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Understanding collision cascades in molecular solids

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Abstract

This paper describes simulations of the sputtering of a molecular solid that uses a reactive potential with both covalent bonding and van der Waals interactions. Recently, the adaptive intermolecular REBO (AIREBO) potential has been developed, which incorporates intermolecular interactions in a manner that maintains the reactivity of the original reactive empirical bond-order (REBO) potential. Preliminary simulations of the keV bombardment of a molecular solid have been performed using the AIREBO potential. Molecules that are initially struck by the bombarding particle break into fragments. The fragments initiate molecular collision cascades leading to the ejection of intact molecules and molecular fragments from the surface. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Theoretical studies of the keV bombardment of organic films on metallic surfaces have contributed to our understanding of the mechanisms governing these processes and have been a guiding force in the interpretation of experimental data and the design of experimental techniques [1]. Many experiments of keV bombardment, however, are performed on thick organic targets. It is not clear that mechanistic insights gained from simulations with organic films on metallic surfaces can be extrapolated to interpret experiments on molecular solids.

In this paper, we describe molecular dynamics simulations of the sputtering of a molecular solid that uses a reactive potential with both covalent bonding and van der Waals interactions. Recently, an interaction potential for hydrocarbons that can model both chemical reactions and intermolecular interactions has been developed [2]. The advantage of this potential is that intermolecular interactions

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have been incorporated while maintaining the reactive nature of the potential. Previous simulations of Ar bombardment of fullerite films [3,4] using a different long-range potential [5] addressed the issues of C atom and molecule ejection.

The molecular dynamics simulations presented here have been performed in order to understand how collision cascades develop which lead to the ejection of molecular species. Do intermolecular or intramolecular interactions dominate in the transfer of energy within the solid? What role do fragments and molecules play in the collision cascade? Do reactions between fragments occur? Does energy released from exothermic reactions in the solid initiate additional collision cascades, thereby increasing the ejection yield?

In order to answer these questions, we have performed molecular dynamics simulations of the bombardment of a benzene molecular crystal with 0.30 keV Xe. The general mechanism for the formation of collision cascades leading to the ejection of intact molecules is beginning to be elucidated. Molecules that are initially struck by the incoming Xe atom are broken into fragments. These fragments then go on to hit neighboring molecules, some of which remain intact and some of which fragment. The process of fragmentation initiates collision cascades between molecules which lead to the ejection of molecules and molecular fragments. In this paper, we first describe the methodology used in the molecular dynamics simulations including a description of the model system and the interaction potentials used. Next, we discuss the results of the simulations and present a sample trajectory that illustrates the mechanisms for ejection.

2. Method

The classical method of molecular dynamics simulations is used to study the system of interest and the details of this method are described extensively elsewhere [6,7]. Once the initial conditions of the system and the potential energy functions to describe the interactions among the atoms and molecules are specified, Hamilton's equations of motion are integrated to determine the position and velocity of each atom as a function of time. From the final positions and velocities of the atoms, the identity and kinetic energy of all ejected species can be calculated. Additionally, the atomic motions leading to the ejection of the molecules and molecular fragments may be analyzed.

The model system is a benzene molecular crystal, which is represented by a microcrystallite of 480 benzene molecules arranged in eight layers of 60 molecules. Figs. 1(a) and (b) illustrate the top and side views of the model system. The benzene crystal structure obtained from X-ray diffraction data [5–8] is orthorhombic with four molecules per

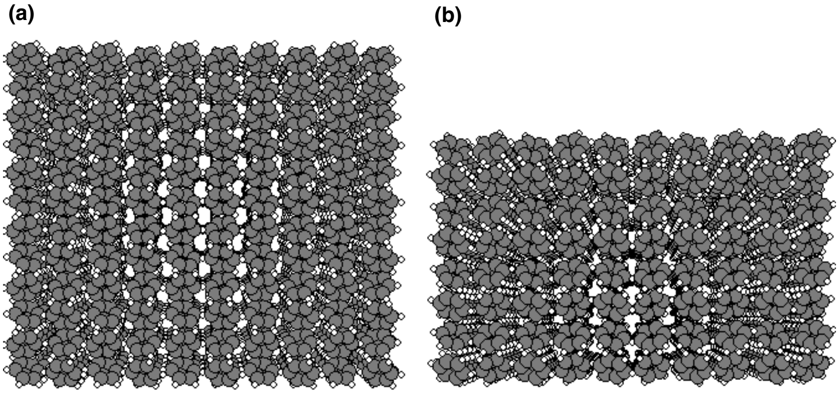

Fig. 1. Model system used in the simulations. The benzene (0 1 0) microcrystallite is composed of 480 molecules arranged in eight layers of 60 molecules. (a) Top view. (b) Side view.

unit cell [8–11]. The positions of the benzene molecules are determined by allowing the crystal to equilibrate at 0 K using an algorithm based on the generalized Langevin equation. The bombarding particle, 0.30 keV Xe, is brought in at normal incidence towards the (0 1 0) plane. A purely repulsive Molière potential is used to model the Xe–C and Xe–H interactions.

The potential energies between all atoms are described by a reactive potential that includes both covalent bonds and intermolecular interactions. Long-range intermolecular energies are included in a manner that allow reactions to take place. The potential is derived from the well-known reactive empirical bond-order (REBO) potential developed by Brenner [12–14], which has been successfully used to model hydrocarbons in the sputtering of organic films on metal surfaces [1]. For our applications, the Brenner potential is modified for hard collisions by attaching a Molière function to the repulsive wall [15]. The REBO potential uses a Tersoff-style potential to describe the covalent bonding among atoms in hydrocarbon systems and varies the bond strength depending on the coordination number, bond angles and conjugation effects. The advantage of the REBO potential is that it is able to model bond breaking and bond formation because atoms may change neighbors and hybridization state. One limitation of the REBO potential is that it does not incorporate long-range intermolecular interactions.

The adaptive intermolecular REBO (AIREBO) potential [2] developed by Stuart, Tutein and Harrison, introduces nonbonded interactions through an adaptive treatment, which allows the reactivity of the REBO potential to be maintained. A possible problem with the introduction of intermolecular interactions is that the repulsive barrier between nonbonded atoms may prevent chemical reactions from taking place. The AIREBO potential corrects for this problem by modifying the strength of the intermolecular forces between pairs of atoms depending on their local environment. For example, the interaction between two fully saturated methane molecules will be unmodified, producing a large barrier to reaction. The carbon atoms in two neighboring methyl radicals, on the other hand, will have a repulsive interaction that is diminished, or even completely absent, allowing them to react. The AIREBO potential yields a cohesive energy per benzene molecule of 0.40 eV. The experimental cohesive energy depends on the temperature of the crystal at which the measurements were done and ranges from 0.45 [9] to 0.507 eV [16].

3. Results

When 0.30 keV Xe bombards the benzene crystal, both molecules and molecular fragments are ejected. In addition, fragments in the solid react to form new species that are subsequently ejected. From these initial calculations, molecules that are directly struck by the impacting projectile do fragment. Some of these fragments collide very gently with neighboring molecules, imparting sufficient energy to initiate motion without fragmentation. More energetic fragments hit neighboring molecules with sufficiently high energy to break covalent bonds and cause fragmentation. Fragments from different molecules can also combine to form new species.

A sample trajectory is shown in Fig. 2, which illustrates the mechanism for fragmentation and the ejection of molecules. At 0 fs, the incoming Xe atom (black) approaches the (0 1 0) plane of the benzene crystal at normal incidence. At 30 fs, the Xe atom has impacted the crystal and has hit two molecules, one in the top layer and one layer below. These two molecules break into fragments. As the molecule in the top layer fragments, it collides with the molecule below it, causing it to fragment as well. At 110 fs, the three fragmented molecules (blue) gently collide with the neighboring molecules, which leads to the ejection of molecules in the top layer (red). At 3000 fs, both molecules and molecular fragments have ejected. Seven stable benzene molecules are ejected with kinetic energies ranging from 0.1 to 0.5 eV. Three molecular fragments are ejected, C_5H_5, C_6H_4 and an unravelled C_6H_6. A reaction takes place between fragments within the molecular solid. A C_5H_5 fragment reacts with a C atom to form a C_6H_5 fragment, which subsequently ejects. From observing animations of the simulations, it appears

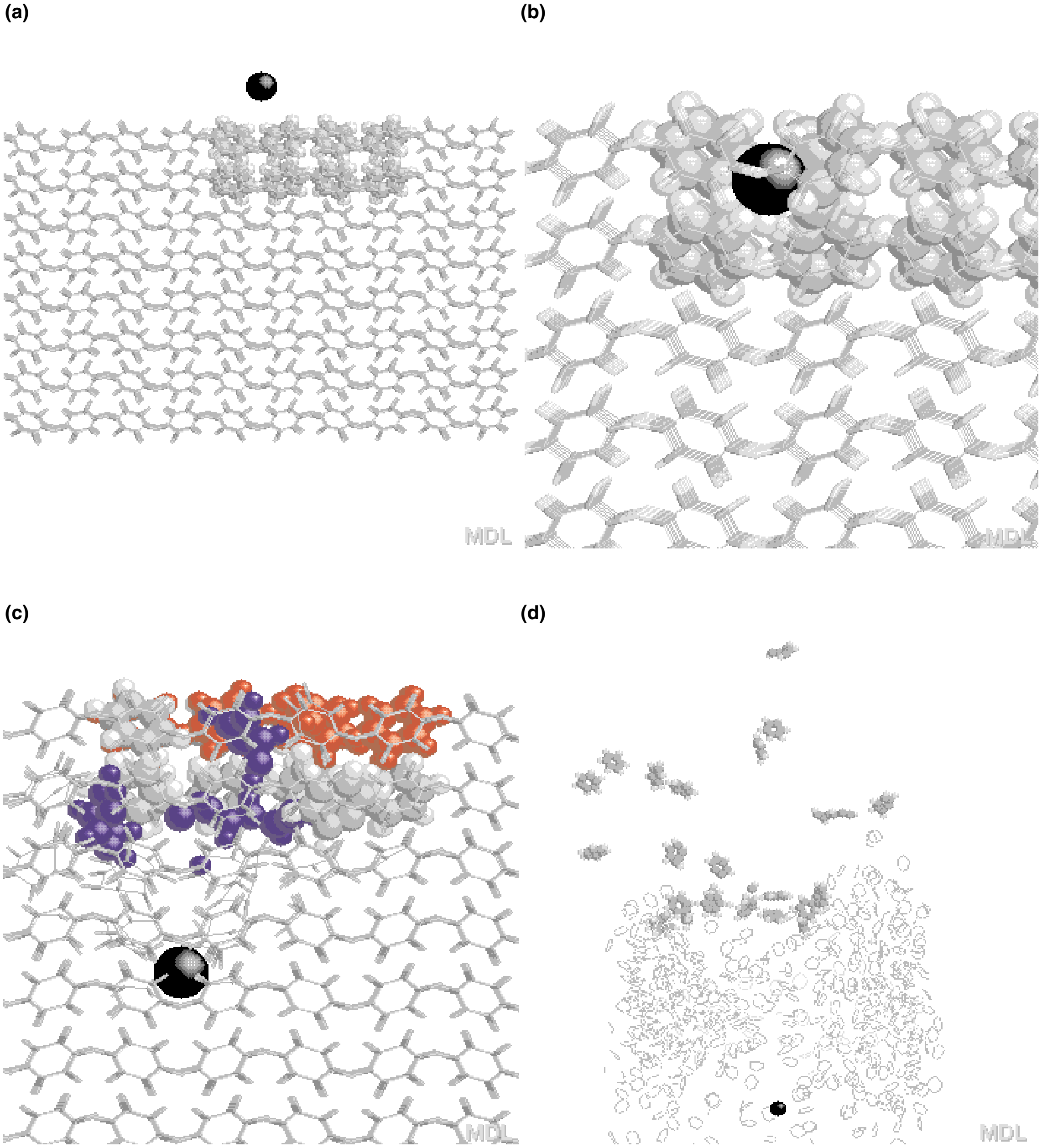

Fig. 2. Illustration of a sample trajectory. Spheres are used to portray the molecules in the affected region of the crystal while wireframes are used to show the remaining molecules in the crystal. Fragmented molecules (blue) initiate gentle collision cascades that lift molecules (red) off the surface. (a) 0 fs. (b) 30 fs. (c) 110 fs. (d) 3000 fs.

that attractive potential energy brings these fragments together. It is plausible that energy released when the radicals combine contributes to the ejection of additional molecular species.

In making the transition from the REBO potential used in previous simulations [1] to the AIREBO potential [2] used here, the cut-off distance in the force calculations increases from ∼2 to

10 Å with a concomitant increase in computer time. For example, a 5 ps trajectory on the molecular solid requires approximately 24 h compared with 3–5 h for a trajectory of an organic film on a metal substrate. A significant challenge is to extend these calculations to more realistic energies of 5 keV, which will require bigger crystals and longer computational times.

4. Conclusions

Preliminary molecular dynamics simulations of the keV bombardment of a molecular solid have been performed with the AIREBO potential. A potential with both intramolecular and intermolecular interactions is used to model the molecular solid. The advantage of this potential is that it incorporates intermolecular interactions while still maintaining the reactive nature of the potential. The model system consists of normal incidence 0.30 keV Xe impacting the (0 1 0) plane of a benzene crystal. With this potential, the cohesive energy per molecule is 0.40 eV, which is comparable to the experimental value.

The purpose of the simulations is to initiate our understanding of how collision cascades develop in molecular solids leading to the ejection of molecules and molecular fragments from the solid. We find that fragments formed by the initial collision can act to further the collision cascade, creating more fragments and putting intact molecules into motion. In addition, we find one radical–radical recombination event that could possibly contribute kinetic energy to the cascade from the exothermicity of the chemical reaction. As we move the simulations towards higher incident energies traditionally used in experiments, we anticipate these events continue to play a role in the collision cascade although their relative importance is presently unknown.

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References

[1] B.J. Garrison, A.D. Delcorte, K.D. Krantzman, Acc. Chem. Res. 33 (2000) 69.
[2] S.J. Stuart, A.B. Tutein, J.A. Harrison, J. Chem. Phys. 112 (2000) 6472.
[3] S. Hobday, R. Smith, U. Gibson, A. Richter, Radiat. Eff. Def. Sol. 142 (1997) 301.
[4] R. Smith, S. Hobday, R. Webb, In: J.L. Duggan, I.L. Morgan, (Eds.), Applications of Accelerators in Research and Industry, AIP Press, New York, 1997, p. 515.
[5] R. Smith, K. Beardmore, Thin Solid Films 272 (1996) 255.
[6] B.J. Garrison, Chem. Soc. Rev. (1992) 155.
[7] B.J. Garrison, D. Srivastava, P.B.S. Kodali, Chem. Rev. 96 (1996) 1327.
[8] E.G. Cox, Proc. R. Soc. A 135 (1932) 491.
[9] E.G. Cox, D.W.J. Cruickshank, J.A.S. Smith, Proc. R. Soc. A 247 (1958) 1.
[10] G.E. Bacon, N.A. Curry, S.A. Wilson, Proc. R. Soc. A 279 (1964) 98.
[11] D.J. Evans, R.O. Watts, Mol. Phys. 31 (1976) 83.
[12] D.W. Brenner, Phys. Rev. B 42 (1990) 9458.
[13] D.W. Brenner, Phys. Rev. B 46 (1992) 1948.
[14] D.W. Brenner, J.A. Harrison, C.T. White, R.J. Colton, Thin Solid Films 206 (1991) 220.
[15] R.S. Taylor, B.J. Garrison, Langmuir 11 (1995) 1220.
[16] H.P. Steinrück, Surf. Sci. 218 (1989) 293.