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Computer simulations of sputtering and fragment formation during keV C₆₀ bombardment of octane and β -carotene

Zbigniew Postawa,^{a*} Michal Kanski,^a Dawid Maciazek,^a Robert J. Paruch^b and Barbara J. Garrison^b

Molecular dynamics computer simulations are used to investigate material ejection and fragment formation during keV C₆₀ bombardment of organic solids composed from small (octane) and medium (β -carotene)-sized organic molecules. Both systems are found to sputter efficiently. For the octane system, material removal occurs predominantly by ejection of intact molecules, whereas fragment emission is a main ejection channel for β -carotene. A difference in the molecular dimensions is proposed to explain this observation. Fragment formation is investigated to answer the question why so few fragments remain in the bombarded solid. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: molecular dynamics simulations; SIMS; cluster bombardment

Introduction

Molecular dynamics computer simulations are an excellent tool for acquiring a better understanding of the mesoscopic processes that occur during cluster bombardment of both inorganic and organic solids.^[1] Through the use of computer modeling, a microscopic view of how projectiles interact with the substrate can be captured.^[1,2] Computational research of the processes induced by cluster projectiles has drawn much attention because such projectiles allow depth profiling of certain organic materials by SIMS.^[3] Study of a material emission and damage formation caused by a cluster bombardment is currently one of the most interesting research endeavors. Computer simulations indicate that during cluster projectile bombardment, molecular fragmentation occurs predominantly in an energized zone located close to the projectile impact, where most of the primary energy is deposited.^[1,4–6] Molecules are fragmented due to collisions with cluster atoms or collisions with other energized molecules or already-formed fragments. Computer studies also indicate that during cluster bombardment, most of the created fragments are ejected. Such a self-cleaning mechanism combined with a lower fragmentation factor associated with a lower kinetic energy per atom is believed to explain why certain organic materials can be depth profiled with cluster ions.^[1,3,6,7] The nature of this self-cleaning is, however, still not fully explained.

In this study, we investigate the effect of the projectile kinetic energy and the size of organic molecules on the ejection efficiency of intact molecules and fragments from atomistic organic solids. Samples composed from small [octane (C₈H₁₈), length ~0.9 nm] and medium [β -carotene (C₄₀H₅₆), length ~2.9 nm] sized molecules were selected to probe the effect of molecular dimension on the ejection characteristics. The organic samples are bombarded by keV C₆₀ projectiles at 45° within a range of kinetic energies to reproduce conditions usually applied in SIMS experiments. Formation of the molecular fragments is

investigated to answer the question why so few fragments remain in the bombarded solid.

Simulation and model

Detailed description of molecular dynamics computer simulations used to model cluster bombardment can be found elsewhere.^[1] 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 atomistic Adaptive Intermolecular Reactive Empirical Bond-Order (AIREBO) potential is used to describe interactions among hydrocarbon species.^[8] This potential describes respectably well reactions among these species,^[9] in particular, dissociation and H addition and abstraction. Of note is that octane is a saturated hydrocarbon molecule with no readily available opportunity for crosslinking, whereas β -carotene has double bonds, which can cross-link. The original organic systems had geometrical configurations and densities equal to the values measured in experiments, i.e. 0.76 and 0.94 g/cm³. Samples were subsequently equilibrated to achieve configurations the most optimal for the potentials used. The calculated density of equilibrated octane and β -carotene samples is 0.76 and 0.81 g/cm³, respectively.

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The comparison of these values with the original ones indicates that the AIREBO potential overestimates density of octane, whereas it underestimates the density of β -carotene. We observe, for instance, that during equilibration procedure, the original length of octane molecules, which have only single bonds, remains unaltered, whereas the length of β -carotene molecules, which have both single and double bonds, is increased by approximately 12%. As AIREBO potential is a very complicated, self-contained unit, the correction of this deficiency is beyond our capabilities. However, although these factors may influence the values of the calculated sputtering yields, they should not affect observed trends. The calculated atomic density of equilibrated octane and β -carotene samples is 104.0 and 86.6 atoms/nm³, respectively, indicating that β -carotene is more open than octane.

The calculated intermolecular binding energy of molecules is approximately 0.6 and 1.3 eV for octane and β -carotene, respectively. The approximate diameter of the hemispherical sample cut-out after equilibration procedure is 38 nm. The model systems contain 57 452 and 12 944 octane and β -carotene molecules, respectively. Rigid and stochastic regions with a thickness of 0.7 and 2.0 nm, respectively, were used around the hemisphere to preserve the shape of the sample and to simulate the thermal bath that keeps the sample at the required temperature and helps inhibit the pressure wave reflection from the system boundaries.^[10] The C₆₀ projectiles were used to bombard the crystal with the kinetic energy ranging between 0.4 and 40 keV and an impact angle of 45°. Such values were selected to reproduce conditions used in the experimental studies. As it had been shown that the efficiency of a cluster sputtering process of organic materials weakly depends on the projectile impact point,^[11] only two impacts were probed. The simulations were run at 0 K target temperature and lasted up to 50 ps, which is long enough to see a saturation in the sputtering yield versus time dependence.

Results

The craters formed by an impact of 20 keV C₆₀ projectiles on octane and β -carotene samples at 45° impact angle are shown in Fig. 1. The coloring scheme (from light/yellow to dark/red) represents the amount of a vertical relocation of organic material. It is interesting to note that while a significant amount of material is removed from both solids as indicated by large dimensions of

the formed craters, the amount of the vertical relocation of organic material that remains in the solids is small, and it is mainly restricted to the volume near the walls of the crater.^[7] Molecular relocation is larger in β -carotene as compared with octane because of a more open geometrical structure of this solid. As a result, material is more compressed, and the crater is larger regardless of the fact that the calculated total sputtering yields are actually comparable for these two solids as indicated in Fig. 2. It should be pointed out, however, that it is still possible that 50 ps is not enough for the systems to return to its equilibrium position, and the crater will relax on still larger time scales than those available here. This process will, however, further reduce the extent of molecular relocation and will additionally support observation that the vertical relocation of organic material after C₆₀ impact is small.

The calculated total sputtering yields expressed in nm³ induced by keV C₆₀ bombardment at 45° incidence are shown in Fig. 2 for octane and β -carotene. There are several interesting observations that can be made from the data presented in this figure. For both materials, the sputtering yield increases linearly with the impact kinetic energy between 1 and 20 keV. The linear dependence of the sputtering yield on the kinetic energy of a projectile has been observed previously and is attributed to a deposition of a projectile kinetic energy in the subsurface volume from where ejection occurs.^[1,12,13] It has been, however, reported in those studies that this dependence deviates at low kinetic energy from a linear form.^[12] As a result, a threshold kinetic energy was introduced, which separates the nonlinear and linear regions. The data presented in Fig. 2 show that the threshold energy is very small in the current case, as the straight lines fitted to the data intersect the beginning of the coordinate system.

The total sputtering yield expressed in nm³ is comparable for both octane and β -carotene, regardless of a different binding energy of these two solids and a different size of molecules forming these materials. It should be pointed out, however, that this observation may be coincidental, and comparison with the data obtained at other organic solids is needed to draw a conclusion that the sputtering yields expressed in the volume representation are similar. The fragmentation process occurs very fast, and within 2 ps, almost 91% of fragments recorded at 50 ps are created in both solids. The fragments are created predominantly by interactions with projectile atoms. It should be pointed out, however, that additional fragmentation will occur also later, for instance, by unimolecular decay of internally excited molecules.^[4] As shown for Polystyrene oligomers, although such process has

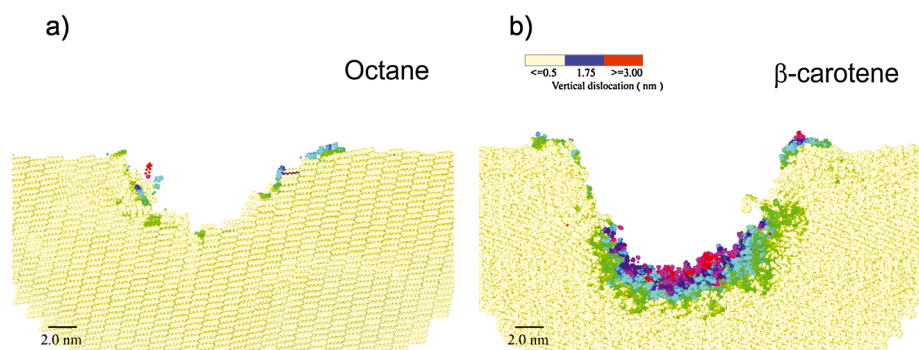


Figure 1. Cross-sectional view of the octane a) and β -carotene b) samples bombarded by 20 keV C₆₀ projectiles at 45° impact angle at 50 ps. The amount of the vertical relocation is represented by a coloring scheme from yellow (≤ 0.5 nm) to red (≥ 3.0 nm). A slab 2.6 nm wide is shown centered at the point of impact.

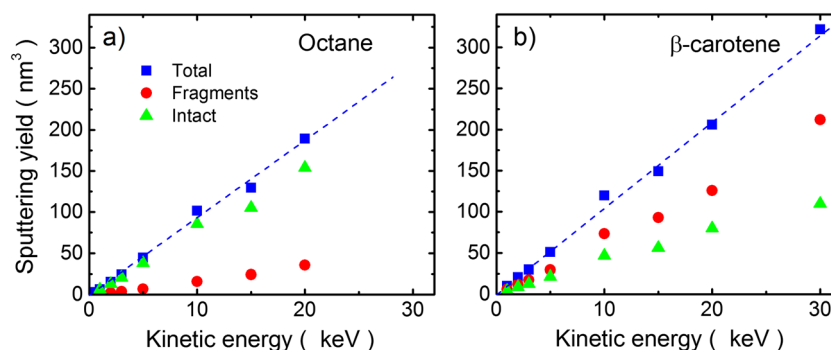


Figure 2. Dependence of the sputtering yield expressed in nm³ of octane a) and β -carotene b) on the kinetic energy of the C₆₀ projectile at 45° impact angle. The total sputtering yield and the sputtering yield of fragments and intact molecules is represented by squares, circles, and the triangles, respectively. Dashed straight lines were fit to the total sputtering yield data.

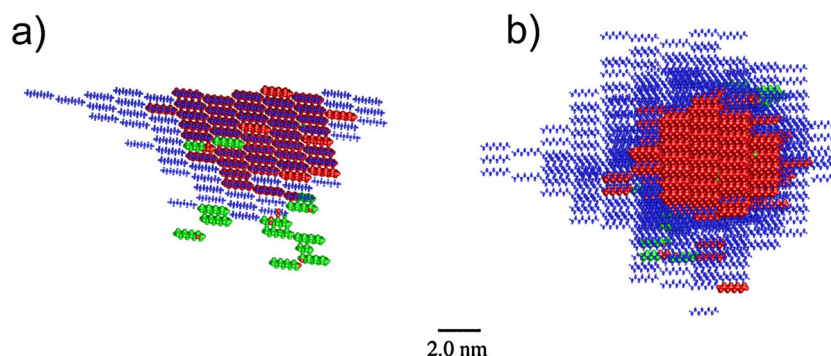


Figure 3. Side a) and top b) views of the initial positions of octane molecules that were ejected by 20 keV C₆₀ projectiles at 45° impact angle as intact molecules (blue) or fragments (thick red) or remained as fragments in the molecular solid (green).

significant impact on ejection of slow molecules, its contribution to the total number of created fragments is less crucial than the contribution of collisional fragmentation.^[4] Therefore, this process will not alter general observations given in the succeeding text. There is a significant difference in the manner the material is being removed from bombarded solids. In case of octane, ejection of intact molecules is a dominant emission channel. For instance, for 20 keV C₆₀ projectiles bombarding octane at 45° at 50 ps almost 85% of matter is ejected as intact molecules. The behavior of β -carotene is different. In this case, most of emitted material (approximately 61%) is removed as fragmented molecules. Inspection of computer animations shows that a difference in the molecular size is mainly responsible for such behavior. Octane molecules are small, approximately 0.9 nm long. It is relatively easy, therefore, to uplift these particles without fragmentation. On the other hand, β -carotene molecules are more than three times longer (~2.9 nm) and contain almost four times as many atoms. Ejection of the larger molecules requires a concerted action of many surrounding particles.^[14] The probability of such correlated action decreases rapidly with the number of particles involved. As a consequence, ejection of intact molecules from this system will be rather small. Moreover, it is also much easier to destroy large molecule as various uncorrelated forces may act on different parts of such structure. Both these processes will result in a lower emission of intact molecules and a higher ejection of molecular fragments from β -carotene as compared with octane.

It has been observed that although many fragments are created during cluster projectile impact, only very few fragments

remain in the bombarded solid.^[4–6,15–17] For instance, our simulations indicate that even for β -carotene, of 1590 fragments (most of them H atoms) created by 20 keV C₆₀ impact, only 91 remain in the solid. As shown in Fig. 3, almost all of the fragments are created in the energized zone located in vicinity of the projectile impact. Such behavior has been reported previously.^[6,7] However, as also shown in Fig. 3, a zone with fragmented molecules is surrounded by a volume from where the intact molecules are emitted. The mechanistic analysis shows that the emission process can be described by a concept of a fluid/gas flow motion, where most of intact molecules are emitted from the corona of the crater by material transport along the walls of the forming crater.^[1,18–20] Such spatial arrangement explains why so few fragments remain in the solid. Although most of the fragments from the central zone are directly ejected, even if some fragments attach to the surrounding material, they will be entrained in a flux of ejecting intact molecules and removed. As a result, only fragments created outside a volume occupied initially by ejecting intact molecules can remain in the solid, but the number of such fragments is very small.

Conclusions

Molecular dynamics simulations have been performed to model bombardment of organic solids of octane and β -carotene by keV C₆₀ projectiles. Because of the relatively small cohesive energy compared with, e.g. metals, the total sputtering yield for both these solids is high. For octane, of the total sputtering yield,

approximately 85% is in intact molecules and the remainder in fragments. For β -carotene, the situation is opposite and most of the emitted material is composed from fragmented molecules. A difference in the molecular size is responsible for such behavior. The chemical damage remaining in investigated solids for a single impact was found to be minor because most of the fragments are either ejected directly or are entrained in a flux of intact molecules that surrounds the volume where molecular fragments are formed by interaction with projectile atoms. We do not observe cross-linking between carotene molecules.

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