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Applications of fullerene beams in analysis of thin layers

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Abstract

Molecular dynamics computer simulations have been employed to model ejection of particles from Ag{1 1 1} metal substrate and thin benzene overlayer bombarded by fullerene cluster projectiles. The sputtering yields are analyzed depending on the size (from C_{20} up to C_{540}) and the kinetic energy (5–20 keV) of a projectile. It has been found that for clean metal substrate bombarded by 15 keV projectiles the maximum ejection is stimulated by the impact of the C_{60} cluster. However, the size of the cluster projectile maximizing the yield depends on the kinetic energy of the cluster, shifting towards larger clusters as the impact energy increases. For a thin benzene overlayer, the yield increases monotonically with the size of the cluster within investigated range of fullerene projectiles and kinetic energies.

Keywords: Sputtering; Cluster bombardment; Organic overlayers; SIMS/SNMS; Molecular dynamics

1. Introduction

Energetic ion beams have become important processing and characterizing tools for a broad segment of the scientific and technological manufacturing sector. In particular, one of the most sensitive surface analysis techniques relies on uplifting of surface constituents by an impact of energetic projectiles followed by a mass analysis of the ionized (secondary ion mass spectrometry—SIMS) and neutral (secondary neutral mass spectrometry—SNMS) surface material. Both these techniques were found to be particularly useful in chemical analysis of organic and biological structures [1]. Cluster projectiles are especially interesting surface probes as it has been found that the sputtering yield can be enhanced when an atomic projectile is replaced by a cluster ion with the same kinetic energy [1]. Computer simulations demonstrate that this effect is caused by a difference in mechanism of energy deposition [2–4]. One of the most interesting and still unresolved questions of the SIMS and SNMS is the optimum size of a projectile that should be used in analysis. In this paper we would like to address this question. A clean silver crystal and a thin benzene overlayer on Ag{1 1 1} are used to investigate the influence of the size and the primary kinetic energy of the fullerene projectiles on the ejection efficiency of atoms and molecules.

2. Model

Molecular dynamics computer simulations used to model particle bombardment are described elsewhere [5]. Briefly, the motion of the particles is determined by integrating Hamilton's equations of motion. The forces among the atoms are described by a blend of pair-wise additive and many-body potential energy functions. The Ag–Ag interactions are described by the MD/MC-CEM potential for fcc metals [6]. The adaptive intermolecular potential, AIREBO is used to describe the hydrocarbon interactions (C–C and C–H) [7]. The interaction of C and H atoms with Ag is described by a Lennard-Jones potential. The model approximating the Ag{1 1 1} substrate consists of a crystallite containing 166,530 atoms arranged in 39 layers. Thin organic overlayer is represented by three layers of benzene adsorbed on the Ag{1 1 1} surface. The adsorption scheme and the potential parameters for benzene molecules were adopted from Ref. [4].

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Special care was taken to eliminate the artifacts associated with the pressure waves generated by the cluster impact as described in Ref. [2].

3. Results and discussion

The total sputtering yields of silver particles ejected from a clean Ag{1 1 1} by 15 keV C_{20}, C_{36}, C_{60}, C_{80}, C_{180}, C_{320}, and C_{540} projectiles are shown in Fig. 1a. For all clusters, the yields are large compared to those obtained due to atomic bombardment [3]. The highest yield is produced by the C_{60} projectile. Dependence of the total yield on the cluster size for three impact energies, 10, 15 and 20 keV, is shown in the inset in Fig. 1a. The dependence is similar for all investigated energies. However, the ejection increases with the impact energy and the maximum sputtering yield shifts towards larger clusters. The mesoscale energy deposition footprint (MEDF) model developed by Russo and Garrison based on the work of Jakas et al. [8] is used to explain the observed trends [9]. The model is based on the idea that the behavior of cluster impact can be approximated by fluid dynamic flow. Russo and Garrison have shown that the energy deposition profile at a time when 90% of the energy is absorbed by the sample is the critical quantity in determining the sputtering yield. There are two main parameters which allow predicting behavior of the bombarded system. First parameter R_{cyl} defines the radius of excitation track made by impinging projectile as well as the depth of a region of this track from which the material is ejected (so called critical depth). The second essential parameter $\tilde{E}$ is the ratio of the average excitation energy within the track to the cohesive energy of the material (2.95 eV for Ag). The model predicts that the ejected material originates from a conical region R_{cyl} deep and $R_{cyl}\tilde{E}^{1/2}$ wide, and the yield is proportional to $R_{cyl}^3\tilde{E}$ [9].

The energy deposition profiles calculated at times corresponding to deposition of 90% of the primary energy (50–150 ps) obtained for 15 keV C_{20}, C_{60}, and C_{180} bombardment of a clean Ag{1 1 1} surface are presented in Fig. 2. As it can be seen, R_{cyl} has the lowest value for C_{20} and is comparable for C_{60} and C_{180}. The calculated values of $\tilde{E}$ are ~1.3, ~2.8, and ~1.9 for 15 keV C_{20}, C_{60} and C_{180}, respectively. The C_{20} projectile creates the narrowest track and the material within the track is weakly excited. Moreover, most of the impact energy is deposited below the critical depth and cannot stimulate any desorption [8,9]. The C_{180} cluster forms energized track comparable to C_{60}, however, the average excitation energy is smaller than for C_{60}. It is not surprising, therefore, that the C_{60} fullerene is the most effective projectile at least for 15 keV bombardment. The values of the sputtering yield predicted by the MEDF model normalized to the yield of the C_{60} cluster are depicted in Fig. 1a by open circles. The error bars represent a fluctuation of 0.2 nm in the value of R_{cyl}. The predicted values agree well with the calculated yields. This indicates that the MEDF model combined with a short-time MD calculations is not only a very powerful tool for elucidating trends in cluster bombardment, but also enables to predict absolute values of the sputtering yield with satisfactory accuracy.

An increase of the impact energy from 15 to 20 keV results in the increase of the excitation energy for all projectiles [9]. However, larger impact energy will also lead to a larger penetration [3]. As visible in Fig. 2, most of the incidence kinetic energy is already deposited below the critical depth for the C_{20} cluster. As a result, increase of the impact energy will have only a small influence on the sputtering yield induced by this projectile, as most of this additional energy will be deposited below the depth contributing to ejection. For the same reason also the ejection stimulated by the C_{60} projectile will be enhanced in

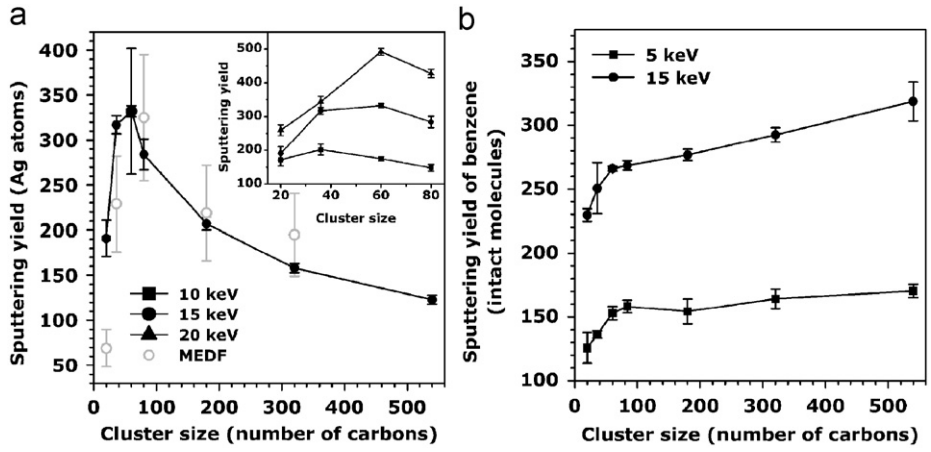

Fig. 1. (a) Total sputtering yield of silver atoms ejected by 15 keV C_n bombardment of clean Ag{1 1 1} crystal, and (b) sputtering yield of intact benzene molecules obtained for 5 and 15 keV C_n ($n = 20$, 36, 60, 80, 180, 320, 540) bombardment of Ag{1 1 1} covered with a thin benzene layer at normal incidence. Open circles depict the total sputtering yield of Ag estimated from the MEDF model, normalized to the yield induced by 15 keV C_{60} cluster. The dependence of the total sputtering yield of Ag atoms on the cluster size and the primary energy of the projectile is shown in the inset to (a).

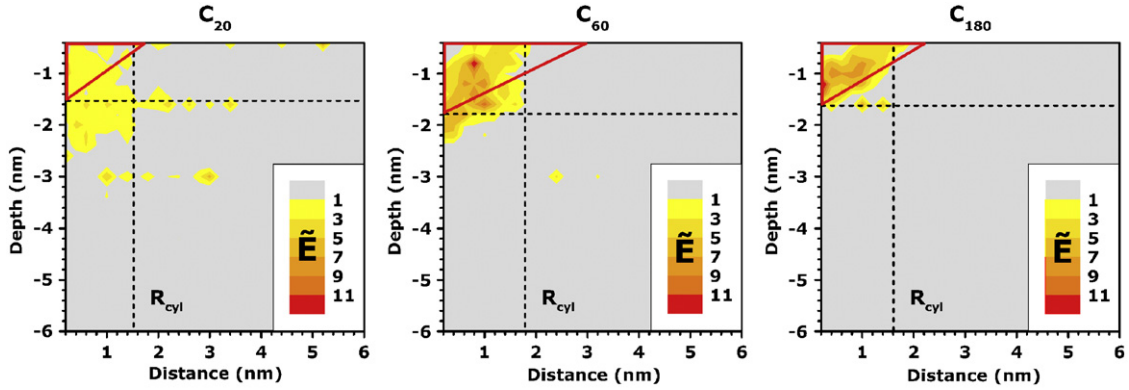

Fig. 2. Energy deposition profiles of 15 keV C_{20}, C_{60} and C_{180} projectiles bombarding a clean surface of Ag{1 1 1} at normal incidence. The figure gives the value of dimensionless parameter $\tilde{E}$ (see text) at the time when 90% of the energy has been deposited. The dashed lines represent the estimate of R_{cyl}. The triangle depicts a crystal volume that will contribute to ejection of silver atoms estimated from the MEDF model [9].

a moderate way as for 15 keV bombardment the energy deposition depth is already exceeding the critical limit. Largest signal enhancement can be expected for the C_{180} projectile because the deposition depth at 15 keV is below the critical limit. This means that all additional energy delivered to the system will be used to stimulate ejection. As a result, the ejection maximum should shift towards larger clusters with larger impact energy, which is indeed observed.

The behavior of benzene overlayer is different from behavior of metal substrate. There is no maximum yield in the sputtering of benzene molecules and the yield increases monotonically with the cluster size as displayed in Fig. 1b. Such behavior is also different from the data obtained for thick benzene crystal bombarded by 5 keV fullerenes, where the most efficient ejection is stimulated by C_{20} clusters [10]. The existence of an organic/metal interface is responsible for the observed differences. Computer animations show that all fullerene projectiles penetrate through a thin overlayer and the amount of energy lost during the penetration increases with the size of the cluster. For small projectiles, like C_{20} or C_{60}, most of the impact energy is deposited in the metal substrate and the organic molecules are emitted predominantly by the interaction with energized substrate atoms [4]. As the cluster size increases, less energy is transferred into the substrate and the role of organic/substrate interactions in molecular ejection decreases. However, at the same time the amount of primary energy deposited in organic overlayer increases. In addition, direct collisions between the projectile atoms and benzene molecules become less energetic, which lowers the probability of molecular fragmentation [4]. Both these phenomena should enhance molecular ejection and compensate for a decreasing efficiency of substrate-related molecular uplifting. MEDF analysis performed on thick benzene sample indicates that the thickness of the layer investigated in the present study is much smaller than a critical depth of molecular ejection [10]. As a result, only the density of deposited energy in the subsurface volume (thin layer), and not the depth of deposited energy is important in our case. The effect of the latter parameter is the reason why the most efficient ejection is stimulated from thick organic solid by a 5 keV C_{20} projectile [10].

4. Conclusions

We have investigated the effect of the kinetic energy and cluster size on the sputtering yield of clean metal substrate and a thin benzene overlayer. It has been shown that within the investigated energy range of 5–20 keV, projectiles with a size close to C_{60} cluster lead to the most efficient ejection from the probed metal surface. The optimal cluster size depends on the impact energy, shifting to larger clusters as the kinetic energy increases. For thin benzene overlayer, the sputtering yield of intact benzene molecules monotonically increases with the size of the cluster. A small layer thickness and the presence of organic/metal interface are responsible for such behavior. Our results indicate that the most optimal ejection conditions are the effect of interplay between the density of deposited energy, energy deposition depth, and the binding energy of the solid and can be predicted by the MEDF model combined with short-time MD computer simulations.

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