

Dynamics of large Ar cluster bombardment of organic solids

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Molecular dynamics computer simulations are used to investigate the ejection process of molecules from a benzene crystal bombarded with keV large Ar clusters. The effect of projectile size, the kinetic energy and the impact angle on the sputtering efficiency is investigated. The results show that although the sputtering yield depends on all projectile parameters, this dependence can be greatly simplified if the sputtering yield per projectile nucleon is expressed as a function of projectile kinetic energy per nucleon. A different dependence of the total sputtering yield on the impact angle has been observed for small and large projectiles. This effect is attributed to a 'washing out' mechanism. For large projectiles most of the organic molecules are ejected by gentle collective action of argon atoms. Proper selection of the projectile parameters allows for achieving conditions where only intact molecules are emitted. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

The introduction of cluster ion sources and the observation that cluster projectiles can significantly enhance the ejection of secondary ions has opened the door to a new and exciting world of three-dimensional depth profiling of organic and biological materials.^[1] Since then, considerable effort has been devoted to find optimal experimental conditions that would allow imaging of the chemical composition of the investigated samples with the highest sensitivity and spatial resolution.^[1] Part of these endeavors is concentrated on finding the best projectile that can accomplish all these goals. Large Ar gas clusters have recently been introduced as promising contenders.^[2,3]

There are several experimental studies that investigated how the ejection efficiency of organic material depends on various parameters of Ar_n ion beam.^[3–7] Some of these studies were conducted by collecting ejected ions.^[3,5,8] It is not clear, however, whether the ionization and ejection processes depend in the same manner on projectile properties. There are few measurements where the total erosion of organic samples was probed at off-normal impact angle.^[4,6,7,9] It has been observed in these studies that the yield is not dependent on the size of the projectile within the investigated range. This observation is different from the data reported for ion emission and predictions of computer simulations performed at normal incidence on coarse-grained organic systems, where a strong dependence on the projectile size is observed.^[10–13]

In this study, we investigate the effect of a projectile size, its kinetic energy and the impact angle on ejection of intact molecules and fragments from an atomistic benzene crystal bombarded by large noble gas cluster projectiles. The results are utilized to explain why simulations performed at normal incidence may not always represent the data obtained with off-normal impact angles.

Model

Details of Molecular Dynamics (MD) computer simulations used to model cluster bombardment are described elsewhere.^[10] The model approximating the benzene crystal consists of 143 750

molecules arranged in a hemispherical sample. The radius of the sample is approximately 21 nm. Rigid and stochastic regions measuring 0.7 and 2.0 nm, respectively, were used around the hemisphere to simulate the thermal bath that keeps the sample at required temperature and prevents pressure wave reflection from the system boundaries.^[10] The forces between hydrocarbon atoms are described by adaptive intermolecular AIREBO potential, which enables modeling bond breaking and bond formation.^[14] 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.^[15] The 5–15 keV Ar_n (*n* = 60, 101, 205, 366, 872, and 2953) projectiles were used to bombard the crystal with an impact angle changing from 0° to 75°. Because it has been observed that bombardment with large polyatomic projectiles is a mesoscopic event and small fluctuations in sputtering yields are expected,^[10] the yields are calculated from the data obtained from two impacts for each set of conditions. The simulations are run at 0 K target temperature.

Results and discussion

The calculated total sputtering yields induced by keV cluster bombardment at normal incidence are shown in Fig. 1(a). There are several trends that can be identified in the data.

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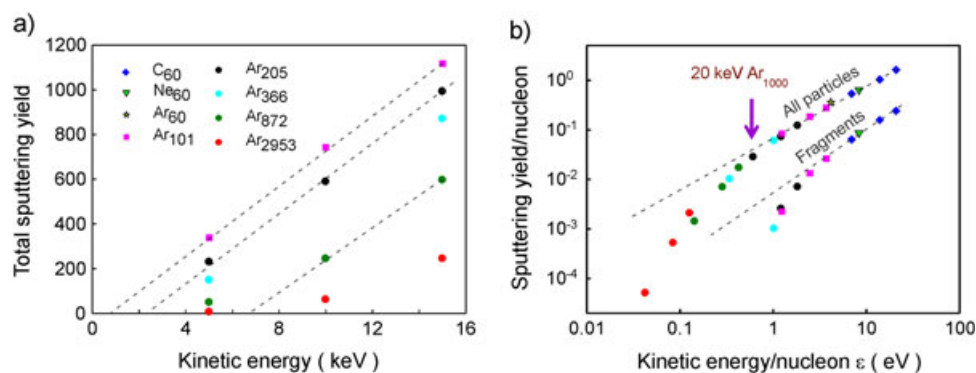


Figure 1. Dependence of (a) the total sputtering yield on the kinetic energy and the size of the Ar_n projectile; (b) the sputtering yield per projectile nucleon on the kinetic energy per projectile nucleon for various projectiles. All calculations are made at normal angle of incidence. Dashed lines represent the fit to the linear part of the dependence. Arrow depicts the kinetic energy per nucleon corresponding to 20 keV Ar_{1000} projectile.

For instance, above a certain threshold, the yield increases linearly with the primary kinetic energy for a given cluster, but when the primary kinetic energy is constant, the yield decreases with the cluster size. In general, however, the erosion efficiency is an entangled function of both the cluster size, total kinetic energy and the energy per atom.^[12,16,17] It has been observed, however, that this dependence can be greatly simplified if the sputtering yield per single nucleon of the projectile is expressed as a function of projectile kinetic energy per nucleon of the projectile – ϵ .^[12,17] Indeed, in this representation, all data points for the total sputtering yield and the yield of fragments collected with various clusters and kinetic energies can be nicely placed on a single curved line as indicated in Fig. 1(b). It is visible that the yield of fragments decreases faster with ϵ . As a result, the ratio of intact to fragment emission increases strongly at low ϵ .

Our results follow the trends observed by Delcorte *et al.* although, actual numbers and rates of decay are different.^[12] This difference is not surprising because their simulations were performed on a system consisting of a coarse-grained polymer and the projectiles were hydrocarbon species. However, as in the study of Delcorte *et al.* two distinct regions can be identified in Fig. 1(b). In the high velocity region the yield per nucleon scales linearly with ϵ as indicated by a dashed line. At low ϵ , the linear region transforms into nonlinear region where the sputtering yield decreases faster with ϵ . The existence of these two regions was attributed to a different velocity at which the primary kinetic energy is deposited.^[12] It is important to point out that all Secondary Ion Mass Spectrometry (SIMS) experiments with Ar clusters performed so far are located in the nonlinear region of the curve, that is, with small KE/nucleon or large cluster sizes.

The general trends observed in experiments where the emission of ionic species is monitored seem to agree with the predictions shown in Fig. 1, although the rate of change depends on a particular system.^[3,7,8] However, this is not the case for experiments where a total amount of removed material is probed.^[6,7] For instance, Rabbani *et al.* have found that, within the experimental accuracy, the erosion rate of cholesterol film for Ar_n projectiles is almost the same for clusters ranging from Ar_{60} up to Ar_{2000} .^[7] This observation does not agree with the trends shown in Fig. 1(a), where the yield decreases significantly with the increase of the cluster size. The data presented in Fig. 1 are compiled, however, for normal incidence, while all experiments have been conducted at 45° impact angle.

The total sputtering yield dependence on the impact angle is shown in Fig. 2 for 10 keV Ar_{101} , Ar_{366} , and Ar_{2953} projectiles. It is evident that the shape of this dependence changes with the cluster size. In the case of Ar_{101} bombardment, the total sputtering yield only slightly increases with the impact angle, has a broad maximum around 40°, and decreases at larger angles. A similar behavior has been observed for fullerene impacts on a coarse-grained benzene solid^[11] and in the studies of large Ar cluster bombardment of metal targets.^[18,19] In the last case, the shape does not change even for large Ar clusters. For Ar_{2953} cluster bombardment of benzene the yield strongly increases with the impact angle and has a maximum around 45° followed by a steep decrease at larger angles. The shape of the impact angle dependence for Ar_{366} projectile exhibits a transitional form from that of Ar_{101} to that of Ar_{2953} .

The shape recorded for Ar_{2953} bombardment resembles the shape of the impact angle dependence reported in numerous studies with atomic projectiles.^[20] 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 that contributes to sputtering. Increase of the impact angle shifts the energy deposition profile closer to the surface. Having more energy in the subsurface region enhances the sputtering yield up to the point where backreflection of the primary kinetic energy becomes important and the yield decreases again.^[20] A similar effect is, however, improbable for medium and large cluster

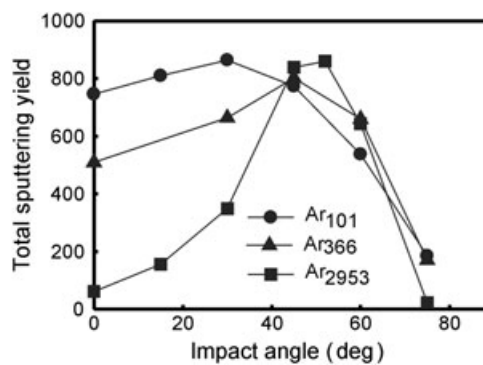


Figure 2. Dependence of the total sputtering yield on the impact angle for 10 keV Ar_{101} (circle), Ar_{366} (triangle) and Ar_{2953} (square) projectiles. Solid lines are drawn to guide the eye.

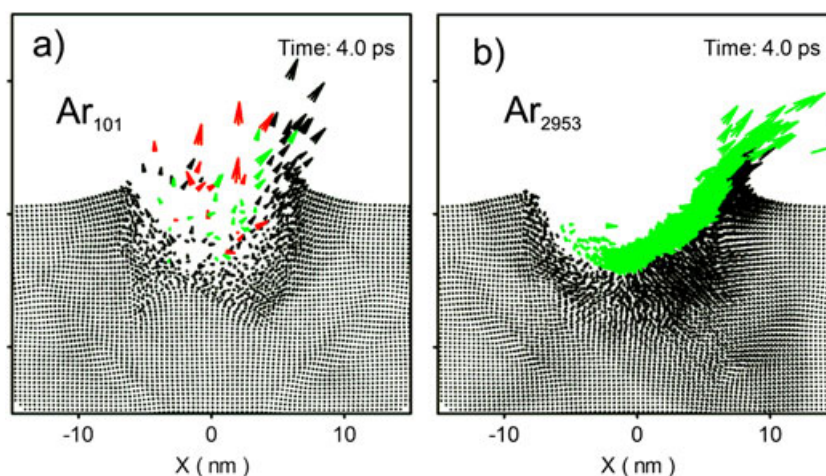


Figure 3. Cross-sectional view of benzene crystal at 4 ps after the impact of 10 keV at a polar angle of 45° (a) Ar_{101} and (b) Ar_{2953} projectiles. Vectors represent the original and final position of the center of mass of system particles at 4 and 4.5 ps. Intact molecules are represented by a black vector, fragments by a red/grey vector, while projectile atoms are depicted by a green/thick black vector. The cross-sectional view is 1.5 nm wide and is centered along the projectile impact point.

keV bombardment because, for these projectiles, almost all of the primary kinetic energy is already deposited in the volume that can efficiently contribute to sputtering.^[21] 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, which is indeed observed for Ar_{101} projectile. However, such scenario cannot explain the yield variation observed for Ar_{2953} .

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 Ar_{2953} cluster as depicted in Fig. 3. It is the interaction of these atoms with benzene molecules that leads to an enhanced ejection of organic particles. In this scheme, system particles are 'washed out' of the crystal. The effect is insignificant for small clusters because of a limited number of projectile atoms that could participate in a 'washing out' process, and the fact that small projectile penetrates into the sample even at relatively large impact angle. As a result, most of projectile atoms quickly lose their original movement direction, as indicated by a large spread to the directions of the arrows shown in Fig. 3. At this point, it is interesting to note that the total sputtering yields observed for Ar_{101} , Ar_{366} , and Ar_{2953} at 45° are indeed similar, as was reported by Rabbani *et al.*^[7]

Similar total sputtering yields does not mean, however, that the ion yields will also be similar at 45° impact angle. The process leading to ejection of ions is still elusive. There are, however, some indications that positive organic ions are formed by association of a parent molecule with a free proton created because of projectile impact.^[22] We see that H atoms compose the most abundant fraction of created fragments. Most of these atoms are, however, ejected. The total number of hydrogen atoms that remain in the bombarded sample decreases quickly with the size of the cluster. For instance, for 10 keV projectiles at 45° impact angle number of created H atoms that remain in the solid is 27.3, 16.6, 3.3, and 0 for Ar_{101} , Ar_{205} , Ar_{366} , and Ar_{872} , respectively. This decrease occurs as a result of a lower density of the energy deposited in the solid, and more efficient cleaning effect of larger projectile. The overall result of this process will be a decrease of the ion yield with the cluster size as observed in experiments. It seems that modification of the total sputtering yield is less crucial in this case.

Conclusions

The effect of projectile size, its kinetic energy, and the impact angle on the ejection of particles from the atomistic benzene crystal bombarded by large noble gas cluster projectiles has been investigated. It has been found that for a normal incidence the yield can be conveniently expressed by reduced coordinates for all investigated kinetic energies and cluster sizes. Decrease of the kinetic energy per nucleon reduces the overall ejection efficiency but it significantly enhances the ratio of ejection of intact molecules to fragments. The shape of the sputtering yield on the impact angle depends on the size of the projectiles. A 'washing out' mechanism that occurs for large projectiles is proposed to account for the observed variations. As a result trends predicted from calculations performed at normal incidence may differ from trends obtained at off-normal impact angle. We do not see a similar effect during Ar_n bombardment of metals, which indicates that the effect is material dependent. It seems that the impact angle around 45° is optimal from the point of view of signal strength and yield variations.

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