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Bombardment induced surface chemistry on Si under keV C_{60} impact

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Abstract

Molecular dynamics simulations of the sputtering of Si by C_{60} keV bombardment are performed in order to understand the importance of chemical reactions between C atoms from the projectile and Si atoms in the target crystal. 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. 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. At 15 keV, the yield of sputtered Si atoms is more than twice the number of C atoms deposited, and there is a net erosion of the solid material.

Keywords: ToF-SIMS; Cluster ion; C_{60}^+; Sputtering; Si

1. Introduction

Secondary ion mass spectrometry (SIMS) experiments have shown that the use of polyatomic projectiles may increase the secondary ion yield by an order of magnitude or more [1–4]. In the past few years, there has been a focus on C_{60}^+ as a primary ion, which demonstrates unique characteristics because of the small energy per atom [5,6]. There is a large enhancement in secondary ion yield with a relatively small amount of damage to the surface. Molecular dynamics simulations of the keV bombardment of Ag [7,8] have compared the sputtering yield and surface damage with Ga and C_{60} projectiles. C_{60} produces a significant enhancement in sputter yield and the damage is confined to a shallower, narrower area of the surface. Recently, a stable, long-lived C_{60}^+ source has been developed that can be focused down to a size of micrometers [9]. Therefore, the C_{60}^+ ion beam shows promise in both imaging [6,10] and depth-profiling applications [6,11]. With the possibility of three-dimensional imaging becoming closer to fruition, there is increasing enthusiasm about the properties of C_{60}^+ as a cluster ion beam [6].

Experiments have measured the sputtering yield produced by the bombardment of Si with 15 keV C_{60}^+ at different angles of incidence. High sputtering yields with minimal damage to the surface were observed [12]. However, there is a problem with C_{60}^+ ions that has caused some concern. Experiments using C_{60}^+ projectiles on a Si target have demonstrated that a buildup of a solid material forms in certain circumstances. Experiments by Gillen et al. [13] of the sputtering of Si with C_{60}^+ showed that the sputtering signal disappears and a buildup of material is produced at low incident kinetic energies. When the incident kinetic energy of C_{60}^+ is increased, the sputtering signal increases.

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 compound, 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. Such bonds are not formed in the pairing of C_{60}^+ with Ag or an organic solid.

There is some debate about the chemical identity of the solid material observed. Recently, a chemical analysis of the material by Fahey et al. [14] indicates that the solid is amorphous carbon. However, it is reasonable to speculate that SiC is formed during the intermediate stages of depth profiling because the strength of the Si–C bond is stronger than the C–C bond. Furthermore, there is a lower concentration of carbon atoms during the initial stages of depth profiling.

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In this paper, molecular dynamics simulations of the sputtering of a Si crystal with a C_{60} projectile are described. In order to examine how the sputtering yield depends on the incident kinetic energy of the bombarding projectile, simulations are performed with kinetic energies ranging from 1 to 20 keV. In addition, the simulations are used to examine the structure of the target crystal after bombardment to determine whether chemical reactions have taken place between the C and Si atoms.

2. Description of the simulations

The classical method of molecular dynamics simulations is used to study the system of interest, and the application of this method to keV bombardment of solids is explained comprehensively elsewhere [15,16]. The model system is a Si{1 0 0} 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 dimensions of the crystal are 200 Å × 200 Å across and 120 Å deep. Simulations were performed with a normal incident C_{60} projectile at kinetic energies ranging from 1 to 20 keV. Only one trajectory was calculated at each kinetic energy. The impact point was chosen to be in the center of the target crystal. All orientations of the projectile are equal because of its symmetry. An empirical many body potential developed by Tersoff [17] 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.

3. Results and discussion

3.1. Sputtering yield

The net result of the C atoms in the projectile and the Si atoms in the target are shown in Fig. 1 as a function of the initial kinetic energy of the C_{60} projectile. The observed difference in the sputtering yield between 15 and 20 keV impact energy is not significant, because the results shown here are for only one trajectory. Further trajectories need to be calculated in order to obtain a clearer picture of the statistical error associated with these values. Nevertheless, the results show a definite trend that is in agreement with experimental observations.

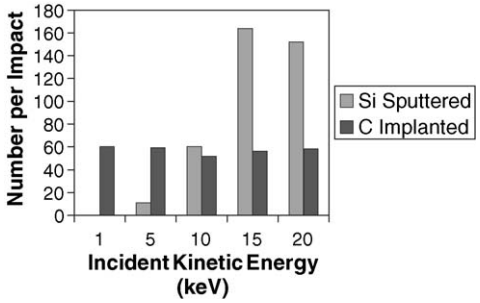

Fig. 1. Number of C atoms implanted and number of Si atoms sputtered from C_{60} keV bombardment of Si at normal incidence.

Nearly 100% 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 incident bombarding energy. However, the sputtering yield of Si atoms depends strongly on the incident kinetic energy of the projectile. At low kinetic energies, the sputtering yield goes to zero. In this case, more atoms are deposited onto the surface by the C_{60} bombardment than the number of ejected atoms, which results in the prediction of a net deposition of solid material. As the incident kinetic energy is increased, the sputtering yield of Si atoms increases, while the number of carbon atoms implanted remains fairly constant. At an incident energy of 15 keV and above, more than twice as many silicon atoms are ejected as the number of carbon atoms implanted into the target, and therefore, the simulations predict a net erosion of the solid material.

3.2. Analysis of the target crystal after impact

Fig. 2 shows a portion of the silicon crystal at 8.3 ps after bombardment with 10 keV C_{60}. The blue spheres represent the carbon atoms from the impinging projectile. It is clear that the projectile has broken up into separate carbon atoms and bonds are formed between the carbon atoms and the silicon atoms in the target. Consequently, nearly all of the carbon atoms from the incoming projectile are incorporated into the target crystal. Carbon forms a stronger bond with silicon than silicon does with itself. Therefore, it is energetically favorable for the carbon atoms to remain implanted in the surface and form bonds with the silicon atoms.

The results of the simulations explain how the net sputtering yield observed experimentally depends on the incident kinetic energy of the bombarding projectile. The atoms in the projectile are trapped by the solid material because of the strong covalent

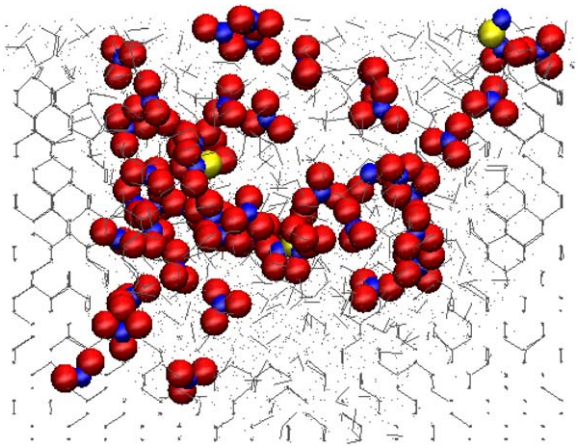

Fig. 2. Side view of the silicon target crystal at 8250 fs after bombardment with a 10 keV C_{60} projectile at normal incidence. The blue atoms spheres are carbon atoms from the incoming projectile. Silicon atoms with one or more carbon atoms as neighbors are shown as spheres. The remaining silicon atoms in the crystal are shown as lines. Silicon atoms with one carbon atom as a neighbor are colored red and silicon atoms with two carbon atoms as neighbors are colored yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

bonds that form. 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.

The structure of this deposit is not clear at the present time due to several reasons. First, the simulations are not carried to large enough times to include recrystallization effects at the end of the collision cascade. Second, the influence of successive impacts onto the same surface area is unknown. In principle, it is conceivable that the incorporation of C into the Si surface leads to a larger average surface binding energy of Si atoms, thereby reducing the initial yields depicted in Fig. 1. In principle, this may lead to a self-poisoning effect, switching from initial erosion to net deposition with accumulation of projectile fluence. As the number of sputtered silicon atoms becomes greater than the number of atoms deposited from the projectile, there will be a net effect of erosion of the target material.

4. Conclusions

Simulations of the bombardment of a silicon crystal with C_{60} are performed in order to explore how the sputtering yield depends on the incident kinetic energy. Chemical reactions occur between carbon atoms from the projectile and silicon atoms in the solid, which result in the formation of strong covalent bonds. Consequently, nearly all of the carbon atoms from the bombarding projectile remain implanted in the silicon crystal. At low incident kinetic energies, a negligible amount of silicon atoms are sputtered from the crystal, and consequently, a net deposit of solid material on the surface is predicted. As the incident kinetic energy increases, the yield of sputtered silicon atoms increases. At about 10 keV, the amount of deposition and sputtering are approximately equal, producing no net change in the quantity of solid material. At 15 keV, more than twice as many silicon atoms are sputtered by the impact as the number of projectile atoms embedded in the crystal, leading to a net erosion of the solid.

The pairing of the C_{60} projectile with the silicon target material results in a unique situation because of the strong covalent bonds that can form between carbon and silicon atoms. The simulations predict that these chemical reactions may in some cases result in the formation of a solid deposit on the surface. This is a good explanation for the peculiar observations that have been made in SIMS experiments with C_{60} on silicon.

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