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Combined molecular dynamics and analytical model for repetitive cluster bombardment of solids

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ABSTRACT

Molecular dynamics simulations of repetitive bombardment of solids by keV cluster beams have generated so much data that easy interpretations are not possible. Moreover, although the MD simulations remove 3–4 nm of material, that is not sufficient material to determine a depth profile. The recently developed steady-state statistical sputtering model (SS-SSM) uses information from the MD simulations and incorporates it into a set of differential equations to predict a depth profile. In this study the distributions that provide the input to the SS-SSM are compared for simulations of 15 keV bombardment of Ag(1 1 1) by C_{60}, Au_3 and Ar_{872} cluster beams.

1. Introduction

In the era before computers were harnessed for modeling various processes, analytic theories provided the basis for understanding phenomena and making predictions. In the case of energetic (keV) particle bombardment, the Sigmund formula predicts that the sputtering yield from an amorphous atomic solid is inversely proportional to the cohesive energy of the solid [1]. This simple relationship is useful for making predictions. Likewise, the Thompson formula for the energy distribution of sputtered particles predicts that the energy at which the peak in the distribution occurs is half of the cohesive energy and that the tail of the distribution goes as $1/E^2$ where E is the kinetic energy of the sputtered particles [2]. The measured energy distribution is often compared to the Thompson formula to determine if a process is considered to be sputtering or thermal. At some point, in the 1960s and 1970s for sputtering, experiments started to provide more detailed and complex data and computers became more powerful, thus we entered into a multiple decade long era in which computer simulations dominated the energetic particle bombardment field as the main theoretical analysis tool.

The energetic particle bombardment field as exemplified by the mass spectrometric approach of secondary ion mass spectrometry (SIMS) has now evolved to a regime where the processes are too big to model with direct microscopic computer simulations. Namely, we are interested in understanding keV cluster bombardment of solids with a goal of modeling depth profiling as is measured in SIMS [3]. Implicit in this objective are multiple individual impacts of 20–40 keV clusters bombarding atomic and molecular solids as well as repetitive bombardment of solids for depth profiling. Analytic theories are not available and the computer simulations are either too big and/or too lengthy.

Our approach has been to develop analytic theories or models that have input based on limited scale molecular dynamics (MD) simulations. Our first effort in this arena was to adapt concepts from fluid dynamics simulations [4] for sputtering by MeV bombardment to develop the mesoscale energy deposition footprint (MEDF) model to predict yields for keV cluster sputtering [5]. The MEDF model uses input from short-time (~100 fs) MD simulations of the cluster bombardment event on the solid of choice to predict successfully the energy dependence of sputtering yields as a function of incident energy from 5 keV to 120 keV of C_{60} and Au_3 bombarding ice [6]. Full MD simulations to predict the yields are computationally intractable. If only short-time information is needed, the sample sizes and the total simulation time are greatly reduced.

The second analytic model that uses input from MD simulations is for modeling depth profiling of delta layers. We have developed a divide and conquer protocol for modeling by MD simulations repetitive bombardment of a solid [7]. These huge calculations, however, only remove 4–5 nm of material in several months of CPU time. Based on the statistical sputtering model (SSM) [8] developed by our collaborators, Krantzman and Wucher, we have developed the steady-state statistical sputtering model (SS-SSM) to take information from the steady-state region of the divide

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and conquer MD simulations of repetitive bombardment of a solid and predict depth profiles [9–11]. Although the input MD simulations still take months of CPU time, with the SS-SSM we can obtain depth profiles tens to hundreds of nm deep. Moreover, the input to the SS-SSM provides a framework for understanding the results of the MD simulations.

Krantzman and Wucher [8,12,13] as well as ourselves [9–11] have previously given examples of how the statistical sputtering models can be used to explain the features of depth profiles of delta layers and how the quantities in the models influence the depth profiles. Here we demonstrate how the input quantities, namely amount of sputtering and displacement per layer explains the essence of the repetitive bombardment calculations of C_{60}, Au_3 and Ar_{872} on a silver target.

2. Description of the calculation

2.1. Molecular dynamics simulations using the divide and conquer protocol

The molecular dynamics (MD) simulations of repetitive bombardment (dynamic SIMS) of C_{60} and Au_3 using the "divide and conquer" protocol [7] have been reported previously [14,15]. In addition, we have unpublished simulations of Ar_{872} bombardment. The target system is Ag(1 1 1) with approximately five million atoms and a surface area of 2800 nm^2 (53 × 53 nm) in a computational cell with periodic boundary conditions. Several incident energies and incident angles were used for each projectile but only the simulations with 15 keV incidence perpendicular or normal to the surface will be discussed here. The simulation starts with a perfectly flat surface, thus there is an induction period before the steady-state region is achieved as characterized by the root-mean-square (rms) roughness being relatively constant and the average surface level receding at a constant rate. Only the latter half of the impact points are in the steady-state region and these are used for generating the input to the SS-SSM.

2.2. SS-SSM

Details of the SS-SSM construction and prescription for evaluating the sputtering and displacements quantities from the MD results are given elsewhere [9,10]. The model is expressed by a set of differential equations for filling factors, i.e. fractional atom populations of system layers, as a function of amount of eroded material in monolayer (ML) units. Each differential equation contains three terms: a sputtering term describing the loss of atoms by sputtering, and two displacement terms describing the loss or gain of atoms by atom relocations to or from other layers. The input quantities are determined as averages relative to the average surface level over all the impacts within the steady-state region of the MD simulation. The selected layer width is a compromise between the spatial resolution and the statistical noise of sputtering and displacement distributions calculated from MD data [9]. In the results presented here, we use a layer thickness of four monoatomic Ag(1 1 1) layers or 0.94 nm which is approximately one nm.

The key connection between the MD simulations and the SS-SSM quantities is the evaluation of the sputtering, Γ_j, and the displacement, $\Delta_{j\to j'}$, terms. The sputtering parameter in its raw form Γ_j denotes the average number of atoms sputtered from j-th system layer per impact, where $j = 0$ represents the average surface level, $j < 0$ and $j > 0$ represent the layers above and below the average surface level, respectively. The displacement parameter $\Delta_{j\to j'}$ denotes the average number of atoms relocated from j-th to j'-th system layer per impact. Naturally, the sum of Γ_j over all j values yields the total sputtering yield in dynamic conditions. As a new concept arising from the SS-SSM, we also define the total displacement yield to be the sum of $\Delta_{j\to j'}$ over all j and j' values except $j = j'$ [10]. We choose displacements between layers parallel to the original surface plane as we are interested in depth profiles. These displacements do not represent lateral motions that have also been observed in the simulations [7,16,17]. Whereas, the total sputtering yield is independent of the chosen layer thickness, the total displacement yield is not. For example, if the layer thickness is chosen sufficiently large, there will be no displacements between layers. Since the displacement yield is not uniquely defined, it cannot be measured experimentally. It does have utility, however, as a single quantity to use when discussing the amount of ion-beam induced mixing in the system per impact for different beam conditions.

3. Results

The usefulness of the SS-SSM lies not only in the ability to predict depth profiles [8–13] but also the description of the simulation data in terms of the sputtering per layer and the displacements between layers as denoted by the Γ_j and $\Delta_{j\to j'}$ distributions. Shown in Fig. 1 are the Γ_j and $\Delta_{j\to j'}$ distributions for 15 keV bombardment of C_{60}, Au_3, and Ar_{872} at normal incidence. It is these distributions that quantify the amount and range of both sputtering and interlayer displacements.

The distributions from the simulations of C_{60} bombardment are shown in Fig. 1a. The sputtering yields per layer are given as the vertical black bars. The most probable sputtering occurs from the average surface level ($j = 0$) and the layer above it ($j = -1$). The range of the sputtering is from $j = -4$ to $j = 3$ with the least sputtering from the tops of the peaks where there are few particles to the bottom of the valleys where it is hardest for particles to eject. The depth range of the sputtering is about the ±2× rms range that corresponds to the exposed surface area. The displacements by one layer up and down are given by the cyan and red curves, respectively. In general, the amount of displacements per layer is greater than the amount of sputtering [9–11]. In this case, the maximum displacement per layer is a factor of four greater than the maximum sputtering per layer. The displacements occur at depths below the sputtering region. Displacement by ±2 layers is typically much smaller than by ±1 layers and in this case is about equal in intensity as the sputtering amount. The final piece of information in Fig. 1a is the dashed curve that corresponds to the fraction of each layer that is neither sputtered nor displaced. This description of the motion of atoms is quite detailed and provides a basis for comparing the motions due to Au_3 or Ar_{872} bombardment.

The distributions for Au_3 bombardment shown in Fig. 1b are, from a distance, rather similar to the ones for C_{60} bombardment. There are a couple of differences, however. First, the sputtering yield for Au_3 is less than for C_{60}. Second, the displacement distributions penetrate deeper into the sample for Au_3 bombardment. This feature is clear from snapshots of Au_3 and C_{60} bombardment on a flat surface [5,18]. The depth profiles for these two systems have been shown previously and C_{60} gives the better depth profiling characteristics for a delta layer [10]. Both the larger sputtering yield for C_{60} and the narrower displacement distribution contribute to the better depth profile. Of note is that the rms roughness for these two cases is coincidentally nearly identical.

The distributions for Ar_{872} bombardment are shown in Fig. 1c. There are significant differences from the previous two distributions. First, the maximum number of displacements per layer is four times greater than for the other two projectiles. Second, the sputtering yields are miniscule. These characteristics are consistent with snapshots of individual impacts on a flat surface [18]. Depth profiling analysis of this system has yet to be performed but initial indications are that the quality would not be good.