

Simulations of C₆₀ bombardment of Si, SiC, diamond and graphite

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Abstract

Molecular dynamics simulations of the 20-keV C₆₀ bombardment at normal incidence of Si, SiC, diamond and graphite targets were performed. The unique feature of these targets is that strong covalent bonds can be formed between carbon atoms from the C₆₀ projectile and atoms in the solid material. The mesoscale energy deposition footprint (MEDF) model is used to gain physical insight into how the sputtering yields depend on the substrate characteristics. A large proportion of the carbon atoms from the C₆₀ projectile are implanted into the lattice structure of the target. The sputtering yield from SiC is ~ twice that from either diamond or Si and this can be explained by both the region of the energized cylindrical tract created by the impact and the number density. On graphite, the yield of sputtered atoms is negligible because the open lattice allows the cluster to deposit its energy deep within the solid. The simulations suggest that build up of carbon with a graphite-like structure would reduce any sputtering from a solid with C₆₀⁺ bombardment.

Keywords: ToF-SIMS; Molecular dynamics simulations; C₆₀⁺; silicon; carbon

1. Introduction

In the past few years, there has been a focus on C₆₀⁺ as a primary ion in secondary ion mass spectrometry (SIMS) experiments, which demonstrates unique characteristics because of the small energy per atom [1-2]. The substantial yield enhancement and reduced substrate damage make it an ideal candidate for molecular depth profiling [1]. However, the results of depth profiling using C₆₀⁺ on Si show puzzling results [3]. At low incident energies, there is no sputtering yield and a carbon deposit is formed on the surface. As the kinetic energy is increased, a sputtering yield is observed, but the yield is extinguished as carbon builds up on the surface. At high incident energies, the deposited carbon produces unusual topographical features on the surface [3].

We have previously reported results from molecular dynamics simulations of a single impact of C₆₀ on Si{100} [4-5] at incident energies ranging from 5 keV to 20 keV at both normal and 45 degree incidence angles. The sputtering yields at 45 degree incidence are greater than those at normal incidence [5], in agreement with experiments by Hill and Blenkinsopp [6]. Almost all of the carbon atoms from the projectile are deposited in the surface and form covalent bonds with the silicon atoms in the target. As the energy is increased, the number of atoms sputtered from the surface exceeds the number of carbon atom deposited by the projectile, and a transition from net deposition to net erosion occurs. This transition occurs at ~12 keV, in agreement with the trend shown in the depth profiling experiments [3].

Numerous studies on the bombardment of C and Si materials with carbon atoms and fullerene projectiles have been performed by Smith, Webb and co-workers [7-12]. Simulations of 1-keV carbon impact onto graphite{1000}, diamond {100} and diamond {111} show very small sputtering yields [7, 8]. Previous molecular dynamics simulations of the bombardment of Si{100} and Si{111} with C₆₀ have shown that Si-C bond formation reduces the sputtering yield, and this effect depends on both the incident angle and surface plane [9-11]. More recently, Webb has described energetic cluster induced adsorption on graphite [12]. Anders et. al. have studied the fragmentation of the C₆₀ projectile and the depth of the cluster range on graphite and fullerite crystals [13].

The simulations described in this paper focus on how the energy density distribution deposited by the cluster impact and the resulting yield depends on the characteristics of the substrate. We performed molecular dynamics simulations of the bombardment of four different substrates composed of Si and C: Si{100}, SiC{100}, diamond{100} and graphite{1000}. The unique feature of these substrates is that the projectile atoms form strong covalent bonds with the target atoms, which results in the incorporation of projectile atoms in the target. The mesoscale energy deposition footprint (MEDF) [14-17] model gives physical insight into how the sputtering yields depend on different characteristics of the substrate. The yield on graphite is essentially zero because of the open nature of the lattice, which allows the entire C₆₀ projectile to penetrate deep into the crystal. The energy deposited is too far below the surface to be effective for producing sputtering.

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 [18]. The {100} face with dimerized surface atoms are used for the Si, SiC and diamond model systems. The micro crystallite 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 crystallite [19]. Simulations of graphite{1000} used periodic boundary conditions in the lateral dimensions and free boundaries in the direction normal to the surface [12].

Simulations were performed with a normally incident 20-keV C₆₀ projectile, which was chosen because it is within the erosion regime, but is still low enough to be computationally feasible. The potentials used to model the Si-Si, Si-C and C-C interactions are described in prior work [4-5], and the potentials used for the graphite simulations have also been described previously [12]. The physical ideas resulting from this model should not be significantly affected by changing the energy of the projectile [4], the angle of incidence [5], the crystal face [7, 10-11] or particulars of the potentials used [11].

3. Results and Discussion

3.1 Sputter and Implantation Yields

In Table 1, results from the molecular dynamics simulations on the four different crystals are reported for a single trajectory of 20-keV C₆₀ bombardment at normal incidence. The number of implanted and sputtered C atoms and the resulting net number of removed C atoms is shown for each substrate. Nearly all of the projectile atoms are implanted in the Si and graphite targets. Consequently, C₆₀ bombardment of Si and graphite will result in a buildup of carbon on the surface. A large fraction of the carbon atoms from C₆₀ are also deposited in the denser targets, SiC and diamond. However, the yield of sputtered carbon atoms is larger than the number of deposited carbon atoms, and there is a net removal of carbon atoms from the surface.

Examination of the total yield of sputtered C and Si atoms from each target shows that SiC has a sputtering yield almost two times greater than that for either Si or diamond. The total sputtering

yield is slightly higher for diamond than for Si, while the sputtering yield for graphite is negligible. By comparing the net number of Si and C atoms gained or lost for each substrate, we can conclude that graphite is the only target that will have a net buildup of material on the surface.

Table 1. Number of deposited C and sputtered C and Si atoms for a single impact. A positive value signifies sputtering (erosion) and a negative number signifies deposition for the net number of atoms.

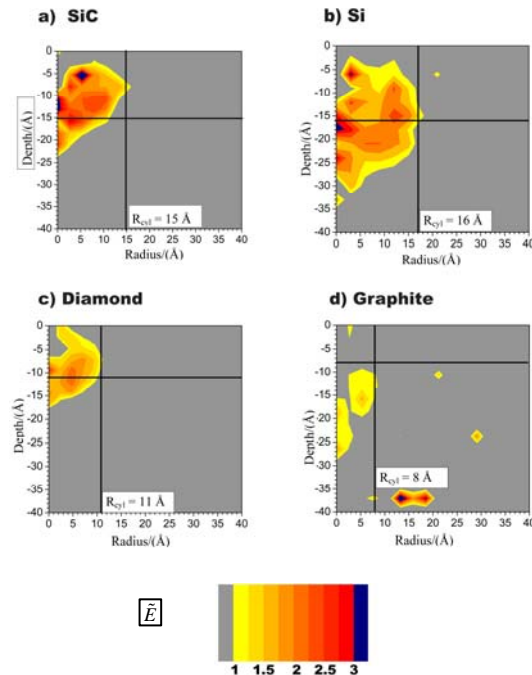
| Crystal | C Atoms Implanted | C Atoms Sputtered | Net C Atoms | C and Si Atoms Sputtered | Net C and Si Atoms |
|----------|-------------------|-------------------|-------------|--------------------------|--------------------|
| SiC | 39 | 228 | + 189 | 506 | + 467 |
| Si | 57 | ----- | - 57 | 185 | + 128 |
| Diamond | 38 | 254 | + 216 | 254 | + 216 |
| Graphite | 60 | 5 | - 55 | 5 | - 55 |

3.2 Application of MEDF model

The mesoscale energy deposition footprint (MEDF) model [14-17] gives physical insight into the differing behaviors of the targets following C_{60} bombardment. The basic ideas and application of the model to simulations of keV bombardment are described in detail elsewhere [15-17]. The trend in yields from the simulations can be understood by examining three critical factors incorporated into this model, i.e., the number density and binding energy of the substrate, and the region where the projectile deposits its energy in the solid.

Contour plots of the average excitation energy deposited within the first 100 fs after impact are shown in Fig. 1. It is evident that the radius and depth of the energy deposition region depend on the target material. In SiC, the energy is deposited in a surface region where it is effective for ejection. In Si, the energy is deposited too deep below the surface to be effective. In diamond, the energy is deposited within a very small region of radius R_{cyl} with much of the energy being deposited below a depth of R_{cyl} . Graphite is a very open substrate and the entire projectile can penetrate into the target leaving no energy in the surface region to promote sputtering.

Figure 1: Contour plots of the excitation energy \tilde{E} for 20-keV C_{60} bombardment of the four substrates. Vertical lines are drawn to show the estimated radius, R_{cyl} , and the horizontal lines depict the depth equal to R_{cyl} .



As explained in detail elsewhere [15-17], the sputtering yield can be estimated by the number of atoms within the initial footprint, a cone with surface radius, $R_s = (\tilde{E})^{1/2} R_{cyl}$, and depth R_{cyl} . In Table 2, the essential factors in the calculation of the MEDF yield are presented along with the MEDF predicted yields and the yields obtained from the simulations. SiC has the highest yield because it has a high number density and the energy is deposited in a relatively wide cylinder with a depth close to the surface. Si has a moderate yield because it has a low number density and the energy is deposited too deep into the target because of its open lattice structure. Diamond has a moderate yield even though it has a high number density, because the energy is deposited in a cylinder with a small R_{cyl} . The yield on graphite is essentially zero because the energy is deposited way too deep in the solid to result in sputtering. The yields from the simulations show a comparable trend to those predicted by the MEDF model.

Table 2. Comparison of sputter yields predicted by the MEDF model and those obtained from the full MD simulations for 20-keV C_{60} bombardment.

| Crystal | Number Density (Atoms·Å ⁻³) | R_{cyl} (Å) | Cohesive Energy (eV) | \tilde{E} | MEDF Yield | Simulation Yield |
|----------|--|---------------|-------------------------|-------------|---------------|---------------------|
| SiC | 0.099 | 14 | 6.165 | 1.5 | 502 | 506 |
| Si | 0.05 | 16 | 4.63 | 1.2 | 264 | 185 |
| Diamond | 0.18 | 11 | 7.37 | 1.2 | 289 | 254 |
| Graphite | 0.11 | 8 | 7.42 | ----- | ----- | 5 |

4. Implications for depth profiling by C_{60} bombardment

The conceptual ideas included in the MEDF model give us a physical understanding of why the sputtering yield with C_{60} depends so dramatically on the characteristics of the target material for Si, SiC, diamond and graphite. These results allow one to make some predictions about depth profiling in silicon by C_{60} . Initially there is the ability to make a SiC like material that will have a larger sputtering yield than Si, although interestingly the volume of material removed for Si and SiC is similar. Upon further bombardment, and possibly enhanced by diffusion processes, a carbonaceous material can develop. The important issue is whether sp^3 hybridized carbon (diamond-like) or sp^2 hybridized carbon (graphite-like) material is formed. If the deposited carbon has a graphite-like structure, the simulations predict the sputtering yield will significantly decrease. Buildup of graphite-like carbon could also occur for organic and carbon based polymers, thus again suppressing the sputtering yields.

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