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Effect of Si–C bond formation in 20 keV C_{60} bombardment of Si

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We have performed molecular dynamics (MD) simulations to investigate the effect of Si–C bond formation on fluence-dependent results in 20 keV C_{60} bombardment of Si. Sputter depth profiling experiments of C_{60} on Si have produced atypical results, which are thought to be caused by the strong covalent bonds that are formed between the C atoms in the projectile and Si atoms in the substrate. A recently developed scheme developed by Russo, *et al*.[8] has been adapted to perform MD simulations of 150 successive impacts of 20 keV C_{60} on Si, which corresponds to a total fluence of 2.64×10^{13} impacts/cm^2. In order to isolate the effects of Si–C bond formation, the same set of trajectories is calculated with and without the attractive Si–C potential energy terms. When Si–C bonds are able to form, nearly all the C atoms from the projectile are incorporated into the substrate. When the possibility of Si–C bond formation is removed, most of the C atoms are backscattered into the vacuum. The cumulative result is that the substrate with Si–C bonds contains a factor of twenty times more C atoms, which are located below the surface.
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Introduction

C_{60} ion beams have been successful for high-resolution sputter depth profiling of metallic multilayer structures.[1] However, when applied to Si, sputter depth profiling experiments by Gillen, *et al*.[2] have shown unique results. No sputtering signal is observed at low-incident kinetic energies. As the incident kinetic energy is increased, a sputtering signal is measured and there is a transition from net deposition to net erosion. However, even at higher-incident kinetic energies when the surface is initially eroded, the sputtering rate steadily decreases until erosion stops and carbon deposition occurs. Similar effects have also been observed during large-scale depth profiling of some organic materials.[3]

Previous MD simulations of single impacts of C_{60} on a Si surface have been able to explain some of the unusual observations[4] Strong bonds can be formed between projectile C atoms and substrate Si atoms, which lead to nearly all the atoms from the projectile being incorporated into the surface. As the incident kinetic energy increases, the sputtering yield of Si increases until it exceeds the number of incorporated C atoms, and there is a transition from net deposition to net erosion. Simulations of C_{60} bombardment were also performed on other group IV materials that may represent the substrate during intermediate stages of depth profiling[5] The MEDF model[6] was used to analyze the results, and it was determined that the yield depends on the region of the energized cylindrical tract created by the impact and the number density of the substrate. The sputtered yield on SiC is a factor of two times greater than on either silicon or diamond, because the projectile deposits its energy in a region effective for sputtering. On graphite, no atoms are sputtered because the open lattice allows the cluster to deposit its energy deep within the solid[7] The simulations suggest that the formation of a carbon deposit with a graphite-like structure would reduce, or perhaps even quench, sputtering from the solid.

The insights gained from these single-impact MD simulations are limited because they cannot model the cumulative result of successive bombardments on the surface. In this paper, the preliminary results of multiple-impacts of 20 keV C_{60} at normal incidence on a single Si microcrystallite are presented. In order to isolate the effect of Si–C bond formation, these results are compared to those obtained from simulations calculated without any Si–C attractive potential energy terms.

Description of the Simulations

The simulations use a 'divide and conquer' scheme developed by Russo *et. al.*,[8] which outlines a protocol for using MD simulations[9] to treat multiple projectile impacts on the same surface area. The entire silicon surface is modeled by a Si(100) crystal with dimensions of 24 nm × 24 nm × 18 nm containing 511 104 atoms arranged in 66 layers of 7744 atoms, with the top layer of Si atoms placed in the (2 × 1) reconstruction. The Si sample is successively bombarded by 20 keV C_{60} projectiles at normal incidence on a set of impact points chosen randomly over the entire surface of the Si crystal. The trajectory for each impact point is run using a smaller cylindrical sample extracted from the major crystal, and then reinserted after the trajectory is complete. An empirical many-body potential developed by Tersoff[10] is used to model the Si–Si, C–C and Si–C interactions. The same set of trajectories is calculated with and without the Si–C attractive terms in the

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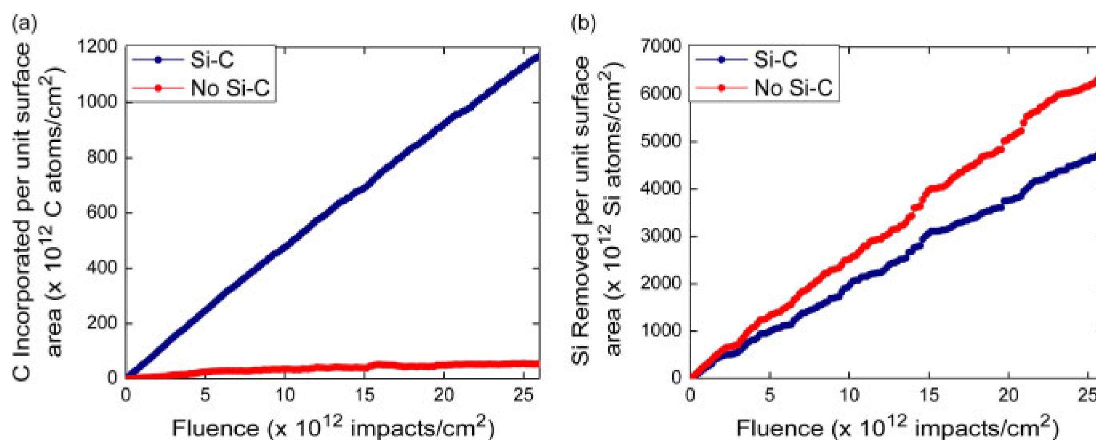

Figure 1. Plots of C incorporation and Si removal as a function of fluence. The legend titles, Si–C and No Si–C, correspond to results from trajectories run with and without the Si–C attractive potential. a) Cumulative number of C atoms incorporated per unit surface area. b) Cumulative number of Si atoms removed per unit surface area.

potential energy function. In order to remove the Si–C attractive portion of the potential, the b_{ij} term for the attractive interaction between Si and C in the pairwise term of the potential (Eqn 1a in Ref. [10]) is set to zero in the Tersoff potential[10] In addition, ω_{ij} is set to zero (Eqn 1d in Ref. [10]), so that there are no Si–C interactions in the many-body terms of the potential. Details about the methodology used in the simulations are described in another paper[11]

Results and Discussion

C incorporation and Si removal

In Fig. 1a), the cumulative number of C atoms incorporated into the substrate per unit surface area is plotted as a function of fluence for the simulations with and without the Si–C attractive potential energy terms. In the simulations with the attractive terms, the average number of C atoms from the projectile left in the substrate after bombardment is 49.9. Without Si–C bond formation, only an average of 7.2 C atoms from the projectile remains after each impact. Furthermore, few of the incorporated C atoms are sputtered during subsequent impacts with the Si–C attractive potential. Without it, 71% of the incorporated C atoms are sputtered during later impacts. The cumulative effect is substantial, and, after 150 impacts, the Si substrate contains 21 times more C atoms when Si–C bond formation is included in the simulations.

The cumulative number of Si atoms removed per unit surface area as a function of fluence is shown in Fig. 1b). After 150 impacts, the cumulative sputtering yield of Si is a factor of one-third greater when the Si–C attractive potential is removed. When Si–C bonds are formed, less Si atoms are sputtered during each impact. Each of the first 10 impacts is, essentially, on a fresh, undisturbed portion of the surface. The average number of Si atoms sputtered per impact during the first 10 impacts is 245 and 297 with and without the Si–C potential, respectively. After 150 impacts, the averages are 184 and 244 Si atoms. Therefore, the greater number of Si atoms sputtered without the Si–C potential is not due to changes in the surface due to accumulation of C atoms in the Si substrate. Interestingly, the difference between the average number is approximately equal to the number of C atoms in the C_{60} projectile. When bonds are formed, the C atoms increase the effective surface binding energy of the Si atoms, thereby decreasing the number sputtered.

Effect of C_{60} bombardment on surface topography and composition

Successive bombardment of C_{60} on the Si substrate results in a significant change in the surface topography. When the C_{60} projectile bombards the fresh undisturbed surface, the impact produces a crater centered at the impact which is surrounded by a rim of Si atoms. The static limit occurs at ∼10 impacts, where there is still little overlap between the disturbed regions. Once C_{60} bombards regions already disturbed by former impacts, a complex and ever-changing topography evolves. Top views of the crystal after 150 impacts are shown in Fig. 2. Si atoms have been moved from below to above the surface, which results in mounds of Si shown by the yellow regions. Erosion has also occurred, which is indicated by the blue, purple and pink regions. In both cases, mounds of Si atoms as high as 3 nm above the surface, and craters as deep as 7 nm below the surface are formed. The number of black points indicates the greater number of C atoms in the substrate when the simulations include Si–C bond formation.

In the near-surface region ranging from 2 nm above and below the original surface height, only ∼5% of the total atoms are carbon with the Si–C attractive potential. Therefore, the simulations have not been run long enough to accumulate enough impacts to make a significant change in the surface composition. In Fig. 1a), the cumulative yield of sputtered Si atoms shows a linear dependence on fluence. Therefore, changes in the substrate due to successive bombardment have not changed the sputtering rate. The simulations are currently running in order to obtain enough impacts to affect the chemical composition of the substrate in the near-surface region.

In order to obtain a better picture of the height of the C atoms in relation to the surface, Fig. 3 shows three-dimensional visualizations of the same crystals shown in Fig. 2. The light gray isosurface represents the boundary between regions with and without Si atoms. The isosurface representation of the surface shows the same mounds and craters illustrated by colors in Fig. 2. The dark gray isosurface representations show the boundaries between regions with and without C atoms. It is clear from the images that the C atoms are below the surface and the number is greater when Si–C bond formation is included.

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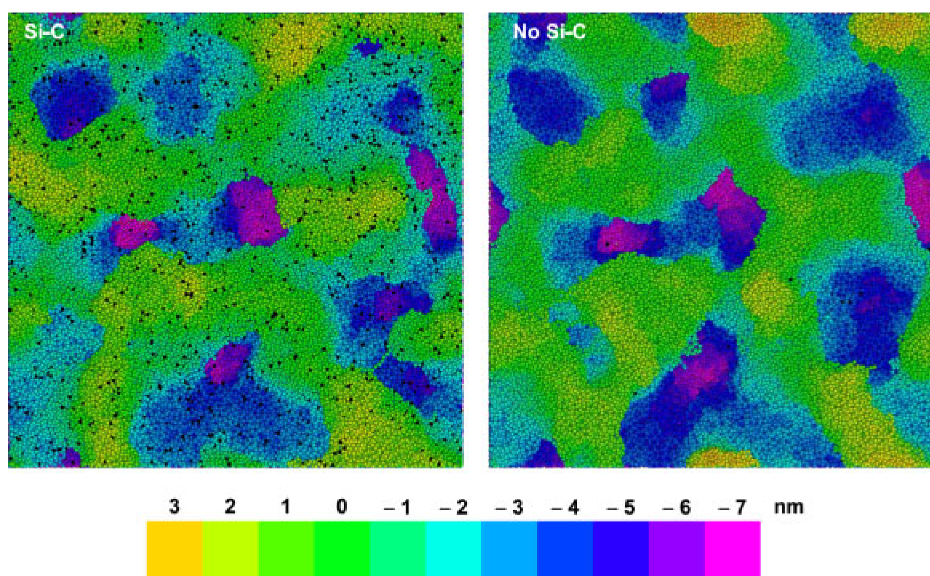

Figure 2. Top view of the entire sample after 150 impacts with atoms colored by height with and without the Si–C-attractive potential. The color scheme is based on the vertical positions of the atoms from a depth of 7.0 nm below to 3.0 nm above the height of the original surface. The black points correspond to the positions of the C atoms incorporated into the substrate.

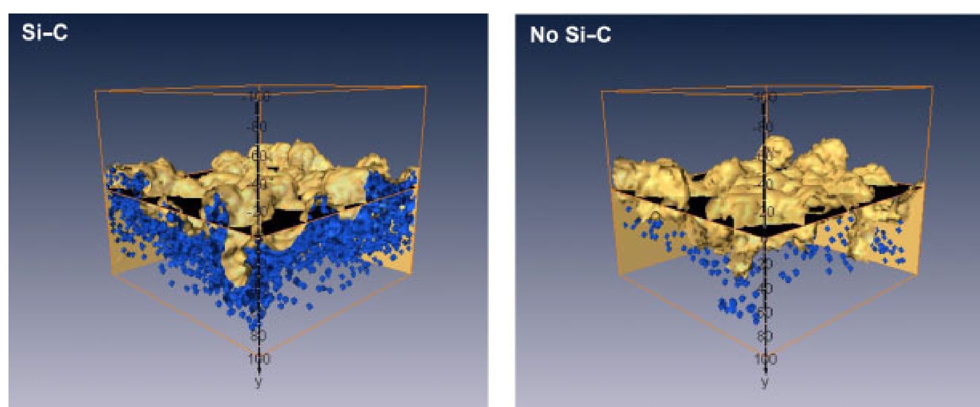

Figure 3. Isosurface representations of the surface after accumulation of 150 impacts. Details are provided in the text.

Conclusion

Implications for sputter depth profiling of Si with C_{60}

In multi-impacts of Si with 20 keV C_{60}, C atoms are incorporated into the substrate because of the strong Si–C covalent bond that can be formed. C atoms implanted upon impact are not sputtered during later impacts because they are covalently bonded to other atoms and are located fairly deep within the surface. As a result, the number of C atoms accumulated in the substrate increases with fluence. From these preliminary simulations, it is clear that the possibility of bond formation between projectile and substrate atoms can lead to an increasing C concentration in a region of the substrate below the surface. Many more impacts are needed make a significant change in the chemical composition of the near-surface region of the crystal.

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References

[1] S. Sun, A. Wucher, C. Szakal, N. Winograd, *Appl. Phys. Lett.* **2004**, *84*, 503.
[2] G. Gillen, J. Batteas, C. A. Michaels, P. Chi, J. Small, E. Windsor, A. Fahey, J. Verkouteren, K. J. Kim, *App. Surf. Sci.* **2006**, *252*, 6521.
[3] G. L. Fisher, M. Dickinson, S. R. Bryan, J. Moulder, *Appl. Surf. Sci.* **2008**, *255*, 819.
[4] K. D. Krantzman, D. B. Kingsbury, B. J. Garrison, *Appl. Surf. Sci.* **2006**, *252*, 6463.
[5] K. D. Krantzman, B. J. Garrison, *J. Phys. Chem. C* **2009**, *113*, 3239.
[6] M. F. Russo, Jr., B. J. Garrison, *Anal. Chem.* **2006**, *78*, 7206.
[7] K. D. Krantzman, R. P. Webb, B. J. Garrison, *Appl. Surf. Sci.* **2008**, *255*, 837.
[8] M. F. Russo, Z. Postawa, B. J. Garrison, *J. Phys. Chem. C* **2009**, *113*, 652.
[9] B. J. Garrison, Z. Postawa, *Mass Spectrom. Rev.* **2008**, *27*, 289.
[10] J. Tersoff, *Phys. Rev. B* **1989**, *39*, 5566.
[11] K. D. Krantzman, A. Wucher, *J. Phys. Chem. C* **2010**, *114*, 5480.

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