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Cluster induced chemistry at solid surfaces: Molecular dynamics simulations of keV C_{60} bombardment of Si

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Abstract

Molecular dynamics simulations of the sputtering of Si by keV C_{60} bombardment have been performed as a function of incident kinetic energy at two incident angles, normal incidence and 45°. Nearly all of the C atoms remain embedded in the surface after bombardment because the C atoms from the projectile form strong covalent bonds with the Si atoms in the target. At low incident kinetic energies, the sputtering yield of Si atoms is small and there is a net deposition of solid material from the projectile atoms. As the incident kinetic energy is increased, the yield of sputtered Si atoms increases. A transition occurs in which the yield of sputtered Si atoms exceeds the number of C atoms deposited, and there is a net erosion of the solid material. A significantly higher sputter yield is observed at an incident angle of 45° than at normal incidence, and therefore, the energy value is lower for the transition from net deposition to net erosion. This phenomenon is discussed in terms of the depth distribution of deposited energy, which is found to be shallower at an incident angle of 45°.
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1. Introduction

Secondary ion mass spectrometry (SIMS) experiments have established that polyatomic projectiles have the potential to greatly increase the sensitivity of static SIMS [1–4]. The recent development of stable, long-lived C_{60}^+ and gold cluster sources that can be focused down to a size of μm [5,6] has inspired a renewed interest in the use of cluster projectiles in SIMS experiments. An advantage of C_{60}^+ over other polyatomic projectiles is the combination of the type and number of atoms in the cluster. There is mass matching between the carbon atoms in the projectile and atoms in targets of organic materials, which has been shown to be an important factor in producing high sputtering yields [7,8]. In addition, the large total number of atoms in the incident C_{60}^+ projectile means that each atom has a relatively small amount of energy, which results in less penetration of the projectile into the surface. Simulations comparing the bombardment of Ag with Ga and C_{60} have demonstrated that the damage produced by C_{60} is shallower and there is less interlayer mixing in the lower layers of the target material [9,10]. Consequently, there has been increasing enthusiasm in exploring C_{60}^+ for both imaging [11,12] and depth-profiling applications [11,13].

In experiments of the 15 keV C_{60}^+ bombardment of Si at angles of incidence of 0, 45 and 60°, Hill and Blenkinsopp have observed high sputtering yields with minimal damage to the surface [5]. However, more recent studies of depth profiling of silicon wafers using C_{60} by Gillen et al. have shown that complications arise because of the deposition of carbon atoms from the projectile into the silicon substrate [14,15]. At low incident kinetic energies, the

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sputtering signal disappears and a buildup of material is produced. When the incident kinetic energy of C_{60}^{+} is increased, the sputtering signal increases until a net erosion of material is observed.

Recently, we have reported results from preliminary molecular dynamics simulations of the bombardment of Si with a normal incident C_{60} projectile as a function of incident kinetic energy [16]. The pairing of C_{60}^{+} as the primary ion with Si as the target material results in a unique experimental system that is in a class by itself. The carbon atoms in the bombarding projectile can make strong covalent bonds with the silicon atoms in the target, which can result in the formation of a strong alloy, SiC. SiC has a greater cohesive energy of 6.165 eV per atom than the cohesive energy of 4.63 eV per atom in pure Si. The simulations predict the formation of strong covalent bonds between the C and Si atoms, which result in nearly all of the C atoms remaining embedded in the surface after bombardment. Such bonds are not formed in the pairing of C_{60}^{+} with Ag or an organic solid. At low incident kinetic energies, little sputtering of Si atoms is observed and there is a net deposition of solid material. As the incident kinetic energy is increased, the sputtering yield of Si atoms increases until the number of Si atoms sputtered from the surface is greater than the number of C atoms from the projectile implanted into the solid and there is a net erosion of material. Previous molecular dynamics simulations of the bombardment of different Si surfaces with C_{60} have shown that Si–C bond formation reduces the sputtering yield, and this effect depends on both the incident angle and the surface plane [17,18].

In this paper, we describe the results of molecular dynamics simulations of the sputtering of Si with C_{60} as a function of incident kinetic energy and angle. Simulations are performed at 45° and normal incidence. Almost all of the C atoms are implanted into the Si target at impact energies up to 20 keV at both impact angles because of the formation of strong Si–C bonds, and therefore, a transition from net deposition to net erosion of the solid material is observed. However, bombardment at 45° produces a greater sputtering yield of Si atoms, which is in agreement with experimental data [5] and molecular dynamics simulations of the sputtering of Si with C_{60} [17] and with Al_n and Au_n ($n = 1$–2) projectiles [19]. These results can be explained by an analysis of the depth distribution of energy deposited by the bombarding projectile.

2. Method

The classical method of molecular dynamics simulations is used and is described extensively elsewhere [20,21]. The model system is a Si{100} microcrystallite containing 248 768 atoms arranged in 23 layers of 10 186 atoms with the top layer of Si atoms placed in the (2×1) reconstruction. The randomly oriented C_{60} projectile is placed at a sufficient distance above the surface that the interaction potential is negligible. The results at each incident kinetic energy are calculated as an average over four trajectories at arbitrarily chosen impact points with the velocity vector pointing either along or under 45° with respect to the surface normal. The size of the crystal with dimensions of $200 \times 200 \times 120\ \text{Å}^3$ is chosen to minimize the effects of the edges of the crystal on the processes essential to the bombardment event. The microcrystallite is surrounded by a heat bath composed of one layer of rigid atoms and two layers of atoms kept at 0 K by a frictional force, which is used to prevent energy induced by pressure waves being reflected from the boundary walls back into the surfaces. This method is explained extensively in previous simulations of the keV bombardment of Ag{111} with C_{60} [9].

An empirical many body potential developed by Tersoff [22] is used to model the Si–Si, C–C and Si–C interactions. The empirical parameters in the potential are fit to the energetics and structure of Si, diamond and SiC. The repulsive potential between Si and C at small interatomic distances is modeled by the Ziegler, Biersack and Littmark (ZBL) potential [23]. An exponential spline function is used to smoothly connect the ZBL potential with the two-body Tersoff Si–C potential [24].

3. Results and discussion

In Fig. 1, the yield of sputtered Si atoms and the number of implanted C atoms are plotted as a function of incident kinetic energy at impact angles of normal incidence and 45°. The standard deviations of the averaged results over four trajectories at each kinetic energy are shown as error bars. At both impact angles, nearly all of the C atoms in the projectile react with the Si atoms in the target material and remain implanted in the solid, regardless of the inci-

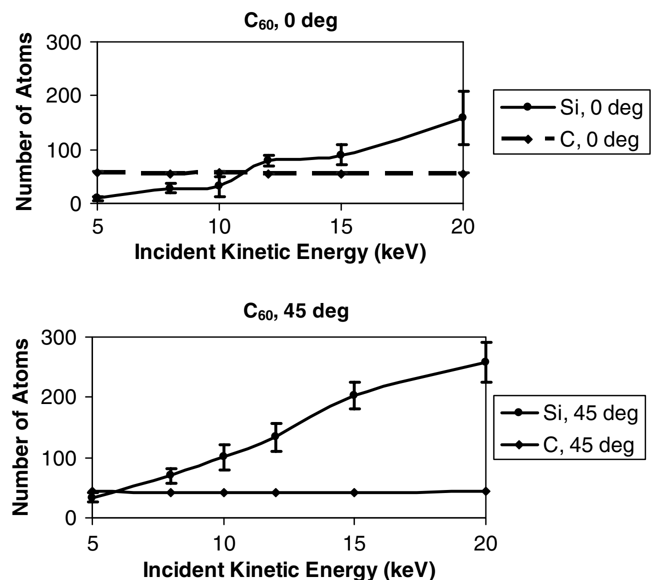

Fig. 1. Average yield of sputtered Si atoms and number of implanted C atoms resulting from the bombardment of Si with a C_{60} projectile as a function of incident kinetic energy and impact angle.

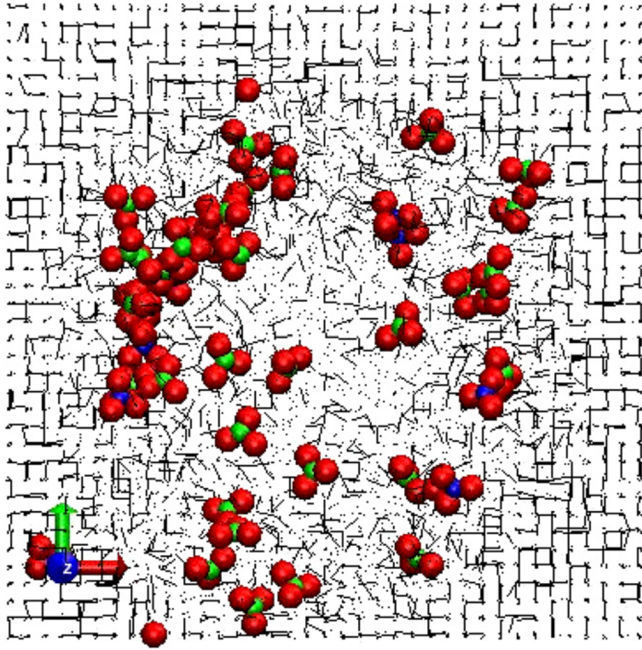

Fig. 2. Top view of the silicon target crystal at 5000 fs after bombardment with a 15 keV C_{60} projectile. at normal incidence. All carbon atoms embedded in the crystal are bonded to silicon atoms. Carbon atoms with three bonds are represented by blue spheres and carbon atoms with four bonds are represented by green spheres. Silicon atoms which are bonded to the carbon atoms are shown as red spheres. (For interpretation of the references to the colour in this figure legend, the reader is referred to the web version of this article.)

dent bombarding energy. The sputtering yield of Si atoms increases with incident kinetic energy. When more C atoms from the C_{60} projectile are implanted into the Si solid than the number of atoms ejected, there is a net deposition of material. As the kinetic energy increases, the number of implanted C atoms is fairly constant, but the yield of sputtered Si atoms increases until a transition is reached and there is a net erosion of material.

Fig. 2 shows a portion of the Si crystal at 5.0 ps after bombardment with 15 keV C_{60} at normal incidence. It is clear that the projectile has broken up into separate C atoms and nearly all of the carbon atoms from the incoming projectile are incorporated into the target crystal. All of the implanted C atoms have bonded to three or four Si neighboring atoms in the lattice. This is not surprising because C forms a stronger bond with Si than Si does with itself, and therefore, it is energetically favorable for Si–C bonds to replace Si–Si bonds.

The dependence of the sputtering yield on the incident kinetic energy can be explained by an analysis of the energy density deposited by the projectile. The volume of the damaged region of the surface can be determined by a visual inspection of the solid surface after the bombardment process. The volume can be estimated as a hemisphere with a radius of 30 Å, which contains approximately 2830 Si atoms. At an incident energy of 5 keV, the C_{60} projectile gives on average of 0.9 eV of potential energy to each atom in this hemispherical zone, which is much less than the binding energy of 4.6 eV. At 20 keV, the C_{60} projectile transfers an average of 4.4 eV per atom in this region, thereby producing a significant number of ejected Si atoms.

At an impact angle of 45°, the sputtering yield of Si atoms is greater and the number of C atoms implanted into the solid is slightly smaller than at an impact angle of normal incidence at all kinetic energies. Consequently, the energy value for the transition from net deposition to net erosion depends on the impact angle. At normal incidence, the yield of ejected atoms does not exceed the number of implanted C atoms until an incident kinetic energy of 15 keV; whereas at an impact angle of 45°, this transition is reached somewhere between 5 and 10 keV.

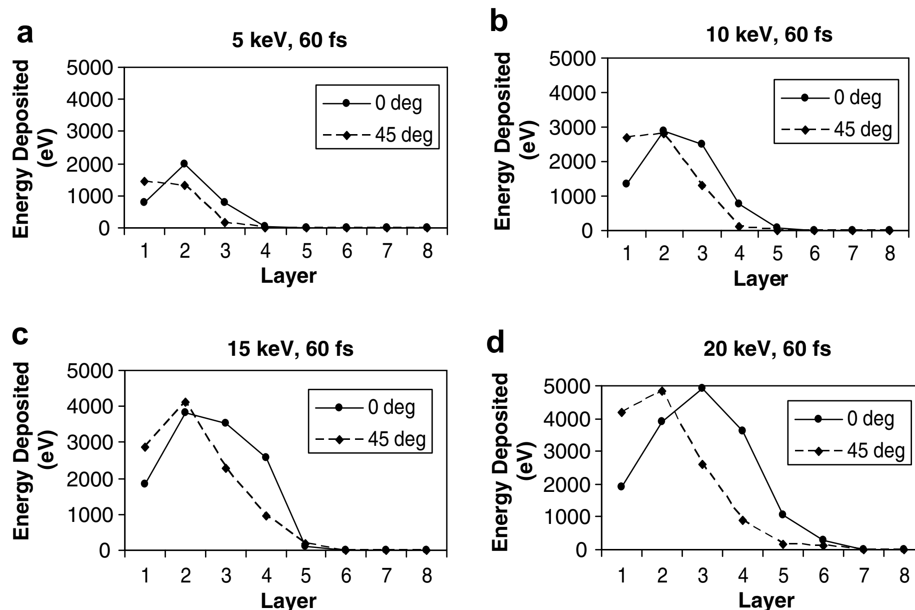

Fig. 3. Depth distributions of the energy deposited by the C_{60} projectile at a time of 60 fs during the bombardment process.

The dependence of the sputtering yield on impact angle can be understood by an analysis of the energy distribution as a function of the layer depth. The majority of sputtered Si atoms are from the two uppermost layers of the Si crystal. In Fig. 3, the total energy transferred at 60 fs is shown as a function of the layer of Si atoms in the crystal. This time is chosen because the depth distribution of the energy early in the bombardment process determines the mechanistic process essential to the sputtering of atoms from the surface [25,26]. The number of the Si layer is shown on the *x*-axis, with "1" being the topmost layer and "8" representing the eighth layer from the top. The energy transfer to atoms below the eighth layer is negligible. At an impact angle of 45°, more energy is transferred to the upper layers of the silicon crystal, thereby producing a greater number of sputtered Si atoms.

4. Conclusions

Molecular dynamics simulations of the bombardment of a silicon crystal with C_{60} are used to understand and interpret the puzzling experimental results. Of greatest concern is the observation at low kinetic energies that the sputtering signal is extinguished and there is a buildup of material on the surface [14,15]. An analysis of the solid surface after the bombardment process shows that the atoms in the projectile are trapped by the solid material. When the number of sputtered silicon atoms is less than the number of atoms in the projectile, then it seems reasonable to assume that a solid material must build up on the surface, leading to a net deposition instead of the typical removal of material observed with other targets. At low incident kinetic energies, the energy per atom transferred by the C_{60} projectile is not sufficient to overcome the binding energy of 4.6 eV. Therefore, chemical reactions between Si and C atoms that lead to the formation of strong Si–C bonds is the underlying reason for the unusual results observed in the bombardment of Si with C_{60}.

The simulations predict that the sputtering yield is greater at 45° incidence than at normal incidence, which is in agreement with experimental data [5]. The majority of sputtered atoms are from the two uppermost layers in the Si crystal. More energy is transferred to the uppermost layers of the crystal when the projectile is brought in at 45°, which leads to a greater number of ejected Si atoms from the surface. Therefore, the simulations predict that the transition energy threshold will be greater at an impact angle of 45° than at normal incidence.

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