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A statistical analysis of the lateral displacement of Si atoms in molecular dynamics simulations of successive bombardment with 20-keV C_{60} projectiles

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ABSTRACT

An important factor that determines the possible lateral resolution in sputter depth profiling experiments is ion induced lateral displacement of substrate atoms. Molecular dynamics (MD) simulations are performed to model the successive bombardment of Si with 20 keV C_{60} at normal incidence. A statistical analysis of the lateral displacement of atoms that originate from the topmost layer is presented and discussed. From these results, it is determined that the motion is isotropic and can be described mathematically by a simple diffusion equation. A "diffusion coefficient" for lateral displacement is determined to be 3.5 $Å^2$/impact. This value can be used to calculate the average lateral distance moved as a function of the number of impacts. The maximum distance an atom may move is limited by the time that it remains on the surface before it is sputtered. After 800 impacts, 99% of atoms from the topmost layer have been removed, and the average distance moved by these atoms is predicted to be 100 Å. Although the behavior can be described mathematically by the diffusion equation, the behavior of the atoms is different than what is thought of as normal diffusion. Atoms are displaced a large distance due to infrequent large hops.

1. Introduction

One of the most commonly used surface analytical techniques is Secondary Ion Mass Spectrometry (SIMS), where bombardment of a solid surface by primary high energy ions leads to a series of complex events that ultimately result in the ejection of secondary ions from the solid. The composition of the sample surface can then be determined by mass spectrometric analysis of the sputtered ions. Lateral two-dimensional images may be obtained by scanning the primary ion beam across the sample and analyzing the sputtered ions pixel by pixel. Characterizing complex multilayer structures is achieved through sputter depth profiling, in which material is systematically removed from the sample by ion induced erosion. After each step of removing approximately 1 nm layer of material, the momentarily exposed surface is analyzed in order to determine the composition of each layer.

Recently, the introduction of cluster ion beams, particularly C_{60}^+, has put SIMS in the spotlight because of the possibility of its application to molecular sputter depth profiling [1]. Experiments show that C_{60}^+ bombardment produces a significant enhancement in sputter yield, i.e., the average amount of material removed from the surface in a single impact. Moreover, chemical damage induced by the ion impact is confined to a shallower region below the surface. The combination of both effects makes C_{60}^+ an outstanding candidate for the three-dimensional chemical characterization of a solid on a molecular level [2–6], thus opening up a large range of applications to both biology and nanotechnology. Both the depth and lateral resolution are factors important in defining the possible success of sputter depth profiling experiments.

In the past 25 years, molecular dynamics (MD) simulations have contributed immensely to our understanding of the processes underlying the bombardment of atomic and molecular solids with keV atomic projectiles [7]. However, these simulations are of limited use in understanding depth profiling experiments because they refer to the "static" case, where an ideal solid surface is exposed to single, decoupled projectile impacts. Simulations capable of modeling processes essential to understanding sputter depth profiling are a major computational challenge because the surface needed to include the results of multiple impacts must be much larger than for a single impact. Recently, Russo et al. have developed a "divide and conquer" protocol to overcome this challenge by dividing the entire surface into sub regions, which are affected individually by different impacts [8]. The trajectories for the sub regions can be calculated separately, which reduces the number of atoms included in the calculation.

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We have applied this method to perform MD simulations of multi-impact bombardment of Si with C_{60} [9,10]. One focus of our previous work on this system has been to understand factors that limit depth resolution by examining the vertical displacement of substrate atoms. A problem with the simulations is that they are computer intensive and it is time-consuming to achieve fluences comparable to those used in experiments. Therefore, we used a statistical sputtering model to extrapolate to fluences beyond those calculated in the simulations.

An important factor that determines the lateral resolution is the distance by which substrate atoms can move laterally – i.e., in a direction parallel to the initial sample surface – across the surface as a result of successive bombardment. In the past, numerous models describing bombardment-induced particle relocation – often termed "ion beam mixing", "cascade mixing", "collisional mixing" etc. – have appeared, ranging from a simple diffusive approach [11] to rather sophisticated Monte-Carlo simulations [12]. MD treatments of this phenomenon have so far been restricted to the static limit, where each projectile impinges onto a perfect crystal surface [13]. In this paper, we re-analyze the data presented in Ref. [9] to study the effect of accumulating projectile fluence on the lateral relocation (i.e., the bombardment induced relocation in any direction parallel to the original surface) of surface atoms. More specifically, we present a statistical analysis of the lateral movement of Si atoms as a function of the number of successive impacts as predicted by multi-impact MD simulations. The results are compared to those predicted by a diffusion-like description of the particle relocation dynamics. The main goal is to derive the "diffusion constant" as the essential parameter of such a macroscopic model from the microscopic MD data and compare the result with simple analytical predictions.

Assuming that the lateral displacement increases with projectile fluence, the maximum possible distance an atom may move could in principle increase indefinitely. However, it is important to remember that there is the competing processing of sputtering, which ultimately removes the atoms from the solid. Therefore, the maximum possible lateral distance a surface atom can be relocated is determined by the length of time it remains on the surface before it is sputtered. Using the MD data in connection with a simple statistical extrapolation, it is possible to determine this quantity, which may be of interest in sputter depth profiling applications.

2. Methods

The classical method of molecular dynamics simulations is used to describe the motion of the atoms as a function of time. The application of this method to model ion bombardment of solids has been discussed in a recent review article [7]. The "divide and conquer" scheme developed by Russo et al. [8] to treat multiple impacts on a single surface has been adopted. A detailed description of the simulations as applied to C_{60} bombardment of Si is described elsewhere [9,10]. 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 large master Si crystal. The trajectory for each impact point is run using a smaller cylindrical sample extracted from the master crystal and then reinserted after the trajectory is complete. The forces between the atoms are modeled using well-established empirical many-body potentials to describe the Si–Si, Si–C and C–C interactions [14].

For the sake of simplicity, the study is limited to the motion of atoms that originate from the topmost monolayer of atoms in the solid. The depth of a monolayer is defined as $d_{\text{layer}} = n^{-1/3}$, where n is the number of density of atoms. In Si, atoms that are less than 2.517 Å below the original surface are classified as being from the top monolayer. If the lateral motion is statistical in nature and the displacement is large compared to that resulting from a single impact, the probability of finding a particular lateral displacement Δr from the atom's original position can be described by [11].

$$p(\Delta r) = \frac{\Delta r}{2Dt} \exp\left(-\frac{\Delta r^2}{4Dt}\right), \tag{1}$$

where the parameter D has the meaning of an irradiation-induced effective diffusion coefficient and t is the time. In the present context, the diffusive treatment is invoked to describe the effect of successive projectile impacts onto the same surface area. Each impact induces massive particle relocation on a very short (picosecond) time scale, which is followed by a comparatively long time before another impact influences the same surface area. Neglecting all particle motion during that intermediate time, the time variable in Eq. (1) can be replaced by the projectile fluence f, resulting in another "diffusion coefficient" D' which has the physical dimensions of area per unit fluence. Using the known surface area $A = (24\ \text{nm})^2$ of our model crystal, the latter can then be characterized by the number of successive impacts, thus yielding a third "diffusion coefficient" D'', which is connected to the specific value of A and is reported in units of area per impact. From this viewpoint, it is irrelevant how much time is used to accumulate a specific fluence f, and Eq. (1) becomes

$$p(\Delta r) = \frac{\Delta r}{2D''N_{\text{imp}}} \exp\left(-\frac{\Delta r^2}{4D''N_{\text{imp}}}\right), \tag{2}$$

where N_{imp} is the total accumulated number of impacts. The average value of the square lateral displacement, $\langle \Delta r^2 \rangle$, depends linearly on f or N_{imp} as

$$\langle \Delta r^2 \rangle = 4D'f = 4D''N_{\text{imp}}. \tag{3}$$

The parameter D'' can then be obtained from the slope of a plot of $\langle \Delta r^2 \rangle$ as a function of N_{imp}.

3. Results

The square of the distance moved by each substrate atom from the topmost layer is calculated and the average value is determined for each impact. If the motion is statistical in nature and can be described by a diffusion equation, Eq. (2) shows that $\langle \Delta r^2 \rangle$ should depend linearly on the number of impacts with a slope equal to $4D''$. Fig. 1 shows a plot of $\langle \Delta r^2 \rangle$ as a function of N_{imp}, and it is seen that a straight line shows a good fit to the data. The slope of the line is 13.9 Å^2/impact, yielding $D'' = 3.5$ Å^2/impact. In order to compare with analytical calculations given, for instance, in Ref. [11], this value can be converted to fluence units by multiplying by the square of the surface area, which results in a value of $D' = 20.2\ \text{nm}^4$. From a simple estimate of the parameters relevant for 500-keV Ar^+ irradiation of copper, Haff et al. arrive at $D \sim 7.8$ Å^2/s for a projectile ion current density of 6×10^{14} ions/cm^2 s. Converted to fluence units, this corresponds to $D' \sim 0.013\ \text{nm}^4$, a value which is much smaller than that determined here. In contrast, experimental data obtained for high-fluence 600-eV Ar^+ bombardment of tungsten [15] reveal $D \sim 1.6 \times 10^3$ nm^2/s at 3.75×10^{17} ions/cm^2 s, yielding $D' \sim 0.43\ \text{nm}^4$. In view of the much larger impact energy along with the fact that cluster projectiles were used here instead of atomic projectiles, the finding of a larger value of D' appears reasonable.

In addition to being displaced, Si atoms in the topmost layer can be removed from the surface by sputtering. With successive bombardment, the number of Si atoms originally from the topmost layer decreases. A plot of the fraction of Si atoms originally from the topmost layer as a function of the number of impacts is shown

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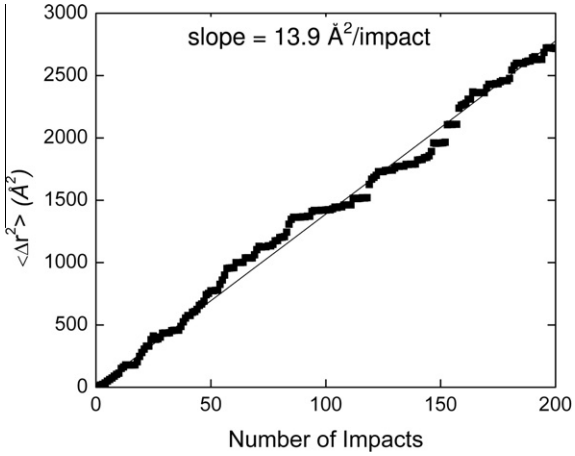

Fig. 1. Linear dependence of the square of the lateral distance on impact number. The average of the square of the distance of each atom from its original value is calculated for each impact point. The data can be fit to an equation for a straight line and is used to calculate the diffusion coefficient, D'', as explained in the text.

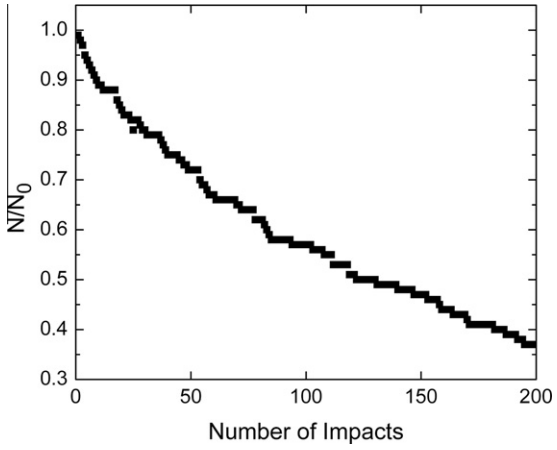

Fig. 2. Fraction of atoms remaining that originate from the topmost layer are shown as a function of impact. After 200 impacts, more than 30% of these atoms are still in the substrate and have not been sputtered.

in Fig. 2. The layers of material are not removed in a sequential fashion, and the fraction of Si from the first layer shows an exponential decrease with the number of impacts. After 200 impacts of 20 keV C_{60}, a total of five monolayer equivalents (ML) of material is removed, but 37% of the atoms originating from the topmost layer are still in the solid sample. From the statistical sputtering model (SSM) developed in Ref. [9], it can be estimated that 20 ML of material must be removed in order to remove 99% of atoms originally located in the topmost layer, which requires approximately 800 impacts. Using the value of D'' determined from Fig. 1, the value of $\sqrt{\langle \Delta r^2 \rangle}$ at this fluence can be calculated from Eq. (3) to be 100 Å. Therefore, the simulations along with the SSM model predict that atoms from the topmost layer can move a maximum distance of about 100 Å before being sputter removed from the surface.

It is interesting to examine the frequency distribution of distance moved per impact for the Si atoms. This is calculated by determining the number of atoms that move a certain distance for each impact and then averaging this value over the 200 impacts. The resulting plot is shown in Fig. 3. From this plot, it can be seen that the dominant peak occurs at the smallest distance of 0–5 Å. Therefore, the atoms have the greatest probability of

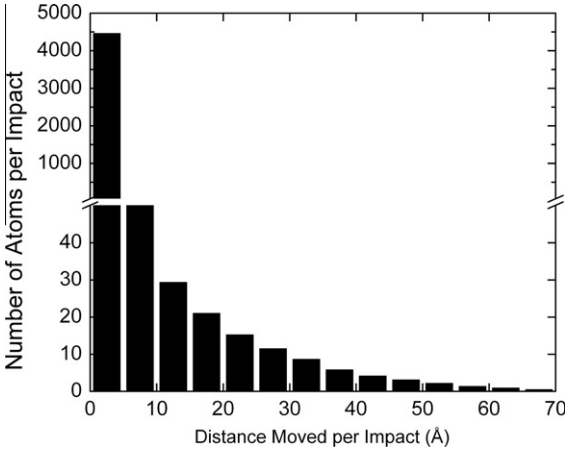

Fig. 3. Distribution of lateral distance moved per impact. Most of the atoms move a small amount during each impact. The frequency of movements of large distances is small.

moving a negligibly small distance, which indicates that most of the atoms are not affected by each impact. This finding is in principle expected, since only a relatively small portion of the total surface area is influenced by a single impact event, leaving many of the surface atoms untouched. Therefore, the first bar in Fig. 3 should in principle be disregarded. The remaining distribution reflects the true probability distribution of individual relocation distances in the course of a single impact event. One can see that relocation over distances up to ~70 Å may occur. Only a few atoms will move such over large distances, and analysis reveals that these atoms must be located close to the impact point.

In order to get an impression of how much the Si atoms move during 200 impacts, the distribution of lateral relocation distance after irradiation to that fluence is shown in Fig. 4. As expected from Eq. (1), the fraction of atoms that move a particular distance Δr increases and reaches a maximum value at $\Delta r = 31.5$ Å. Again, it is seen that the maximum relocation distance is of the order of 100 Å as evaluated above. In order to examine the consistency of the diffusive approach, the prediction of Eq. (2) is fitted to the MD data as indicated in Fig. 4. The best fit is found for a value $D'' = 2.7$ Å^2/impact (solid line in Fig. 4). If the value of 3.5 Å^2/impact determined from Eq. (3) is inserted, we find a slightly worse fit (dotted line in Fig. 4). In both cases, however, the general features of the relocation distribution are reasonably well reproduced by

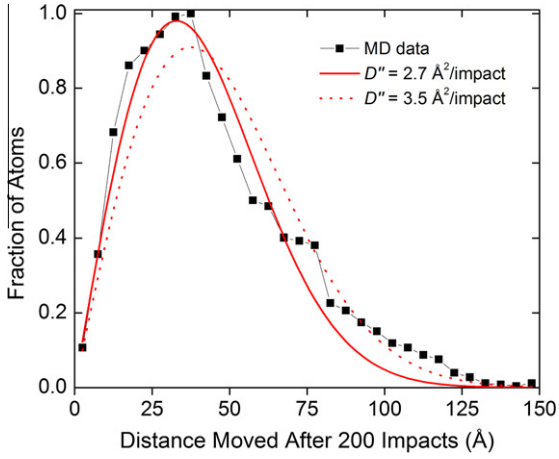

Fig. 4. The distribution of the lateral distance moved after 200 impacts of non-sputtered Si atoms. The most probable distance moved is 31.5 Å.

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Eq. (2). Note, however, that although the lateral motion of atoms can be formally described by the diffusion equation, the motion identified by the molecular dynamics simulations does not behave in the way diffusion is normally characterized. The total distance travelled is not a result of an accumulation of even, small hops over each impact. Rather, the distance moved is small during most of the impacts. During a few impacts, the atoms move a large distance (see Fig. 3), and these large hops make the greatest contribution to the total distance moved.

4. Conclusions

The lateral relocation of the atoms from the original topmost layer in the solid can be described mathematically by a simple diffusion equation. The value of the "diffusion coefficient", D, can be used to determine the average displacement as a function of time, or, in this case, the number of impacts. Atoms are not removed sequentially from the solid and 37% of atoms from the topmost layer are still in the solid after 200 impacts in which a total of five ML equivalents of material have been removed. We find that surface atoms can be laterally relocated by a total distance of the order of 100 Å before being removed by sputter erosion.

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