculated with the ReaxFF potential. The values were compared with the reference data to verify whether this potential gives correct predictions. The results are presented in the [Supporting Information](#). We observe some deviations between the bond energies predicted by ReaxFF and the reference data. However, the differences always remained below 10% of the reference data.

A detailed description of the MD method can be found elsewhere.<sup>19</sup> The shape and size of the samples are chosen based on visual observations of energy transfer pathways stimulated by impacts of C<sub>60</sub> projectiles. As a result, hemispherical samples with diameters of 40, 32, and 26 nm for polystyrene, silicon, and diamond, respectively, are used. These samples contain 1 621 182, 432 449, and 823 719 atoms. The calculated densities of these samples are 1.097, 2.334, 3.54 g/cm<sup>3</sup> and agree well with the experimental values of 0.96–1.04, 2.33, and 3.5–3.53 g/cm<sup>3</sup> for polystyrene, silicon, and diamond, respectively. Rigid and stochastic regions near the external boundaries of the sample with thicknesses of 0.7 and 2.0 nm, respectively, were used to simulate the thermal bath that keeps the sample at the required temperature to prevent reflection of pressure waves from the boundaries of the system and to maintain the shape of the sample.<sup>20,21</sup> The simulations are run at the 0 K target temperature in an NVE ensemble and extend up to 50, 20, and 20 ps for polystyrene, silicon, and diamond, respectively, which is long enough to achieve saturation in the ejection yield vs time dependence. Impacts of 20 keV C<sub>60</sub>, Ar<sub>872</sub>, and Ar<sub>1000</sub> were modeled at a 45° incidence angle relative to the surface normal to comply with the experimental conditions used in ref 22. The two different Ar clusters, differing about 10% in size, were chosen to get an idea on the possible effects of non-monodisperse size distribution of the clusters since in real experiments clusters exhibit a distribution around the nominal size. Simulations are performed with the Large-scale Atomic/Molecular Massively Parallel Simulator code,<sup>21</sup> which was modified to describe sputtering conditions better. Numerical solution of the equation involved in the proposed model was performed by means of a Python-based script, developed on purpose. We simulated the D-SIMS depth profiles of 100 nm-thick PS thin films deposited onto a Si substrate. The primary ion beam current was 1 nA, rastered over 500 × 500 μm<sup>2</sup>. Experimental results have been replicated as in ref 22.

## RESULTS AND DISCUSSION

In the MD-TR model, the position of the bombarded surface is kept invariant so that the erosion process is represented as a “travel” of the underlying material toward the surface. The sputtering rate is represented by the travel velocity (*v*) of the inner target layers toward the surface. When the material moving toward the surface enters the layer altered by the ion beam, it is redistributed by ion-beam mixing and, also, ion-beam-induced chemistry is triggered. The partial differential

equation describing the evolution of the concentration profile, *C*(*z*, *t*), of a certain species during a sputter-profile experiment can be written as

$$\frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C) - \nabla \cdot (vC) + R \quad (1)$$

where *C* is the volumetric atomic concentration of the species composing the target material, expressed in atoms/nm<sup>3</sup>. If the sputtering area is kept constant during the simulations, only the traveling direction *z* (normal to the surface plane) must be considered; thus, the unit of *C* is atoms/nm. For the reconstruction of the depth profile, the model is using the so-called sampling depth, which takes into account the fact that atoms ejected by a single projectile impact can be initially located also below the surface. SIMS intensities (*I*(*t*)) are calculated by the following equation

$$I(t) \propto \int_0^\infty C(z, t) \cdot e^{-z/(\lambda)} dz \quad (2)$$

where *λ* is the extent of the sampling depth distribution, which is known to be of the order of interatomic distances.

The quantity (*v*) is equivalent to the erosion rate expressed in nm/s. If we express the flux (*φ*) of projectiles in ions nm<sup>−2</sup> s<sup>−1</sup> and the volumetric sputtering yield (*Y*) in nm<sup>3</sup>/projectile, we can write

$$v \left[ \frac{\text{nm}}{\text{s}} \right] = Y \left[ \frac{\text{nm}^3}{\text{projectile}} \right] \cdot \phi \left[ \frac{\text{projectile}}{\text{nm}^2 \text{s}} \right] \quad (3)$$

The dominant quality of the transport and reaction model is the capability to simulate depth profiles of reactive target layers, such as those constituted by organics or polymers. For example, during depth profiling of the organic target by monatomic beams or during the bombardment of polystyrene-like polymers by means of C<sub>60</sub> primary beams, the intensity of fragments characteristic of the original polymer is readily lost.<sup>23</sup> Even in the case of sputtering of thick samples by means of large argon clusters, damaging is not negligible so far.<sup>24</sup>

Focusing on the specific case of the depth profiling of a polystyrene layer deposited onto a silicon substrate, based on the simplified assumption that the instantaneous erosion rate is equal to the weighted mean between the erosion rates of the intact and fully damaged material, we can write

$$v = v_{\text{PS}} C_{\text{PS}} + v_{\text{c}} C_{\text{damage}} + v_{\text{Si}} C_{\text{Si}} \quad (4)$$

where *v*<sub>PS</sub>, *v*<sub>c</sub>, and *v*<sub>Si</sub> are the erosion velocities of the pristine polystyrene, damaged material, and silicon substrate, respectively. *C*<sub>PS</sub>, *C*<sub>damage</sub>, and *C*<sub>Si</sub> are the normalized relative concentrations of target atoms that, inside the altered layer, pertain to undamaged polystyrene repeating units, to the damaged material, and to the silicon substrate, respectively. In the present application of the MD-TR model, the volumetric sputtering yields of *Y*<sub>PS</sub>, *Y*<sub>c</sub>, and *Y*<sub>Si</sub> are obtained by MD simulations performed on polystyrene, diamond (chosen as a representative of the fully damaged, carbonlike material formed upon beam irradiation), and silicon, bombarded with C<sub>60</sub>, Ar<sub>872</sub>, or Ar<sub>1000</sub> projectiles. It should be noted that the choice of diamond as a representative of a fully damaged polymer is probably too extreme, while an amorphous carbon or a C–H cross-linked network would be more realistic. However, the generation of a truly amorphous system for MD simulation is very difficult and, on the other hand, the good agreement of

our MD-TR simulations with experimental results (see *infra*) indicates that the choice of diamond is acceptable.

The volumetric sputtering yield values, calculated by MD simulations, are reported in Table 1.

**Table 1. Volumetric Sputtering Yield (nm<sup>3</sup>/ion) from MD Simulations**

|         | C <sub>60</sub> | Ar <sub>872</sub> | Ar <sub>1000</sub> |
|---------|-----------------|-------------------|--------------------|
| PS      | 84              | 99                | 93                 |
| Si      | 6               | 2                 | 0.8                |
| diamond | 1.9             | 0.011             | 0.011              |

The quantity **D** in eq 1 is a function that takes into account the ion-beam-induced mixing in the altered layer region. In the present simulation, surface roughening is neglected. The mixing term **D** in eq 1 is related to the ion-beam-induced motion of particles in the collision cascade, which can be described by analogy with the self-diffusivity process. Strictly speaking, we should also consider the lateral component to the diffusion. In simulating a depth profile of a laterally homogeneous system, however, we can neglect the lateral component and, consequently, the model is reduced to a unidimensional one along the traveling direction *z* (normal to the surface plane). By analogy with the unidimensional random walk model for diffusion, the units of **D** is nm<sup>2</sup>/s. To extract the per impact ion-beam-induced diffusion (*D'*) from the MD simulations, we divide each simulated sample into the equally spaced slices along the *z*-axis. For each slice, we calculated a sum of the total square displacements along the *z*-axis of all atoms located initially in a given slice multiplied by the volume occupied by the displaced atom. For a slice *i* of a width *dz* at depth *z<sub>i</sub>*, this can be expressed by the following equation

$$D'[z_i] = \sum_{j=1}^{N_i} dz_j^2 V_j / dz \quad (5)$$

where *N<sub>i</sub>* is the total number of atoms in the given slice, *dz<sub>j</sub>* is the total displacement of the *j*th atom along the *z*-axis, and *V<sub>j</sub>* is the atomistic volume occupied by this atom calculated from a modeled sample density. Final diffusion can be obtained with a simple multiplication by the flux

$$D = D' \varphi \quad (6)$$

Figure 1 shows such distribution, obtained from simulations, after the impact of each primary ion (Ar<sub>1000</sub>, Ar<sub>872</sub>, and C<sub>60</sub>) on the three target materials (PS, Si, and diamond, respectively). Note that, in the case of Ar clusters, a mass spread of ±10% does not have a significant impact on the *D'* distribution.

The function **R** in eq 1 incorporates beam-induced reactions occurring in the region involved in the interaction with the

beam. Since the aim of the model is that of simulating the molecular depth profile, we are interested in estimating the evolution, with projectile fluence, of the surface concentration of the undamaged material. In view of this, **R** can be interpreted as a numeric function representing the sink of the reacted portion (*C<sub>react</sub>*) of the original material in the simulated volume at each simulation step *Δt*. It is worth noting that at each iteration step of the simulation (involving the solution of the transport and reaction differential equation) the concentration of the unreacted material changes due to the formation of damaged material so that **R** will change with ion fluence.

We assume that the ion-beam-induced reactions occur in the same region where the beam-induced mixing is active. Thus, we write

$$R(z) = -\frac{D(z)}{\int_0^\infty D(z)dz} \frac{\Delta C_{\text{react}}}{\Delta t} \quad (7)$$

where  $\frac{D(z)}{\int_0^\infty D(z)dz}$  is a factor representing the normalized numeric function *D*, obtained from MD simulations as described above. The negative sign accounts for the fact that **R** is a sink term, which decreases the amount of pristine material. To estimate the atomic fraction of material that underwent some modification, we count, at the end of the MD simulation, (i) the number of C–H bonds that were turned into C–C bonds (indicating the formation of cross-links during the time scale of the simulation) and (ii) the number of atoms that exhibit a number of bonds lower than those they had in the original polymer. The latter quantity provides an indication about the concentration of reactive species (such as radicals) that, in turn, can evolve in damaged material on a time scale longer than that considered in the MD simulation. Table 2 reports the

**Table 2. Atomic Portion of the Reacted Material per Single Ion Beam Impact**

|                                    | C <sub>60</sub> | Ar <sub>872</sub> | Ar <sub>1000</sub> |
|------------------------------------|-----------------|-------------------|--------------------|
| free H atoms                       | 24              | 3                 | 0                  |
| reactive carbon atoms <sup>a</sup> | 675             | 180               | 104                |
| C–H bonds converted to C–C         | 2               | 0                 | 0                  |
| <i>C<sub>react</sub></i>           | 701             | 183               | 104                |

<sup>a</sup>C atoms that at the end of MD simulations display less bonds than the pristine material.

atomic portion of the reacted material per single ion beam impact, in the case of C<sub>60</sub>, Ar<sub>872</sub>, and Ar<sub>1000</sub> projectiles. Results indicate, in agreement with experimental results,<sup>25–27</sup> that C<sub>60</sub> induces much greater damage into polystyrene compared to Ar clusters. We observe that the amount of atoms participating to newly formed C–C bonds or that remain reactive (carbon

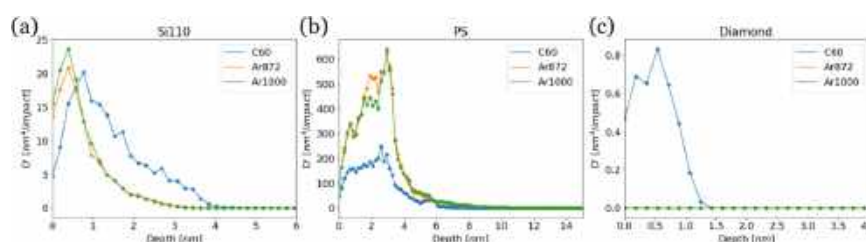


**Figure 1.** Distribution along the depth of ion-beam-induced diffusion stimulated by the impact of each primary ion (C<sub>60</sub>, Ar<sub>872</sub>, and Ar<sub>1000</sub>) in (a) silicon, (b) polystyrene, and (c) diamond targets. Note that, according to MD results, the considered Ar clusters do not modify the diamond target.

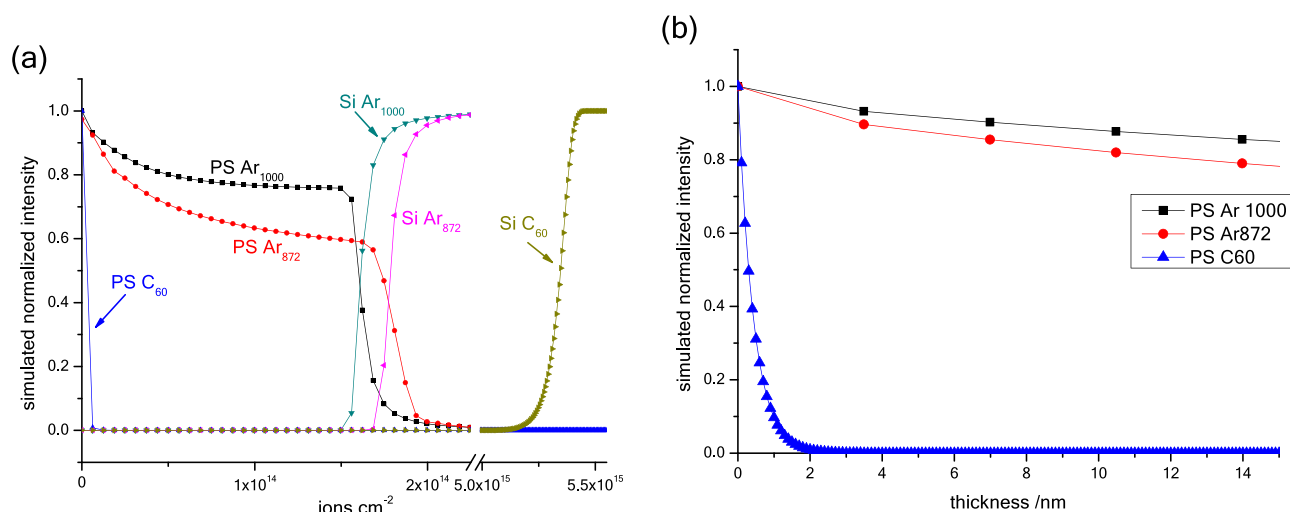


**Figure 2.** Simulated depth profiles of polystyrene on silicon obtained by Ar<sub>872</sub>, Ar<sub>1000</sub>, and C<sub>60</sub> primary ions as a function of ion fluence (a) and depth (b).

atoms with “missing” bonds or free H atoms) represents a small fraction (0.512% for C<sub>60</sub>, 0.057% for Ar<sub>872</sub>, and 0.036% for Ar<sub>1000</sub>) of the atoms that experienced the primary ion impact (please refer to Figure 1) and remained in the target at the end of the MD simulation (i.e., that were not sputtered away).

However, as we will see in the following (Figure 2), the 1 order of magnitude difference between C<sub>60</sub> and argon clusters can account for the different behavior of the two kinds of a projectile in terms of damage since the reactive species (most of them, presumably, radicals) can produce cross-linking in polystyrene. This is consistent also with previous findings, obtained in a different experimental context, showing that a few ion-beam-induced cross-links can induce an irreversible sol–gel transition in polystyrene.<sup>28–30</sup>

As it is evident from the simulated profiles reported in Figure 2, the model is able to reproduce the essential characteristics of the experimental profiles,<sup>25</sup> namely, the initial drop of molecular signal intensity, which is very pronounced in the case of C<sub>60</sub> and much lighter in the case of the largest argon cluster, as well as the strong differences in the primary ion dose needed for reaching the interface.

Table 3 reports the average volumetric sputtering yields for a 100 nm-thick PS film, obtained by means of the MD-TR

**Table 3. Volumetric Sputtering Yields (Average) and Depth Resolution Calculated by the MD-TR Model for a 100 nm-Thick PS Film**

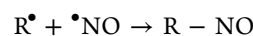
|                                    | C <sub>60</sub> | Ar <sub>872</sub> | Ar <sub>1000</sub> |
|------------------------------------|-----------------|-------------------|--------------------|
| Y (nm <sup>3</sup> /ion)           | 2               | 77                | 87                 |
| depth resolution (nm) <sup>a</sup> | 118             | 16                | 19                 |

<sup>a</sup>Depth resolution was calculated by the usual<sup>31</sup> 16–84% intensity method.

model using the rise of the substrate signal. Considering that the single-impact sputtering yields (as obtained from MD simulations, see Table 1) are rather similar for C<sub>60</sub> and the two considered Ar clusters, it is clear that the much smaller average sputtering yield obtained in the case of C<sub>60</sub> is due to the damage produced in the target by C<sub>60</sub> ions. The value of 2 nm<sup>3</sup>/ion obtained by the MD-TR model for polystyrene

sputtering with C<sub>60</sub> primary ions is in reasonable agreement with the experimental finding of 0.5 nm<sup>3</sup>/ion for PS<sup>25</sup> and <0.2 nm<sup>3</sup>/ion for a similar system.<sup>26</sup> In other words, the MD-TR model is able to fill the gap between the experimentally determined yields and those calculated by MD simulations, thanks to the introduction of the reactivity term. Interestingly, also in the case of Ar clusters, the MD-TR model gives rise to lower average sputtering yields (ca. 30 and 7% lower than those reported in Table 1 for Ar<sub>872</sub> and Ar<sub>1000</sub>, respectively), but in reasonable agreement with the figures (107 nm<sup>3</sup>/ion for Ar<sub>872</sub> and 94 nm<sup>3</sup>/ion for Ar<sub>1000</sub>) obtained by extrapolation, according to the equation proposed by Seah,<sup>32</sup> of experimental data obtained by Rading et al. in slightly different conditions.<sup>25</sup> Also, the predicted trend of reduction of sputtering yield (larger for the smaller cluster) is in agreement with the expected increase of damage at higher energy per component atom of the cluster. Moreover, we observe that a deterioration of the depth resolution at the interface accompanies the case (C<sub>60</sub> projectile) where large damage accumulation occurs, as observed in systems with PS-like behavior.<sup>26</sup>

According to Table 2, the main contribution to the ion-beam-induced damage is the production of reactive species such as H atoms or C species with “dangling bonds” that may undergo successive reactions. In the case of polystyrene, these reactions produce an increasingly cross-linked material. Many of these reactive species can be regarded as radicals. Recently, some of us demonstrated that nitrogen monoxide (NO), a well-known radical scavenger, is able to reduce strongly the damage of PS-like polymers in C<sub>60</sub>-SIMS depth profiling experiments.<sup>22,26</sup> Since the MD-TR model can include any chemical reaction occurring inside the altered layer, we included NO radical scavenging. We assumed that the reactive radical species R• produced during a cluster impact, whose amount is estimated from the MD simulation (see Table 2), are quenched by the reaction with NO molecules with the formation of stable, unreactive species



accordingly to a 1:1 stoichiometry. Thus, eq 5 becomes

$$R(z) = -\frac{D(z)}{\int_0^{\infty} D(z) dz} \frac{\Delta(C_{\text{react}} - C_{\text{NO}})}{\Delta t} \quad (8)$$

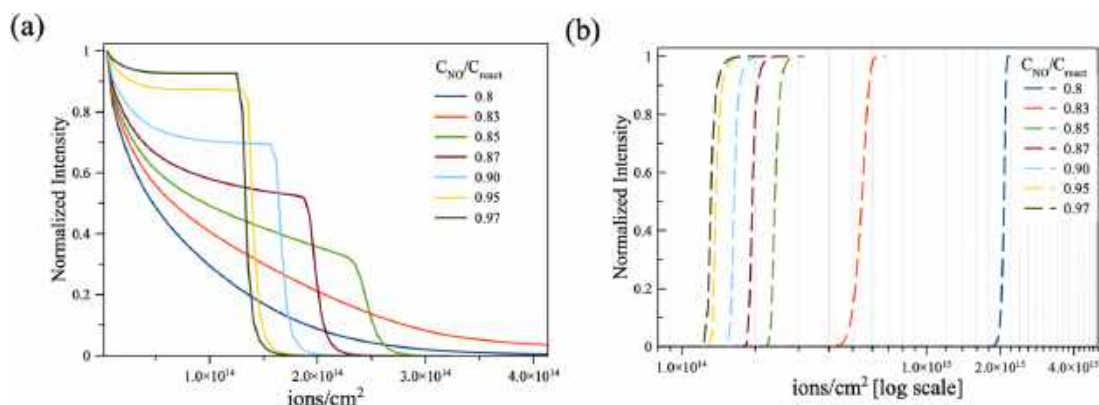


**Figure 3.** Simulated  $C_{60}$ -SIMS depth profiles of a 100 nm-thick film of polystyrene on silicon. Polystyrene (a) and silicon (b) intensities were calculated at different levels of  $C_{NO}/C_{react}$  ratios.

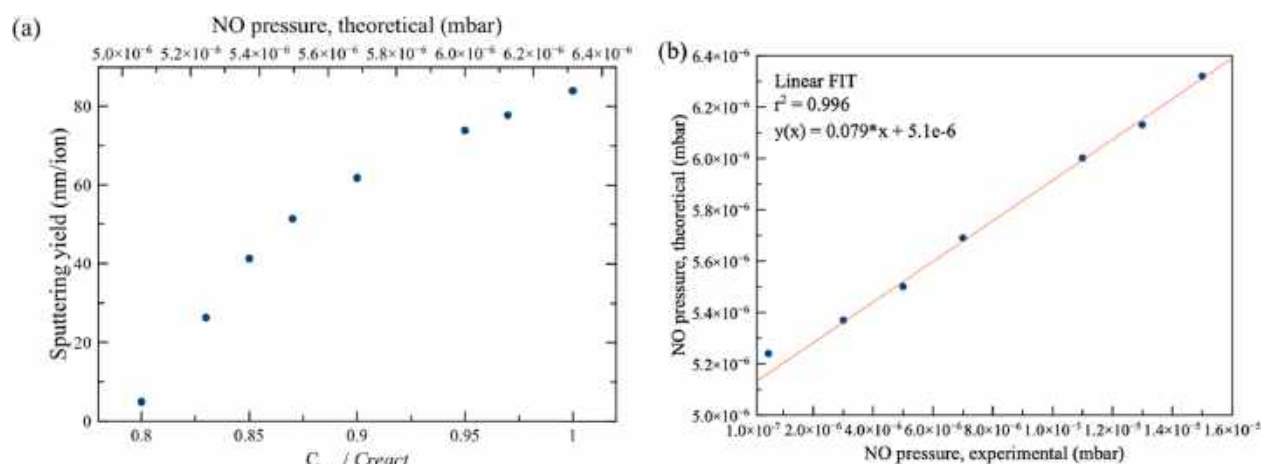


**Figure 4.** (a) PS sputtering yield (20 keV  $C_{60}$  projectile) as a function of  $C_{NO}/C_{react}$ . The top X-axis shows the NO partial pressure computed as described in the main text. (b) Linear regression of the theoretical to experimental NO partial pressure.

where  $C_{NO}$  represents the number of nitric oxide molecules reaching the surface during the simulation step  $\Delta t$ .

Figure 3 reports the simulated depth profiles of silicon and polystyrene in the case of  $C_{60}$  projectiles at various  $C_{NO}/C_{react}$  ratios. For the sake of simplicity, we assumed that (i) the probability that a NO molecule reacts with a beam-produced radical is unitary and (ii) such probability is independent of the location of the radical inside the (remaining) modified material. Also, we assume (iii) that the quenched macromolecular radicals will continue to behave, under ion impacts, in the same way as the original polymer.<sup>13</sup>

In agreement with the data obtained in NO-assisted  $C_{60}$  depth profiling of PS and PS-like polymers,<sup>22,26</sup> simulation shows that the higher the NO amount, the faster the erosion process and the better the shape of the molecular depth profile of PS.

To correlate theoretical findings with experimental results, we estimated the number of NO molecules hitting the surface per time unit by means of impingement rate at several NO pressures

$$\frac{\text{molecules}}{\text{cm}^2 \text{ s}} = \frac{N_A P}{\sqrt{2\pi M R T}} \quad (9)$$

where  $N_A$  is Avogadro's number,  $P$  is the NO partial pressure in the analysis chamber,  $M$  is the NO molar mass,  $R$  is the ideal gas constant, and  $T$  is the temperature.

Figure 4a shows the trend of PS sputtering yield as a function of the NO/radical ratio as obtained from the simulation. In the same figure, the top X-axis shows the corresponding NO partial pressures, computed according to eq 9. In Figure 4b, we report the correlation between theoretical and experimental pressures needed for obtaining the same sputtering yield volume. In the range of NO pressures considered, correlation is linear, with a slope of about 0.1. This means that to obtain a certain effect on the sputtering yield the experimental NO pressure must be increased about 10 times more than expected from the simulation. We believe that this discrepancy is related to the approximation that NO molecules can access quantitatively all of the radicals produced in the altered layer so that the predicted overall efficiency of NO in "killing" the radicals is overestimated (unity instead of ca. 0.1). Also, we must note that the linear correlation between calculated and experimental NO pressures is verified when significant amounts of NO ( $C_{NO}/C_{react} > 0.8$ ) are considered. Indeed, the nonzero value of intercept in Figure 4b has no physical meaning and it indicates that the linear behavior cannot be extrapolated at very low NO pressures. Clearly, although the qualitative agreement between the previsions and the experiment is promising, additional elaboration and refinements are needed on this point.

In conclusion, the integration of the results of molecular dynamics simulations in a transport/reaction model was used

for the prediction of the SIMS depth profile. In particular, the model allows the simulation of the SIMS depth profiles of organic samples under cluster primary beam irradiation and is able to take into account ion-beam-induced reactions and the effect of reactive gas dosing.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01653.

List and energetics of the selected chemical reactions essential for our studies leading to C–H or C–C bond cleavage calculated with the ReaxFF potential (PDF)

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# Intuitive Model of Surface Modification Induced by Cluster Ion Beams

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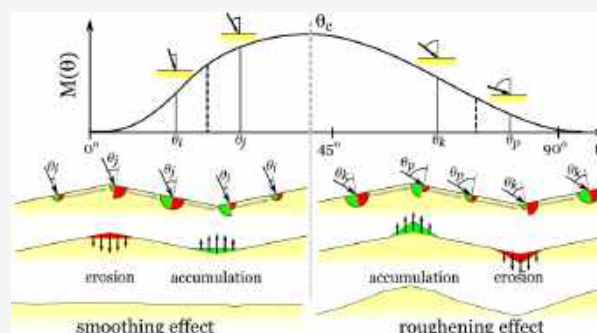
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**ABSTRACT:** Topography development is one of the main factors limiting the quality of depth profiles during depth profiling experiments. One possible source of topography development is the formation of self-organized patterns due to cluster ion beam irradiation. In this work, we propose a simple model that can intuitively explain this phenomenon in terms of impact-induced mass transfer. By coupling our model with molecular dynamics simulations, we can predict the critical incidence angle, which separates the smoothing and roughening regimes. The results are in quantitative agreement with experiments. It is observed that the problems arising from topography development during depth profiling with cluster projectiles can be mitigated by reducing the beam incidence angle with respect to the surface normal or increasing its kinetic energy.



Surface-sensitive techniques such as Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy (AES) combined with ion-induced material removal can be used to create spatial maps of the chemical composition of materials in a process called depth profiling. This approach has been successfully applied to many systems both inorganic and organic.<sup>1–3</sup> The main problem of depth profile acquisition is the degradation of resolution with a time of analysis.<sup>4</sup> There are two main factors in play here: topography development<sup>5,6</sup> and ion-beam-induced material alteration.<sup>4,7,8</sup> The latter issue is virtually solved by the introduction of large gas cluster ion beams (GCIB).<sup>9–11</sup> The topography development problem can be mitigated by sample rotation.<sup>5</sup> However, this approach limits analysis to depth dimension only because lateral spatial information is averaged out.

One possible source of topography development during ion irradiation is so-called spontaneous pattern formation where self-organized nanoscale ripples appear on the surface of the sample during the bombardment.<sup>12,13</sup> Over the years, there has been a substantial theoretical effort to develop models capable of qualitative and quantitative prediction of the surface evolution.<sup>12–21</sup> However, all available models have two main drawbacks concerning depth profiling with cluster projectiles. One is that none of these models have been applied to this type of projectiles or organic samples. All theoretical and almost all experimental research has been done with monatomic projectiles and inorganic samples. Only few experiments with cluster projectiles have been performed so far.<sup>22–25</sup> Another problem is that proposed theoretical models

have a complicated mathematical formulation, which makes it difficult to develop adequate physical intuition regarding the phenomenon in question. Without proper understanding, countering the emergence of undesirable surface roughness during depth profiling is difficult.

In this manuscript, a simple model, based on a concept of mass transfer, is proposed to predict the conditions favorable for the formation of ripples on the solid surfaces bombarded by cluster projectiles. The unique beauty of this model is that, despite its simplicity, it can predict these conditions with good accuracy. Furthermore, it makes it easy to comprehend why surface roughness, which we equate to ripple formation, will increase or decrease under given experimental conditions.

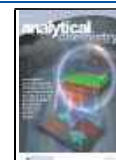
## SIMULATION DETAILS

The molecular dynamics computer simulations are used to model the effect of argon cluster bombardment of gold and silicon samples. General information about MD simulations can be found elsewhere.<sup>26</sup> Briefly, the motion of particles is determined by integrating Hamilton's equations of motion. Forces among particles are described by following potentials: the Lennard-Jones potential splined with KrC to accurately

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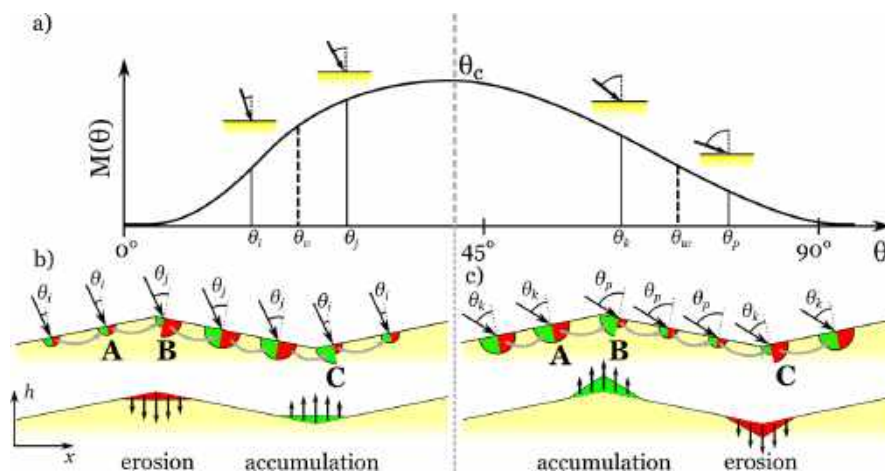


**Figure 1.** (a) Idealized effect of the incidence angle  $\theta$  on the mass transfer function  $M(\theta)$  for a bombardment by cluster projectiles and schematic visualizations of the effect of mass transfer on the sample topography in regions where  $M(\theta)$  increases (b) or decreases (c) with  $\theta$ . Green and red quarters represent the global mass inflow and outflow for a given node, respectively. Black tilted arrows represent directions of the impacting projectiles, and the symbols,  $\theta_i, \theta_j, \theta_k, \theta_l, \theta_m$  describe local incidence angles. The global incidence angles are  $\theta_v$  and  $\theta_w$ .

describe high energy collisions is used to describe Ar–Ar interactions.<sup>27</sup> The Tersoff potential splined at a short distance with ZBL potential<sup>28</sup> is used to describe forces between Si atoms,<sup>29</sup> while EAM force field is used for Au atoms.<sup>30,31</sup> Finally, the ZBL potential is used to represent collisions between Ar–Au and Ar–Si atoms.<sup>28</sup> The simulations are performed with the LAMMPS code.<sup>32</sup>

The values of the mass transfer function  $M(\theta)$  for different projectile parameters (kinetic energy, incidence angle) are extracted from MD trajectories. The divide and conquer approach developed for modeling depth profiling is used. This approach has been described in detail previously.<sup>33,34</sup> Briefly, a master sample is prepared as a cuboid with periodic boundary conditions imposed in  $x$  and  $y$  directions. The size of the master sample for silicon and gold equals to  $40 \times 40 \times 30$  nm and  $42 \times 42 \times 32$  nm, respectively. These samples contain 2.45 and 3.4 million atoms, respectively. Then, an impact point on the surface is selected randomly. A hemispherical region with a radius of 19 nm centered at this impact point is subsequently cut out from the master sample and used to simulate an impact of an Ar<sub>3000</sub> cluster with a given kinetic energy and incident angle for 25 ps. The sample is subsequently quenched for 10 ps in order to maintain the desired temperature; it was equal to 0 K in the present study. After each simulation, all sputtered atoms are removed, the mass transfer function is calculated, and the remaining (nonsputtered) atoms are reinserted into the master sample. Subsequently, a new point of impact is randomly selected, and the cycle is repeated. For each combination of the kinetic energy and incident angle, a series of 50 simulations are performed, which corresponds to a fluence of approximately  $3 \times 10^{12}$  impacts/cm<sup>2</sup>, and the final value of the mass transfer function is calculated as an average. Four test studies corresponding to the incidence angles of  $30^\circ$ ,  $35^\circ$ ,  $45^\circ$ , and  $50^\circ$  are performed on a silicon sample with a 10 times larger number of impacts to probe the effect of the projectile fluence on the mass transfer function dependence on the angle of incidence. While the amplitude of this dependence varies with the number of impacts, its shape (position of maximum) remained the same. Repetitive bombardment setup has been chosen to avoid strain introduced by a single impact.

The effect of projectile parameters (kinetic energy, incidence angle) on mass transfer can be obtained from molecular dynamics simulations. The mass transfer function is defined as

$$M = \sum_i V dx_i \quad (1)$$

where  $V$  is the volume occupied by an individual atom,  $dx_i$  is the displacement of the  $i$ th atom in the  $x$ -direction caused by the projectile impact, where the  $x$ -direction is the azimuthal direction of the incoming projectile, as proposed in ref 19. The ion beam density at the bombarded surface decreases with the angle of incidence  $\theta$  due to the increase of the ion beam spot size on the irradiated surface. To account for this phenomenon, the results from the MD simulations should be normalized by the following formula:

$$M(\theta) = M_{\text{MD}}(\theta) \cos(\theta) \quad (2)$$

where  $M(\theta)$  is the angle-dependent mass transfer function, and  $M_{\text{MD}}(\theta)$  is the mass transfer calculated from the molecular dynamics simulations.

## RESULTS AND DISCUSSION

The process of sputtering is believed to have a minor effect on the ripple formation during cluster projectile bombardment.<sup>35,36</sup> It is postulated that the mass transfer stimulated by impact of a projectile is of critical importance in this case.<sup>35–37</sup> In order to understand its influence, we begin by posing a question: what effect will a mass transfer near a surface have on its topography? To answer this question, we introduce a simple two-dimensional model, where the surface is represented by a set of discrete nodes, as shown in Figure 1. The coordinate system in this model is selected in such a way that the azimuthal direction of the ion beam is the  $x$ -axis, as depicted in Figure 1. Incoming projectiles are directed toward the macroscopic surface at the same global angle of incidence. This angle is equivalent to the experimental incidence angle. However, the global incidence angle usually does not represent the actual angle of incidence at a given node, because the real surface is never flat. In real samples, the local incidence angle should be defined relative to the surface normal at the point of projectile impact. It depends on the global angle of incidence

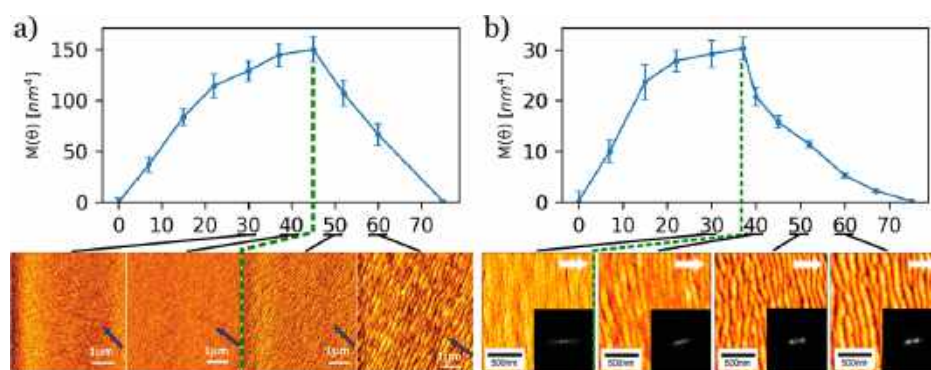


**Figure 2.** Angle-dependent mass transfer functions for (a) silicon and (b) gold samples sputtered by 30 keV Ar<sub>3000</sub>. The AFM images show experimentally measured topography of the sample<sup>23,24</sup> at respective angles. The dashed green line depicts a location where the smoothing/roughening transition should be observed under reasoning presented in the text. The AFM images are reproduced with permission from refs 23 and 24 and are licensed under a Creative Commons Attribution (CC BY) license.

and the local surface inclination. The magnitude of these effects is proportional to the inclination of the  $M(\theta)$  function for a given global incidence angle, so, for the cases where a plateau is reached, the mass redistribution will not influence surface topography.

After the projectile impact, the matter is transferred from one node to another. Our model is based on global mass transfer along the  $x$ -axis. For a cluster projectile impact at a flat surface along the surface normal, the same amount of material is transferred, on average, to the left and right neighbors of the bombarded node.<sup>35,36</sup> Therefore, from the point of view of a global mass transfer along the  $x$ -axis, the resulting mass transfer is zero. For the off-normal angle of incidence, the mass is transferred along an azimuth of the incoming beam.<sup>36</sup> The global mass transfer is no longer zero along the  $x$ -axis. The amount of mass transferred from a bombarded node increases initially with an increase of global incidence angle. However, the mass transfer must drop eventually, because no mass is transferred for the 90° incidence angle since the projectile never hits the sample. Based on these considerations, the value of the mass transfer function at a given node  $M(\theta)$  should depend on the local angle of incidence  $\theta$ , as shown in Figure 1a. There is a specific angle  $\theta_c$ , which will be called a critical angle, where  $M(\theta)$  has a maximum. This angle separates two regions, where  $M(\theta)$  increases and decreases with the incidence angle.

Three possible surface morphologies should be considered to investigate the temporal evolution of the bombarded surface. The surface can be flat, convex (hill), or concave (hole), near a point of projectile impact. An example of a surface exhibiting all these cases is shown in Figure 1b,c. The total amount of material transferred into and outside a given node is depicted as radii of the quarter-circles. Green and red quarters represent the mass inflow and outflow for a given node, respectively. For the off-normal incidence, the mass is transferred in the  $x$ -direction. In our model, this means that for a given node, the mass inflow occurs only from a node on the left, while the material is moved to the node on the right. A flat section of a surface represented by node A in Figure 1b,c is the simplest situation to discuss. In this case, the local angle of incidence at nodes A-1 and A is identical. As a result, the amount of material incoming and outgoing from node A is the same, as represented by quarters of the equal radii. Consequently, the height of node A is not affected relative to its neighbors, and the morphology does not change at this

point. The situation is different for convex and concave surfaces represented by nodes B and C, respectively. In the case of a convex surface, the local incidence angle  $\theta_j$  or  $\theta_p$  at node B is larger than the local incidence angle  $\theta_i$  or  $\theta_k$  at node B-1. The opposite situation occurs for node C.

The final mass balance at nodes B and C depends on the shape of the  $M(\theta)$  function. In the case where, for a given global incidence angle,  $M(\theta)$  increases with  $\theta$ , as depicted in Figure 1b, the mass inflow from the node B-1 is smaller than the outflow from node B, because  $\theta_j > \theta_i$ , therefore,  $M(\theta_j) > M(\theta_i)$ . The mass is removed, and the height of node B decreases, as indicated by downward-pointing vertical arrows. For a concave surface (node C), the situation is the opposite. More mass is transferred into node C than removed from it. As a result, the depth of this depression decreases. Considering both these effects, the global surface roughness will decrease for the impacts presented in Figure 1b.

Similar reasoning can be applied for the impact conditions where the  $M(\theta)$  function decreases with  $\theta$ . This case is depicted in Figure 1c. However, now the conclusions will be opposite to the situation shown in Figure 1b. While the relationship between  $\theta_p$  and  $\theta_k$  remains the same, that is,  $\theta_p > \theta_k$ , now  $M(\theta_p) < M(\theta_k)$ . Therefore, the global transfer to node B in Figure 1c is positive, while the mass is removed from node C. As a result, the elevation of the hill increases while the depression becomes more profound, which leads to an increase of the surface roughness. It is evident that the incidence angle corresponding to the maximum of the  $M(\theta)$  function separates the surface smoothing and roughening regimes.

Experimental results describing the effect of the incidence angle on the ripple formation during the Ar<sub>3000</sub> bombardment of silicon and gold surfaces<sup>23,24</sup> are used to verify the predictions of the proposed model. The shapes of the mass transfer functions calculated from molecular dynamics (MD) computer simulations are shown in Figure 2. The AFM images presenting experimentally measured topography of the sample at respective global incidence angles are shown below the graphs of individual  $M(\theta)$  function. The experimental data show that the ripples begin to form above 40° and 30° at silicon and gold surfaces, respectively. The critical angles obtained from the calculated  $M(\theta)$  functions for the same systems are 45° and 40°, respectively. It is evident that the transition from a smooth to a rough surface correlates very well with the value of the critical angle. This agreement proves that our model, regardless of its simplicity, is working correctly and

corroborates the hypothesis that the mass transfer is predominantly responsible for an angle-dependent roughening/smoothing phenomenon during cluster projectile bombardment.

So far, only the effect of the incidence angle on the surface roughness was discussed. However, the kinetic energy of cluster projectiles may also influence the surface roughness. In fact, it has been shown that, at very low energies per atom, ripples appear in organic samples bombarded by gas cluster projectiles.<sup>25</sup> This process leads to fast degradation of the depth resolution with depth.<sup>6,25</sup> The problem was eliminated by increasing the projectile kinetic energy (energy per projectile atom). Unfortunately, the RMS roughness has not been directly measured in that paper.<sup>25</sup> Nevertheless, it has been established that the buildup of the surface roughness is the main factor limiting the achievable depth resolution.<sup>6,11</sup> Therefore, a possibility to achieve a better depth resolution indicates that the surface roughness must decrease with the increase of the kinetic energy per atom.

Angle-dependent mass transfer functions calculated for several kinetic energies of Ar<sub>3000</sub> projectiles, bombarding the silicon surface, are shown in Figure 3 to probe the effect of the

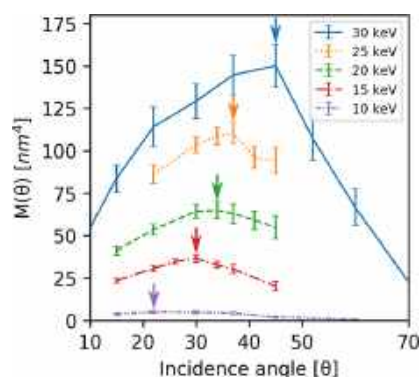


**Figure 3.** Angle-dependent mass transfer functions for silicon, bombarded by Ar<sub>3000</sub> with different kinetic energies. For each incidence energy, the location of the maximum is highlighted by an arrow.

primary kinetic energy. Silicon is very different from the systems investigated in ref 25 where organic multilayers were analyzed. Therefore, no quantitative agreement between theoretical and experimental data can be expected. Nevertheless, similar trends should be observed in both these studies. It is evident that the value of the critical angle, which separates smoothing from roughening conditions, indeed shifts toward larger incidence angles with the increase of the projectile kinetic energy. It is expected, therefore, that at low projectile kinetic energy, the critical angle is below the incidence angle used in the experiment (45°), and the surface will be roughened. However, when kinetic energy is increased, the value of the critical angle  $\theta_c$  shifts toward larger values, leading to a decrease of roughness due to the elimination of ripple formation.

## CONCLUSION

We have shown that ripple formation during cluster ion beam irradiation, which we equate to surface roughening, can be explained by impact-induced mass transfer with a simple and intuitive model. The main conclusion from our model is that the transition between smoothing and roughening regimes can

be explained by the location of a maximum, called the critical angle, of an angle-dependent mass transfer function. If the incidence angle is lower than the critical angle, the mass transfer will have a smoothing effect, and if it is higher, the roughness will increase. Due to the nature of this function, the location of the maximum is expected to be around 45°. This finding has substantial practical importance because the incidence angle of a sputtering beam is 45° in a majority of commercially available apparatuses. We suggest that shifting the incidence angle closer to the surface normal by even a few degrees will have a beneficial impact on the quality of acquired depth profiles. Furthermore, we have shown that the increase of the cluster impact energy shifts the critical angle toward larger values. This observation suggests that the roughening problem, for some cases, can be resolved by increasing the kinetic energy of the beam. Finally, it should be mentioned that the proposed model works both for inorganic and organic samples. In this paper, we have focused on inorganic materials because results discussing the effect of the angle of incidence on the ripple formation are only available in the literature for such samples. We need such results to validate the predictions of our model. However, it should also be emphasized that our model can only be used to predict the onset of ripple formation during surface bombardment by cluster projectiles. Both the experimental results and computer simulations show that for these projectiles process of mass transfer prevails over sputtering.<sup>23,24,34,36</sup> As a result, sputtering can be ignored as it was done in our model. A similar approach cannot be applied to atomic missiles for which mass transport is much smaller due to the significantly smaller projectile size and momentum. Both the existing theories and experimental data indicate that the effect of sputtering cannot be ignored for these projectiles.<sup>12–21</sup>

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### Notes

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