

Sputtering of a coarse-grained benzene and Ag(111) crystals by large Ar clusters – effect of impact angle and cohesive energy

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Molecular dynamics computer simulations are employed to investigate the role of the substrate cohesive energy on the impact angle dependence of the sputtering yield for Ar₆₀ and Ar₂₉₅₃ projectiles bombarding a benzene molecular solid and a Ag(111) atomistic sample. A different dependence of the total sputtering yield on the impact angle is observed for small and large projectiles for benzene, while a similar dependence is observed for Ag(111). It is demonstrated that the increase of the cohesive energy leads to a significant decrease of the total ejection signal for both Ar₆₀ and Ar₂₉₅₃ projectiles. The shape of the impact angle dependence, however, is much less sensitive to this parameter. The 'washing out' mechanism and the structural differences of the irradiated samples are proposed to be responsible for the different shapes of the impact angle dependence. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Time-of-flight secondary ion mass spectrometry is a powerful tool for chemical characterization of solids. More than a decade ago, it was observed that ion beams composed of cluster projectiles may have significant advantages as compared to atomic projectiles, especially in three-dimensional chemical analysis of organic and biological samples.^[1,2] Since then, a wide variety of cluster projectiles have been employed and tested. Currently, popular projectiles include large argon clusters as it has been reported that they can achieve a successful depth profile in several cases where smaller cluster projectiles have failed.^[3,4] While the database of experimental results is growing fast,^[3–9] still not much is known about processes occurring during Ar cluster bombardment of organic materials. To date, only a limited number of computer studies have been performed on these systems.^[10–14] It has been reported recently that the shape of the impact angle dependence of sputtering yield changes significantly with the size of the projectile bombarding organic samples.^[11,14] For clusters containing less than approximately 200 atoms, the total sputtering yield only slightly increases with the impact angle, has a broad maximum, and decreases at angles above approximately 40°. A similar behavior has been observed in studies of Ar cluster bombardment of metal and semiconductor targets.^[15–17] It is interesting to note that in this case, the shape remains the same even for large Ar clusters. However, for Ar₈₇₂ or Ar₂₉₅₃ cluster bombardment of benzene, the yield strongly increases with the impact angle, has a maximum around 45° followed by a steep decrease at larger angles.^[11,14] Such behavior was confirmed recently by experimental measurements performed with Ar₂₀₀₀ on polymer samples.^[18] It has been proposed that a 'washing out' mechanism is responsible for the observed differences.^[11,14] It has been also speculated that this mechanism should be pronounced in materials with low cohesive energy^[11]

In this study, we investigate the effect of the sample cohesive energy on the shape of the impact angle dependence of sputtering of coarse-grained benzene and Ag(111) crystals bombarded by Ar₆₀ and Ar₂₉₅₃ cluster projectiles. The cohesive energy of the samples was artificially changed from 0.5 eV (real value) to 2.9 eV for benzene and from 2.9 eV (real value) to 0.5 eV for Ag(111). The results are utilized to get a better insight into processes that accompany large noble gas cluster bombardment of various materials.

Model

Details of the MD computer simulations used to model cluster bombardment are described elsewhere.^[10] The model approximating the benzene crystal consists of 307 366 molecules arranged in a hemispherical sample. The radius of the sample is approximately 26 nm. Samples of the same size are used for Ag(111). Rigid and stochastic regions measuring 0.7 and 2.0 nm, respectively, are used around the hemisphere to simulate the thermal bath that keeps the sample at the required temperature and prevents pressure wave reflection from the system boundaries.^[10] In this study, we use the coarse-grained approach to model the benzene solid. This technique has proven to significantly decrease simulation time

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while giving results similar to the data obtained with a full atomistic model.^[19] Each coarse-grained benzene molecule is represented by six CH particles with the mass of 13 amu. A Lennard-Jones potential is used to describe the interaction of CH-CH particles located in different molecules. The CH-CH interaction inside a single benzene molecule is described by a Morse potential. Details of a coarse-grained method and appropriate values for the Lennard-Jones and Morse potential parameters can be found elsewhere.^[19] The interactions between Ar atoms in the projectile and between Ar atoms and all other particles in the system are described by a Lennard-Jones potential splined with KrC potential to properly describe high-energy collisions.^[20] Interactions between Ag atoms are described by a pairwise Morse potential.^[21] In spite of the deficiency associated with its pairwise nature, the Morse potential is used in this case because it allows for an easy modification of the cohesive energy. Cohesive energy of investigated crystals is artificially changed from 0.5 eV to 2.9 eV for benzene and from 2.9 eV to 0.5 eV for Ag(111) by modification of the depth of intermolecular (benzene) and interatomic (Ag) potential well. The 15 keV Ar₆₀ and Ar₂₉₅₃ projectiles are used to bombard the crystal with an impact angle changing from 0° to 75°. The simulations are run at 0 K target temperature.

Results and discussion

The sputtering yield dependence on the impact angle is shown in Fig. 1 for two different cohesive energies and for 15 keV Ar₆₀ and Ar₂₉₅₃ irradiating benzene (a,b) and Ag(111) (c,d) crystals. The yield is multiplied by the cohesive energy to be able to present all data on the same scale. The shapes of the distributions recorded for both projectiles for silver, as well as for Ar₆₀ projectile for benzene, show are similar (Figs. 1a,c,d) and differ from the shape of the angular spectra recorded for Ar₂₉₅₃ bombarding benzene (Fig. 1b).

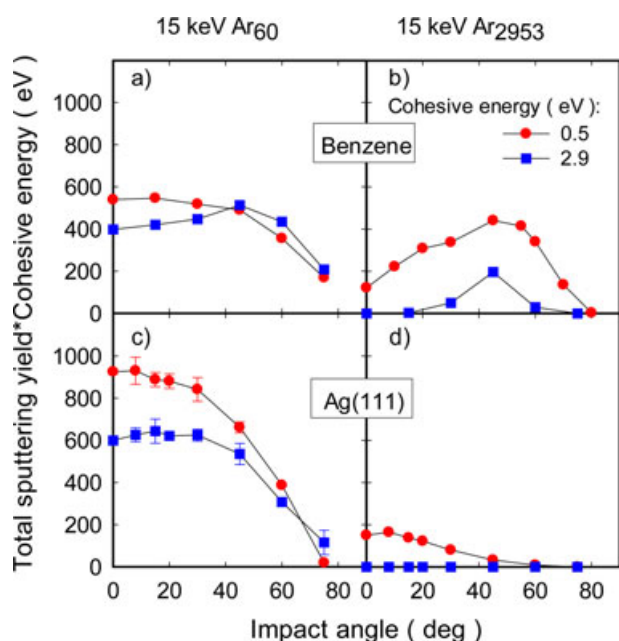


Figure 1. Dependence of the total sputtering yield multiplied by the cohesive energy on the impact angle and the substrate cohesive energy (0.5 eV – circle, 2.9 eV – square) for 15 keV Ar₆₀ and 15 keV Ar₂₉₅₃ bombarding surface of benzene (a, b) and Ag(111) (c, d) crystals. Solid lines are drawn to guide the eye.

In the former cases, the total sputtering yield only slightly increases with the impact angle, has a broad maximum, and decreases at angles above 40°. A similar shape has been reported in other studies with large Ar clusters performed at metal and semiconductor surfaces.^[15–17] For 15 keV Ar₂₉₅₃ bombardment of the benzene system, however, the behavior is different. In this case, the yield strongly increases with the impact angle, has a maximum around 45° followed by a steep decrease at larger angles. A similar dependence was observed for 15 keV Ar₈₇₂.^[11]

The shape recorded for Ar₂₉₅₃ bombardment of benzene resembles the shape of the impact angle dependence reported in numerous studies with atomic projectiles.^[22] The physics behind these two cases is, however, quite different. For keV atomic projectiles, a significant portion of the primary kinetic energy is deposited below the volume in the substrate that contributes to sputtering. Increase of the impact angle shifts the energy deposition closer to the surface. Having more energy closer to the surface enhances the sputtering yield. At some point, however, backreflection of the primary kinetic energy becomes important and the yield decreases again.^[22] For medium and large cluster keV bombardment, almost all of the primary kinetic energy is already deposited in the volume that can efficiently contribute to sputtering.^[23] As a result, the yield can only slightly benefit from the modification of the deposited energy profile, and the resulting distribution should be rather flat over a wide range of angles and decrease at larger angles where energy backreflection starts to dominate. Such behavior is indeed observed for the Ar₆₀ projectile bombarding benzene or the Ar₆₀ and Ar₂₉₅₃ projectiles bombarding the silver crystal.

It is evident from Fig. 1b that something different is occurring in the bombardment of benzene by the Ar₂₉₅₃. In this case, almost all the primary energy is deposited in the volume that contributes to particle ejection even for normal incidence. However, the mechanistic analysis of atomic movements shows that at off-normal impact angles, an intense flux of Ar atoms is 'sliding' over the right side of the crater for the Ar₂₉₅₃ cluster as shown in Fig. 2b.^[11,24] It is the interaction of these atoms with benzene molecules that leads to an enhanced ejection of organic particles. In this scheme, the system molecules are 'washed out' of the crystal. The effect is insignificant for small clusters due to a limited number of projectile atoms that could participate in a 'washing out' process, and to the fact that small projectile penetrates into the sample at the same impact angle as shown in Fig. 2a.^[11,14] As a result, for these small projectiles, a flux of correlated Ar atoms is not formed.

The main consequence of a modified cohesive energy is a change of the total emission. The effect of this quantity on the shape of the impact angle dependence is much less pronounced. Emission of benzene molecules stimulated by 15 keV Ar₂₉₅₃ impact at off-normal impact angles is still dominant even for the benzene system with a cohesive energy of ~2.9 eV as shown in Fig. 1b. Also, the shape of the impact angle dependence is preserved for Ag(111) with the cohesive energy lowered to the value typical for benzene, as indicated by Fig. 1c. Although, a correlated flux of backreflected Ar atoms is visible for the Ar₂₉₅₃ projectile bombarding silver, in this case, it does not lead to significant material removal at off-normal impact even from a sample having low cohesive energy as shown in Fig. 1d. Both these observations clearly indicate that lower cohesive energy cannot be responsible for different shape of impact angle dependence observed for Ar₆₀ and Ar₂₉₅₃ projectiles on benzene.

There are several major differences between benzene and silver crystals. One is a cohesive energy which is much lower for

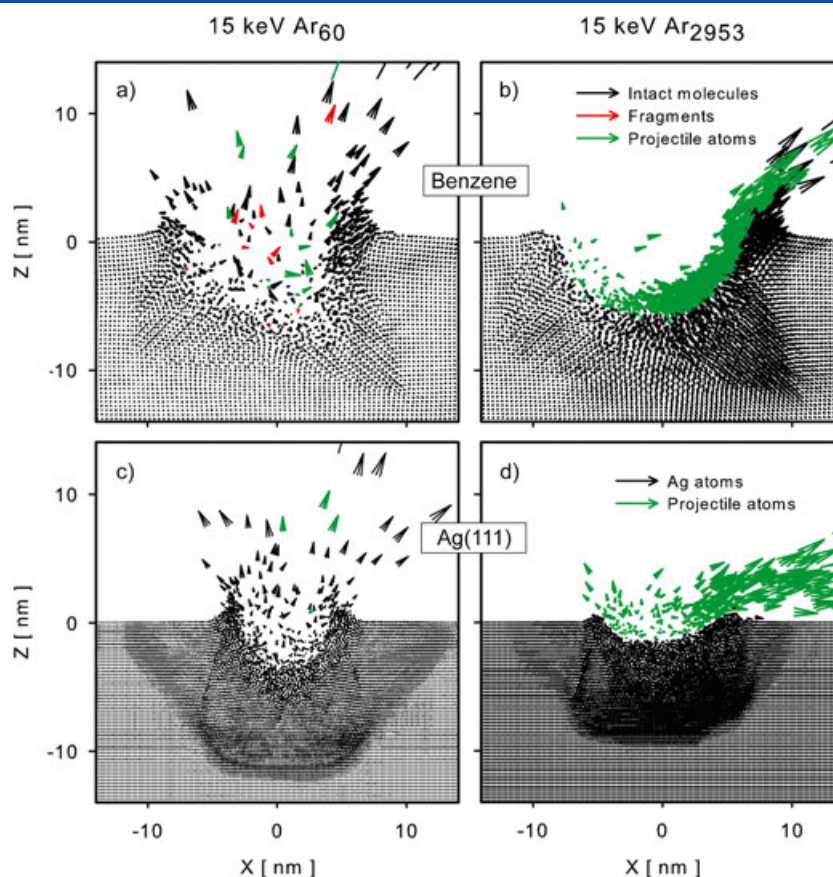


Figure 2. Cross-sectional view of benzene (a,b) and Ag crystals (c,d) with cohesive energy of 0.5 eV at 4 ps after the impact of 15 keV Ar_{60} (a,c) and 15 keV Ar_{2953} (b,d) projectiles at a polar angle of 45° . Vectors represent the original and final positions of the center of mass of system particles at 4 and 4.5 ps. Intact molecules and Ag atoms are represented by black vectors, fragments by red vectors, while projectile atoms are depicted by green vectors. The cross-sectional view is 1.5 nm wide and is centered along the projectile impact point.

benzene (~ 0.5 eV) as compared to silver (~ 2.9 eV). The second difference is the material structure. The benzene crystal is more open and is composed of molecules, while Ag is denser and is composed from atoms. As a result, from the point of view of a flux of backreflected Ar atoms, the benzene crystal should be seen as a more textured substance, as compared to Ag sample. Ar atoms in the backreflected flux may 'catch on' benzene molecules imparting more kinetic energy to these particles. We speculate, therefore, that this difference is responsible for the observed strong material removal stimulated by Ar_{2953} projectiles bombarding benzene at large impact angle.

Conclusions

The role of sample cohesive energy on the shape of the impact angle dependence of the total sputtering yield stimulated by an impact of 15 keV Ar_{60} and Ar_{2953} was investigated. It is shown that modification of the cohesive energy leads predominantly to a change of the total sputtering yield. Modification of this quantity has, however, a minor influence on the shape of the impact angle dependence of the sputtering yield. Therefore, it is concluded that low cohesive energy of benzene is not responsible for a strong material removal observed at off-normal impact angles for large Ar projectiles bombarding molecular benzene, but rather material structural properties are responsible for this phenomenon.

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