MOLECULAR DYNAMICS INVESTIGATIONS OF ENERGETIC
CLUSTER BOMBARDMENT OF METAL-ORGANIC INTERFACES
AND ORGANIC SOLIDS

A Dissertation in
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by
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ABSTRACT

The objectives of this dissertation are two-fold and are related by the underlying theme of utilizing molecular dynamics simulations to investigate the different types of damage inflicted on substrate materials by the impacts of energetic clusters. Accumulation of such damage can lead to unsuccessful secondary ion mass spectrometry depth profiling experiments.

The first objective is to develop and test a methodology for incorporating reactions in cluster bombardment simulations, which has been shown to be difficult due to the high computational cost of such simulations. Initially, a reactive force field used to describe the interactions between atoms was tested for its ability to model reactions related to the build-up and removal of damage during depth profiling experiments of two organic polymers. Next, a protocol for a mixed resolution model was designed that partitioned a test sample of solid benzene into atomistic and coarse-grained regions. The atomistic region incorporated interactions described by a complex reactive potential, and the coarse-grained region’s interactions were described by simple two-body potentials. Test simulations showed that the dynamics of cluster bombardment transferred smoothly between the regions of the mixed resolution system. Finally, as a proof of principle, the molecular benzene system was used in simulations of energetic C$_{60}$, Ar$_{18}$ and Ar$_{60}$ cluster bombardments to analyze the overall differences in sputtering yields and damage formation. The results from the C$_{60}$ bombardment were also used in an investigation that successfully determined the relationship between C$_{60}$ and Ar in cobombardment experiments.
The second objective of this dissertation is to elucidate through MD simulations the difficulties in SIMS depth profiling experiments of metal-organic interfaces. By performing C$_{60}$ bombardment simulations on systems composed of varying metal overlayer thicknesses on an organic substrate, the dynamics related to the early ejection of substrate molecules along with the implantation of metal clusters in the substrate were uncovered. Results from these simulations provide a clear picture of the dynamics occurring in the SIMS depth profiling experiments.

The work presented in this dissertation is beneficial to the theoretical and experimental advancement of the SIMS field. The mixed resolution model has shown that both a reactive atomistic and coarse-grained description of a system can be used together in cluster bombardment simulations to greatly reduce their computational cost, which will enable its use in simulations to elucidate the chemical effects of cluster bombardment. For SIMS experimentalists, the simulations of the cluster bombardment of metal-organic interfaces have presented a microscopic view of the dynamics occurring during the bombardment process. A microscopic view that reveals the problems that must be overcome to successfully analyze materials that incorporate metal-organic interfaces with the SIMS technique.
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Chapter 1

Introduction

Since their inception, molecular dynamics (MD) computer simulations have been applied to a wide array of areas of research in order to collaborate with experimentalists in interpreting their data and propose new experiments. The field of secondary ion mass spectrometry (SIMS) has greatly benefited from the microscopic view of the experiment that MD simulations have provided.\textsuperscript{1-11} For instance, MD simulations have been instrumental in describing some of the key advantages of the use of cluster over atomic ion beams in SIMS experiments.\textsuperscript{2,9,12-17} These advantages have enabled cluster ion beams to be used in depth profiling and 3D imaging SIMS experiments of molecular solids such as polymers,\textsuperscript{18} biological materials\textsuperscript{19} and organic electronic devices.\textsuperscript{20} The chemistry and dynamics resulting from the interactions of clusters impacting these and similar materials can have significant effects on the outcomes of the SIMS experiments. As with the initial MD studies of cluster bombardment of primarily atomic solids, MD simulations can play an important part in elucidating the chemical and dynamic effects associated with cluster bombardment of molecular solids. Modeling such systems can however be challenging due to the sizes of the systems, complex number of interactions and the computational cost of including chemistry in the MD simulations. Therefore, the developments of new computational methodologies and simulation systems are required if MD simulations are to be used to investigate experimental SIMS phenomena associated with such complex molecular samples. The underlying theme of this dissertation is the development and
application of methods that will extend MD simulations to systems that are of interest to the SIMS community.

Prior to discussing how the theme of this dissertation will be implemented, first, a brief overview of the SIMS experiment with some historical notes on atomic vs. cluster ion beam use in SIMS experiments will be presented. Then some examples of how results from MD simulations of cluster bombardment can be directly correlated to SIMS experimental data will be given. Lastly, the importance of the different types of damage that can result in the bombarded solid as relates to depth profiling SIMS experiments will be highlighted.

1.1 SIMS Experiment

1.1.1 Technique

Secondary ion mass spectrometry (SIMS) is a surface analysis technique for studying solids and thin films that provides elemental and molecular information. The advantages SIMS has over other surface sensitive techniques are its ability to study samples neat or “as-received”, its sub-micrometer imaging capability, and its excellent surface sensitivity.17 These advantages have resulted in SIMS having a long history of use in the semi-conductor industry21 and to SIMS being applied to a wide array of materials such as polymers,18 nanomaterials20,22 and biological structures23-25

The SIMS technique uses an ion gun to direct an energetic beam of ions (i.e. primary ions), in the thousands of electron volts range, at a sample surface. The primary
ions can be atomic (e.g. Ar\(^+\), Cs\(^+\), Ga\(^+\)) or cluster ions (e.g. SF\(_5\)\(^+\), C\(_{60}\)\(^+\), Ar\(_{x}\)\(^+\)). The impact of the primary ions initiates collisional motion in the sample from which species are desorbed from the surface in what is called the sputtering process. Depending on the composition of the substrate, the sputtered species can be atoms, molecules or molecular fragments in a neutral, positive or negative ionic state (Figure 1-1). The sputtered ionic species (i.e. secondary ions) are directed into a mass analyzer, that determines each of the ion’s mass to charge ratio from which the sample can be identified.\(^{26}\) Also, the sputtered neutral species can greatly outnumber the sputtered ions, which has led to an extension of the SIMS technique called secondary neutral mass spectrometry (SNMS) where postionization of the neutral species (such as with a laser beam) can greatly increase the sensitivity of the SIMS experiment.\(^{27-29}\) Although, it is the use of high energy ion beams that enables the SIMS technique to be extended to the cutting-edge imaging experiments.
By moving the primary ion beam over the sample surface in a raster pattern, a 2D image can be taken of the sample, where every pixel of the image represents a recorded mass spectrum. To differentiate the domains of a biological sample in a 2D image, a high-spatial resolution is necessary. Currently, spatial resolutions to the sub-50 nm range have been attained with Bi$_3^{2+}$ clusters. The primary ion beam can also be used to erode away the surface layers. The collection of mass spectra as the primary ion beam sputters away the surface layers is called depth profiling an example of which can be seen in Figure 1-2 for the depth profiling of a sample composed of 1 nm thick layers, referred to as delta layers, of the organic molecule Irganox 3114 interspersed between 50 to 100 nm
Irganox 1010.\textsuperscript{31-33} The sharp peaks in Figure 1-2 clearly indicate the positions of the Irganox 3114 delta layers for depth profiling with Ar\textsubscript{1700} primary ions.\textsuperscript{33}

The combination of depth profiling with 2D imaging has led to one of the unique experiments in SIMS. During the depth profiling process, 2D images can be taken from which pixels can then stacked to form a 3D image\textsuperscript{34,35} as can be seen in Figure 1-3 for the 3D biochemical image of freeze-dried oocyte.\textsuperscript{19} The ability of energetic particles to depth profile is dependent on the nature of the interaction of the particle with the surface during impact and through the sputtering process. For instance, the interaction of atomic and cluster projectiles with the impacted surface are very different and give cluster ion beams advantages over atomic beams in certain applications. Over the past decade much experimental and theoretical work has been done to elucidate the processes related to cluster/surface interactions.

Figure 1-2. Left, depth profile of Irganox 3114/1010 sample with M\textsubscript{3114}—R\textsuperscript{−} secondary ion signal plotted against primary ion dose. The sharp peaks of the delta layers are indicators of excellent depth resolution being achieved. Right, schematic showing the structure of multilayered Irganox sample on silicon wafer.\textsuperscript{33}
Figure 1-3. Left, schematic of the stacking of 2D images used to generate a 3D image. Right, 3D image of freeze-dried oocyte where color scale is normalized for the total counts per pixel for the cholesterol peak at m/z 369.19

1.1.2 Early Cluster SIMS Experiments

Two advantages of using primary cluster over atomic ion sources were first identified by Applehans & Delmore over 20 years ago.36 They found that cluster beams yielded simplified mass spectra and extended the mass range that could be analyzed. Gillen et al. would use SF$_5^+$ and small carbon clusters (C$_x^-$, x = 2-10) to investigate the depth profiling capabilities of clusters compared to atomic beams.37,38 Depth profiles of organic thin films showed a significant increase in secondary ion intensity and a reduction in beam-induced damage in the substrate; whereas, for atomic primary ions or for small clusters like C$_2^-$ that behave like primary atomic ions, the secondary ion signal was quickly lost as can be seen in Figure 1-4.38 The glutamate signal produced by the larger C$_8^-$ cluster, in Figure 1-4, reaches a steady-state that indicates the continued removal of material, and the signal only drops off when the interface with the underlying
substrate is reached. It was hypothesized that the larger cluster was able to clean up the damage created by the cluster’s impact with the surface and that the distribution of the cluster’s kinetic energy over all the atoms of the cluster led to a more efficient transfer of energy to the surface upon impact, thus resulting in significantly higher sputtering yields. However, a microscopic view of what was occurring on the molecular level was lacking. A resource that the SIMS community could turn to, to provide such a view, were MD simulations. MD simulations had been successful in describing the collision cascade events produced by atomic projectiles impacting a solid surface.\textsuperscript{39-41} The MD simulations successfully provided a clear picture of the extent and depth of damage that resulted from the collision cascades initiated by atomic bombardment; thus, MD simulations were tasked to describe the cluster/solid interaction for energetic cluster bombardment of solid surfaces as well.

![Figure 1-4](image_url)

Figure 1-4. Time dependence of molecular ion emission for the parent molecular ion of a glutamate thin film bombarded with $\text{C}_2^-$ and $\text{C}_8^-$ cluster ion beams.\textsuperscript{38}
1.2 Molecular Dynamics Simulations

1.2.1 MD Basics

Before illustrating how molecular dynamics (MD) simulations have helped elucidate cluster bombardment and how results from MD simulations have correlated with experimental SIMS data thus providing validation of the use of MD to model cluster bombardment, it will be helpful to have some basic idea of what MD simulations are. Also, some mention should be made as regards to using classical mechanics and force fields or interaction potentials in MD simulations. How to actually perform MD simulations can be found elsewhere.42-44

Molecular dynamics simulations describe the evolution of a system of particles with respect to position and time through the application of Newton’s equation of motion that can be expressed as the following second-order differential equation:

\[ m_i a_i = m_i \frac{d^2 r_i}{dt^2} = F_i = -\nabla V(r_i), \text{ for } i = 1, ..., N \]  \hspace{1cm} (1-1)

or equivalently, as two first-order differential equations:

\[ m_i \frac{dv_i}{dt} = F_i \]  \hspace{1cm} (1-2)

\[ \frac{dr_i}{dt} = v_i \]  \hspace{1cm} (1-3)

where \( m_i \) represents mass and \( r_i, v_i, a_i \) and \( F_i \) are the position, velocity, acceleration and force of the \( i^{th} \) atom in an \( N \) atom system and are all vectors in three dimensions. The interaction potential, \( V(r_1, r_2, ..., r_N) \), is generally a function of the positions of all the atoms. By solving the equations of motion using algorithms based on finite difference...
methods, the positions and velocities of the atoms of the system can be calculated for a future time.

The atoms are assumed to be in their lowest electronic state throughout their motions. This is due to the classical nature of Newton’s equation of motion where no quantum effects are included and no excited electronic or ionic states are taken into account. Therefore, ionization events that are an integral part of SIMS experiments are not part of the MD simulations. The lack of quantum effects limits some avenues of investigation with respect to using MD simulations to model cluster bombardment; however, the nuclear motions of the atoms is at the heart of many processes, and their importance in elucidating some the key dynamical processes associated with cluster bombardment will be seen later.

How realistically the motions of the atoms of the system are described is directly dependent on the interaction potential, \( V(r_1, r_2, \ldots, r_N) \). Theoretically, the interaction potential could be described by the forces evaluated from the solution to the Schrödinger equation within the Born Oppenheimer approximation for each configuration of atoms in the system. Such calculations are still well beyond current computational technology for systems of hundreds of thousands of atoms. Therefore, interaction potentials are described by equations with functional forms that can represent the solution of the Schrödinger equation. The parameters to the equations are fit to experimental or quantum mechanical data. There is not a universal interaction potential that describes the chemistry and physics of every system well. The validity of a simulation is determined by a comparison of the results with experimental findings and depends fundamentally on the questions the simulation is trying to answer.
1.2.2 Cluster Vs. Atomic Bombardment

MD simulations conducted by Postawa and coworkers produced an excellent graphical presentation of the differences between atomic and cluster bombardment and can be seen in Figure 1-5 for the bombardment of an Ag{111} solid by 15 keV Ga in the left column and 15 keV C$_{60}$ on the right. The descending snapshots show the progression of the bombardment process over 29 ps. The layers of the systems are colored according to the Ag atoms original positions relative to the surface height. The projectile atoms are colored black and for Ga, can clearly be seen penetrating deep into the solid, to at least twice the depth of the bottom of the crater formed by the C$_{60}$ impact, which is due to the high kinetic energy of the Ga atom in conjunction with its small size and high mass. As the Ga is penetrating the solid, it is impacting Ag atoms that can start collision cascades. The impacted Ag atoms then proceed to impact other atoms, which in turn leads to other atomic collisions. Dissipation of the kinetic energy of the colliding atoms eventually causes the collision cascades to stop. The collision cascades cause a large amount of damage along the atomic projectiles path. For an atomic crystalline solid, damage is restricted primarily to mixing (i.e. the displacement of atoms or molecules from their original positions in the solid matrix). The mixing in Figure 1-5 caused by Ga can be seen from the displacement of the particles between different layers according to the layer colors. Even though the Ga impact causes a lot of vertical motion between the Ag layers, there are very few Ag atoms sputtered, on average $21 \pm 2$ Ag atoms per impact. Sputtering by the C$_{60}$ cluster is on average $327 \pm 5$ Ag atoms. Thus, it would take 15
more 15 keV Ga impacts to produce the amount of sputtered Ag atoms as a single C\textsubscript{60} impact.

Figure 1-5. Snapshots from MD simulations of 15 keV Ga and C\textsubscript{60} bombardment of a Ag\{111\} surface at normal incidence. The cross-sectional slices of the systems sequentially follow the bombardment process for 29 ps. The atoms are colored by original layers in the substrate. The projectile atoms are black.\textsuperscript{9}
The dynamics of the projectile solid interaction are obviously quite different for the Ga atom and the C\textsubscript{60} cluster as can be seen from Figure 1-5. Upon impact with the surface, C\textsubscript{60} produces a plume of ejection, which causes a crater to begin to form. Ag atoms flow upwards and outwards resulting in the formation of a crater rim. When the kinetic energy has dissipated, a crater that is roughly 2 nm deep remains with the mixing confined to a ~1.5 nm band extending from the crater wall. The greater crater depth with respect to the width of the mixed region shows how subsequent C\textsubscript{60} impacts can remove the damage from previous impacts thus demonstrating how depth profiling experiments are possible. Juxtaposed to this description is the amount of damage to the Ag solid that would occur from 15 additional impacts of Ga that would be necessary to generate a similar sputtering yield to one C\textsubscript{60} impact, demonstrating why in general atomic ion beams cannot be used for depth profiling. It is clear that the Ga and C\textsubscript{60} bombardment simulations provided valuable information for the SIMS community; however, the simulations also yielded an important link between the cluster bombardment simulations and SIMS experiments.

1.2.3 Simulations Agree with Experiment

Although Figure 1-5 gives us a qualitative picture of the differences in atomic vs. cluster bombardment; it is important to validate that the MD simulations are providing reasonable results by making comparisons to experimental data. Two such cases are for the comparison of the kinetic energy distributions of sputtered silver monomers and dimers for both the above Ga and C\textsubscript{60} bombardment simulations and SIMS experiments.
with similar initial conditions, and the work done by Brenes et al. in confirming the mechanisms of sputtering for small organic molecules generated from energetic $C_{60}$ bombardment by comparing experimental and simulated polar angle distributions of sputtered molecules in conjunction with vector plots produced from the MD simulations.\textsuperscript{45}

The kinetic energy distributions from MD simulations and experiment for silver monomers and dimers sputtered by 15 keV Ga and $C_{60}$ are shown in Figure 1-6 a-d, where the normalized signal of the sputtered species are plotted versus the sputtered species kinetic energy in eV. Kinetic energy distributions for experimental 15 keV Ga bombardment show the Ag dimers are sputtered with lower kinetic energies than the corresponding Ag monomers and that the dimer spectrum drops off faster than for the monomer in the high-energy portion of the spectrum (Figure 1-6c). The same trends for sputtered Ag monomers and dimers are also seen in the kinetic energy distributions from the 15 keV Ga bombardment simulations (Figure 1-6a). The kinetic energy distributions for sputtered Ag monomers and dimers from 15 keV $C_{60}$ bombardment however do not follow these trends. The results from both the experiment and simulation show that the Ag dimers on average have larger kinetic energies than the monomers (Figure 1-6b, d). From these results, we see that the relative peak positions for the Ag monomer and dimer distributions interchange when going from Ga atomic to $C_{60}$ cluster bombardment, and the MD simulations’ ability to represent this behavior is evidence that the simulations are correctly modeling the bombardment process. Moreover, these data are clear evidence that the physics of cluster bombardment is distinct from the physics of atomic bombardment.
Figure 1-6. Kinetic energy distributions for silver monomers (solid lines) and dimers (dashed lines) sputtered by 15 keV Ga and C\textsubscript{60} bombardment at normal incidence produced by experiment (c, d) and by MD simulations (a, b).\textsuperscript{9,46}

Comparison of the energy resolved polar angle distributions of sputtered intact molecules from 20 keV C\textsubscript{60} cluster bombardment at normal incidence of benzo(a)pyrene and MD simulations of 20 keV normal incidence C\textsubscript{60} bombardment of solid benzene is an
example of how results from MD simulations agree with experimental data for cluster bombardment of small molecular solids and how the microscopic view supplied by the MD simulations were able to explain the trends in the data and confirm the fluid flow mechanism of ejection. The energy resolved polar angle distributions for the sputtered intact molecules are shown in Figure 1-7. A peak at \( \sim 30^\circ \) for all kinetic energies is superimposed on an over-cosine type background. By decomposing the polar angle distributions for all kinetic energies into high and low kinetic energy regimes shows that the off-normal peak at \( \sim 30^\circ \) is due to emission of high energy molecules; whereas, the over-cosine component is primarily from emission of low kinetic energy molecules as seen in Figure 1-7. Agreement between the polar angle distributions for the MD simulations and SIMS experiments indicate that the simulations are correctly modeling the \( \text{C}_{60} \) bombardment process, but in order to explain the mechanism of ejection, it is necessary to look at vector plots from the MD simulations showing the velocities and directions of molecules and fragments ejecting at 2 and 8 ps after cluster impact as seen in Figure 1-8. The vector plots show that the majority of high energy molecules are ejecting early in the sputtering process at off-normal angles from the crater rim indicating a fluid flow mechanism of ejection. The 8 ps vector plot shows that the over-cosine emission is from the low-energy desorption of intact molecules from the crater walls. The vector plots therefore account for both the energy resolved polar angle distributions and the total polar angle distributions and confirm the fluid flow mechanism of molecular ejection. The ability to tie MD results to experimental SIMS results provides a foundation for applying MD simulations to other processes related to cluster bombardment such as the creation of other forms of cluster induced damage.
Figure 1-7. Polar angle distributions of intact organic molecules sputtered by 20 keV C_{60} bombardment at normal incidence. Signal intensity is plotted versus emission angle and as a function of emission energy; (a) measured experimentally for benzo(a)pyrene molecules with all energies (black line), 0-3.8 eV (red line) and above 3.8 eV (blue line), and (b) calculated from MD simulations for coarse-grained benzene molecules with all energies (black line), 0-1.26 eV (red line) and above 1.26 eV (blue line). See reference for details concerning energy choices.\textsuperscript{45}
Figure 1-8. Vector plots from MD simulations of a 20 keV $C_{60}$ impact at normal incidence of coarse-grained benzene at (a) 2 ps and (b) 8 ps. The vector tail depicts the molecule or fragment’s position at the given time while the vector head depicts its position 0.3 ps later. The emission angle and/or lateral relocation of the molecule or fragment is indicated by the vector’s direction while the length corresponds to the molecule or fragment’s kinetic energy.\textsuperscript{45}

1.3 Damage Accumulation during Depth Profiling

In Section 1.1.2 we saw that continued build-up of damage to the substrate from primary ion impacts was hypothesized to be the cause of signal loss during SIMS depth profiling experiments with atomic and small cluster primary ions. The MD simulations of Ga and $C_{60}$ impacting an atomic Ag\{111\} surface shown in Figure 1-5 provided some evidence for this by the extensive mixing caused by atomic bombardment over cluster bombardment.\textsuperscript{9} The MD simulations also suggested that a clean-up mechanism for the
primary ion induced damage could be at work during cluster SIMS depth profiling. An analytical model was developed by Cheng, Wucher and Winograd that describes how damage to the substrate could be linked with the sputtering process to produce a successful or unsuccessful depth profile.\textsuperscript{47} A schematic of the erosion model is depicted in Figure 1-9,\textsuperscript{47} where \( F \) represents the flux of intact molecules into (\( F_{\text{supply}} \)) and out of (\( F_{\text{sputter}} \)) an altered layer of thickness (\( d \)). The damage formation is represented by (\( F_{\text{damage}} \)). A system that is able to reach a steady state; wherein, the disappearance rate (\( F_{\text{sputter}} \)) caused by the removal of intact molecules and the supply rate (\( F_{\text{supply}} \)) or recovery of undamaged molecules through surface erosion, reach an equilibrium, and thus no further damage is accumulated results in a successful depth profile.\textsuperscript{18,47}

![Figure 1-9. Schematic diagram of the erosion model. \( F \) represents the flux into and out of the altered layer of thickness \( d \).\textsuperscript{47}](image)

As was seen in Figure 1-4, not all materials can be depth profiled by all types of clusters. In some cases, the damage in the altered layer increases faster than succeeding


cluster impacts can remove the damage (i.e. $F_{\text{damage}} > F_{\text{sputter}}$), which results in the eventual loss of signal. For instance, $C_{60}$ cannot depth profile the polymers polystyrene (PS) and polyamides, yet can depth profile poly(methyl methacrylate) (PMMA).\textsuperscript{18,48} The damage that is inhibiting depth profiling of PS by $C_{60}$ is believed to be chemical damage resulting from the formation of a carbonaceous overlayer that may involve a network of cross-linked polymer chains.\textsuperscript{18} Alternatively, the depth profiling of PMMA is hypothesized to be assisted by the ease with which PMMA forms small gas molecules through unzipping reactions of the polymer chains.

Very few MD studies have been performed that have studied the effects of chemical damage from cluster bombardment.\textsuperscript{4,49} This is primarily due to the computational cost of utilizing MD potentials that can model chemical reactions. The cluster bombardment simulations that have been run have been for short times and thus do not include all the dynamics of the cluster bombardment event.\textsuperscript{4,49} These simulations were not able to capture the final topography of damage in the solid or the eventual sputtering of reacted molecules. Clearly, the formation of and removal of chemical damage are important processes in molecular depth profiling, and methods to employ reactive MD potentials in cluster bombardment simulations could assist in uncovering such processes.

Another type of system that $C_{60}$ has difficulties depth profiling through, are metal overlayers on organic substrates.\textsuperscript{20,50} The $C_{60}$ depth profiles for a 15 nm Ag film on 650 nm of trehalose with a Si substrate is displayed in Figure 1-10.\textsuperscript{50} The interfaces in Figure 1-10 are marked by dashed lines. Following the traces from left to right with increasing $C_{60}^+$ fluence is in the direction of erosion of the sample. Several points were made by
Cheng and coworkers concerning the plots. First, the trehalose signal is reduced an order of magnitude compared to the depth profile of trehalose with no metal overlayer. Secondly, the Ag signal sharply rises at the interface where normally it would be decreasing through the interface as the Ag overlayer is eroding; the authors attribute this to possible matrix effects. Also, the Ag signal monotonically decreases yet persists through the extent of the trehalose layer. A final point to be made is that the trehalose signal appears well before the Ag/trehalose interface is reached indicating that the Ag overlayer is being penetrated much earlier than would be expected. It appears as though many complex processes are occurring in the depth profile and could be due to a combination of mixing and chemical damage.
Figure 1-10. Depth profiles of secondary ion intensities vs. $C_{60}^+$ fluence of Ag/Tre/Si film. The trehalose fragment ion is the $m/z$ 163 signal.\textsuperscript{50}

1.4 Goals of this Dissertation

The previous discussions have related the importance of the ability of MD simulations to elucidate phenomena related to energetic cluster bombardments of solids, and also the critical effects that the different forms of damage induced by energetic cluster ions has on SIMS depth profiles of organic solids. The goals of this dissertation are twofold and are concerned with extending MD simulations to the problems of damage formation by energetic cluster bombardment. To investigate the chemical reactions associated with the cluster bombardment of polymers requires the use of a
computationally expensive reactive potential. In order to use such a potential in cluster bombardment simulations that incorporate the full dynamics of the bombardment event, methods need to be developed that reduce the simulations’ computational time. Therefore, the first goal of this dissertation is to define and test a methodology to incorporate reactive MD potentials in simulations of energetic cluster bombardment that will be able to describe the full dynamics of the event in a computationally tractable time and test the methodology by using cluster bombardment simulations on an organic solid. The second goal of this dissertation is to apply MD simulations to a system that has raised important experimental questions as relates to dynamic SIMS and that will broaden the scope of the type of systems and time frames modeled by MD cluster bombardment simulations. Such systems are provided by metal-organic interfaces that are analogous to the C60 depth profiling experiments shown in Figure 1-10. Cluster bombardment simulations of metal-organic interfaces will be used to describe the processes of sputtering and mixing that are so far unique to that type of system. The analysis will yield some hypotheses on depth profiling through such systems.

1.4.1 Incorporating Reactive MD in Cluster Bombardment Simulations

Several problems arise when attempting to incorporate chemical reactions in MD cluster bombardment simulations that capture the full dynamics of the cluster bombardment process. First, since kinetic energies above 20 keV for the primary cluster ion are commonly employed in SIMS experiments, we would like simulations of cluster bombardment to be close to this range. However, this can be difficult considering that the
higher the kinetic energy, the faster the motions the impacted particles will have, and the smaller the time step will have to be in order to capture the correct motions of the particles. This fact is especially troublesome for molecular organic samples that contain hydrogen atoms, due to the high vibrational frequency caused by the much lighter mass of hydrogen; this effect can be minimized by using the more massive tritium form of hydrogen. Molecular organic solids also tend to have low binding energies. Therefore, for higher keV cluster impacts, the range of motion is much greater, which results in larger system sizes (i.e. over a million atoms) and longer trajectories to capture the full dynamics of the cluster bombardment event.

The evaluation of the forces is the most costly part of every integration step and depends on the number of particles, the range of the forces and the complexity of the force field.\textsuperscript{51} Incorporating a reactive MD force field is extremely costly in computer time. For example, the system energy for the ReaxFF force field is made up of the following nine partial energy terms.

\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tor}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \]  

(1-4)

Where the partial energy terms from left to right are for: bonding, over-coordination, under-coordination, valence angle term, energy penalty for an atom with two double bonds, torsion angle, conjugated systems, nonbonded van der Waals interaction and coulomb interactions.\textsuperscript{52} The combination of the high kinetic energy, large system size and the complex reactive potential is why a cluster bombardment simulation of 15 keV \( \text{C}_{60} \) on solid benzene using the adaptive intermolecular reactive empirical bond order potential (AIREBO) implemented in a serial computer code would take roughly 5 months for a 50
ps trajectory.\textsuperscript{51,53,54} Clearly, better methods need to be found to make the simulation times more reasonable.

1.4.1.1 Mixed Resolution Model

The length and time scales of MD simulations can be increased by applying coarse-grained or reduced representations to the simulation system. In a coarse-grained representation two or more atoms are represented by a single bead or particle as seen in Figure 1-11 for molecular benzene, where the C-H moiety is depicted as one bead.\textsuperscript{55,56} The reduction in computational time for a coarse-grained MD simulation is due to fewer particles in the system and thus the reduction in the number of interactions that need to be calculated. Also, typically simple two-body potential functions are used to describe the particle interactions, which simplifies the calculation. Lastly, H atoms are combined within a bead with a heavier atom so that the high vibrational frequencies of the H atoms are removed from the simulation thus allowing larger timesteps. Recently coarse-grained representations have been combined with an atomistic representation in multiscale MD simulations.\textsuperscript{57}

The multiscale MD approach by Nielsen et al. uses a switching function based on the interaction distance between an atom and a coarse-grained particle to scale the interaction potential between the two particles.\textsuperscript{57} This method has the advantage of being able to describe atomistic effects in a region of interest while reducing the computational cost by applying coarse-graining to a region that does not need the same detailed description. The multiscale simulation then is able to take advantage of the benefits of
coarse-grained MD simulations with the exception of the timestep increase since lighter elements would still be present in the atomistic region.

An alternative simplified approach to the Nielsen et al. multiscale method would be to modify the simplified two body potential describing the interaction between coarse-grained particles to describe the interaction between atoms and coarse-grained particles. This is the method that has been applied to cluster bombardment of solid benzene in Chapters 3 and 4 and is called the mixed resolution model.

![Figure 1-11. All atom (AA) representation of benzene (left), with carbon represented as light green spheres and hydrogen as silver spheres. The coarse-grained (CG) benzene representation is on the right with blue spheres representing a carbon and its bonded hydrogen atom as one bead.](image)

### 1.4.1.2 Parallel Programming

An alternative to using the mixed resolution model for reducing the computational time of cluster bombardment simulations is to employ parallel programming; a programming method that divides the computer code into independent parts, which can
be executed on different processing units.\textsuperscript{51} Therefore, the costly force calculations of the cluster bombardment simulations can be divided among the processors, thus greatly reducing the required computer time. The gains in computer time, from the addition of more processing units, do not scale linearly after a certain number of processors have been added. Several factors are involved in the loss of linearity and include the fact that not all parts of the computer code can be made parallel, the increase in information exchange between nodes and processors, the efficiency of the computer algorithm and the quality of the computer code. However, these deficiencies are small in comparison to the gains in computer time that can be realized. As evidence, the serial version of the sputtering code used for cluster bombardment simulations by the author was parallelized by Zbigniew Postawa and used in the cluster bombardment simulations of metal-organic interfaces (Chapter 5), which encompassed the full dynamics of the cluster bombardment event while in part using the reactive AIREBO potential. The simulations lasted from 1 to 6 weeks.

1.4.2 Cluster Bombardment of Metal-Organic Interfaces

A similar system to that represented in the depth profiles of Figure 1-10, composed of a metal overlayer on an organic substrate, is an organic light-emitting diode or OLED, which has a metal cathode, typically aluminum, exterior to multiple layers of organic and organometallic layers. SIMS techniques such as depth profiling and 3D imaging are envisioned to be useful in analyzing and developing such OLED devices; however, at present, successful depth profiles of such material have required the removal
of the metal cathode as was done for the acquiring the 3D image of the OLED in Figure 1-12. The depth profiles of Figure 1-10 give experimental clues to why the metal cathode is being removed before the SIMS experiments. With the continued advancement of the science of materials, it is not hard to imagine the possibility of the development of layered organic devices with embedded metal layers (i.e. not easily removed) that would need the analysis techniques provided by SIMS. The determination of the effects of cluster bombardment of metal-organic interfaces is therefore an excellent candidate for MD cluster bombardment simulations.

To relate single cluster impacts to depth profiling experiments of metal-organic interfaces, it is necessary to mimic the depth profiling by utilizing decreasing thicknesses of metal overlayers on the organic substrate. The simulations become more challenging computationally as the metal overlayer thickness is decreased since the underlying substrate size must be increased concurrently so that the simulation will be able to capture all of the relevant dynamics related to cluster bombardment. Due to the system sizes (i.e. \( \sim 10^6 \) atoms), and the complex mix of potentials to describe all the atomic interactions; it is necessary to use a parallel programming computational methods to make these simulations tractable. The combination of both computational and system challenges provided an excellent opportunity to extend MD simulations to an important area of dynamic SIMS research.
Figure 1-12. Dual beam 3D analysis of an active matrix OLED display.\textsuperscript{20}

1.5 Overview

The work associated with the development of a mixed resolution model incorporating a reactive potential will be presented in Chapter 2, 3 and 4. Chapter 2 will describe testing of the reactive force field ReaxFF to determine its validity as relates to reactions that can occur in the energetic cluster bombardment of PMMA and PS. Chapter 3 covers the testing of the mixed resolution model applied to a solid benzene system. Chapter 4 utilizes the mixed resolution model of the benzene system to investigate the sputter yield, total chemical damage and the location of chemical damage associated with the cluster bombardments by three clusters with different initial properties. The work on cluster bombardment of metal-organic interfaces will be presented in Chapter 5. Chapter
6 will summarize the work presented in this dissertation and provide some thoughts on possible future work.

1.6 References


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Chapter 2

Strategies for Modeling Diverse Chemical Reactions in Molecular Dynamics Simulations of Cluster Bombardment

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2.1 Introduction

Many experimental factors have been found to contribute to the success or failure of SIMS depth profiling experiments of polymers such as the energy, angle and type of primary cluster ion beam, fluence rate and temperature. A leading cause of signal loss in depth profiling experiments of polymers is believed to be the formation of carbon layers, possibly caused by the cross-linking reactions that can occur between polymers strands. Much of the polymer degradation chemistry that could be involved in the formation of these carbon layers is already known; however, a full description of the chemical processes that are involved in maintaining signal intensity in a depth profiling experiment of organic compounds has not yet been determined. One polymer that can successfully be
depth profiled is poly (methyl methacrylate) (PMMA). This polymer is known to readily form small gas molecules such as CO and CO$_2$ upon decomposition. One hypothesis, thus, is that small gas formation can lead to successful depth profiles. Molecular dynamics simulations can be used to investigate the chemical processes that are occurring during a depth profiling experiment of organic substrates and thus give insight into the validity of the current assumptions and hypotheses concerning signal loss in these experiments.

Molecular dynamics simulations have been used to explain many of the physical phenomena that occur during both atomic and cluster bombardment experiments, and recently the adaptive intermolecular reactive empirical bond-order (AIREBO) potential has been used to investigate the chemical reactions that occur upon C$_{60}$ bombardment of organic substrates such as solid octane and octatetraene. The MD simulations using the AIREBO potential have shown that, for a 5-20 keV C$_{60}$ bombardment of octane and octatetraene, the chemical reactions occur in the region of the cluster impact, and the reacted atoms are either in the gaseous plume formed or deposited on the crater walls. The simulations on octane and octatetraene have provided valuable information on where and on what time scale the reactions are occurring during C$_{60}$ cluster bombardment. Although these simulations provide insight into the reaction region, small gas formation is not a reaction channel of octane and octatetraene. Two model systems that are suitable for testing whether the efficiency with which small gas molecules are formed affects depth profiling experiments are the organic polymers PMMA and polystyrene (PS) since PMMA can form small gas molecules and PS can undergo cross-linking reactions in a cluster bombardment experiment. A reactive atomistic potential that is parameterized for
the elements constituting both the polymers PMMA and PS is the ReaxFF\textsuperscript{6} potential developed by van Duin.\textsuperscript{7}

Before ReaxFF should be used in MD simulations of C\textsubscript{60} cluster bombardment of PMMA or PS, it was essential that ReaxFF be tested to see if it can model the reactions that are expected to occur during such simulations with acceptable reaction energies. The results of the ReaxFF testing will be presented in this paper.

2.2 Computational Method

ReaxFF is a atomistic reactive empirical bond order potential that is able to model the formation and dissociation of bonds by using a continuous relation between bond order and bond distance.\textsuperscript{6} Bonds are dissociated smoothly by defining all valence related terms in the potential using the bond order.\textsuperscript{6} ReaxFF has been parameterized to model reactions between atoms of many types of elements, not only including H, C and O, but also N, B, Si, Pt, and others.\textsuperscript{6-13} Because ReaxFF is parameterizable, it is possible that many different types of substrates and primary ion beams could be modeled in a simulation of a depth profiling experiment using ReaxFF potentials.

To test ReaxFF’s ability to model the reactions that could occur during a C\textsubscript{60} cluster depth profiling experiment of PMMA, ReaxFF was used to simulate a number of PMMA degradation reactions that had previously been simulated with the Gaussian 03 program using quantum mechanical methods by Conforti and Garrison.\textsuperscript{14} Figure 1 shows the bond cleavages that can occur during PMMA degradation reactions, which can result in the formation of small gas molecules such as CO, CO\textsubscript{2} and various other radicals.\textsuperscript{14}
The Norrish Type IA process occurs when the C-C bond in the ester side chain is cleaved; Norrish Type IB process cleaves the ester C-O bond. The ester methyl group can undergo ester elimination, and Norrish Type II processes occur when a C-C bond on the main chain is cleaved. For modeling a potential cross-linking reaction that can occur in polymers such as PS, the energy for the cycloaddition of two ethylene molecules to form cyclobutane was calculated using ReaxFF.

![Figure 2-1. PMMA monomer unit showing bond cleavage points for the different types of degradation reactions.](image)

The ReaxFF code was used with parameters for C, H and O and was initially developed to investigate the high-temperature gas-phase oxidation of hydrocarbons. The geometries for the reactants were obtained by constructing and minimizing the structures with Gaussian 03. The reactant geometries given by Conforti and Garrison were also used for an additional check on the minimized geometries and were found to be in close agreement for the PMMA degradation reaction energies. All the reaction energies were calculated by incrementally changing the distance between reacting atoms until the
relevant bonds were either broken or formed. With each change in interatomic distance between reacting atoms, the structure was minimized to ensure that a local minimum in the reaction pathway was not missed.

2.3 Discussion

When considering the suitability of a computational method for modeling C\textsubscript{60} depth profiling experiments of polymers, it was important to take into account the computational difficulties of such simulations, such as the physical and chemical effects caused by the cluster bombardment can occur over a volume of the substrate containing hundreds of thousands of atoms, the high energy impact of the cluster can cause the formation of many electronic excited states creating a multitude of reaction pathways and a large variety of reactions can also occur from the many types of diverse fragments formed by both the cluster and substrate. At this time, there is not a computational method that can solve all of these problems simultaneously; therefore, compromises must be made to develop a computationally feasible method. The large system size needed for such simulations rules out the possibility of considering the possible excited states formed. Also, as shown with simulations of C\textsubscript{60} bombardment of octane and octatetraene,\textsuperscript{5} a reactive potential alone is too computationally expensive; therefore, it is necessary to coarse grain the part of the system that is devoid of reactions.

The testing performed has shown that ReaxFF is capable of modeling the formation of gas molecules and cross-linking reactions with reasonable reaction energies. By combining ReaxFF with a coarse grained potential, it will be possible to investigate
those chemistries believed to be involved in maintaining signal intensity in C$_{60}$ depth profiling experiments of organic compounds. A protocol must then be developed for the simulation of cluster bombardments that takes into account the compromises just mentioned so that simulations will be computationally tractable. It will therefore be necessary to create a system wherein those atoms that do not react will be described by a coarse grained potential. Far fewer calculations are required to describe the behavior of the coarse grained particles, and this will shorten the simulation time considerably compared to using a reactive potential to describe the entire system. ReaxFF will be used for the atoms that are within a cylinder below the C$_{60}$ cluster impact point that has a radius of 20 Å and a depth of 40 Å. The cylinders dimensions were based on the simulations of 20 keV C$_{60}$ bombardment of octane and octatetraene using the AIREBO potential, which showed that the reacted atoms were contained in a cylinder of the dimensions given above, by the completion of the chemical reactions during the simulations.$^5$ An interaction potential will be necessary to describe the interactions between the coarse grained particles and atoms.

It is believed that using this protocol will enable the modeling of C$_{60}$ depth profiling experiments of polymers such as PMMA and PS, which in turn will allow the investigation of the physical and chemical phenomena that cause signal loss in organic depth profiling experiments. Such investigations could possibly lead to generally applicable conditions for successfully depth profiling organic compounds.
Figure 2-2. Comparison of the reaction energies calculated using ReaxFF (blue) and quantum mechanical calculations (purple) and experimental data (green) for the simulations of PMMA degradation reactions (top 6 reactions) and for the cyloaddition reaction of two ethylene molecules to form cyclobutane (bottom reaction).

### 2.3 Conclusion

It has been proposed in this paper that the efficiency with which small gas molecules are formed is a leading contributor to the success or failure of a C$_{60}$ depth profiling experiment of an organic substrate. To investigate this claim, a protocol has been developed for simulating these experiments using molecular dynamics, which involves the combining of a coarse grained potential with the reactive atomistic potential ReaxFF. The suitability of using ReaxFF in the simulation C$_{60}$ depth profiling experiments was confirmed by comparing the ReaxFF results for the simulation of PMMA degradation reactions with results from quantum mechanical calculations and by
comparing ReaxFF results for the cycloaddition reaction of two ethylene molecules to form cyclobutane with experimental results

### 2.4 References

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Chapter 3
Mixed Resolution Model for C_{60} Cluster Bombardment of Solid Benzene

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3.1 Introduction

Molecular dynamics (MD) simulations have been able to provide microscopic insights into many of the physical phenomena that occur during the sputtering process,\(^1\) where energetic particles strike a surface ejecting atoms or molecules depending on the target. The changes in how the target's surface is modified and the changes in sputtering yields caused by the differences in the incident particles such as size, energy and angle of incidence have been successfully elucidated by MD simulations of cluster bombardment for various atomic and molecular solid targets.\(^2\)-\(^8\) Many of these phenomena of the sputtering process have been related to secondary ion mass spectrometry (SIMS), an application of sputtering where the ionized sputtered particles (secondary ions) are detected by a mass spectrometer.\(^9\) Recently, MD simulations have been probing how sputtering is affected by multiple particle bombardments as applied in depth profiling experiments, where successive layers of the target are removed by continued
bombardment.\textsuperscript{10} Depth profiling is an important component of the promising field of SIMS 3-dimensional imaging. The especially exciting aspect of the 3D imaging SIMS experiments using energetic C\textsubscript{60} projectiles is that they can be performed on molecular solids and obtain chemically specific information about molecules.\textsuperscript{5}

MD simulations of sputtering have primarily concentrated on the physical phenomena associated with sputtering; however, in the case of molecular solids, ignoring chemical effects could lead to an incomplete picture of the sputtering process. For example, using the reactive AIREBO\textsuperscript{11} potential for MD simulations of C\textsubscript{60} cluster bombardment of four hydrocarbon solids showed that the hydrogen to carbon ratio influences the degree of cross-linking that occurs between carbon atoms of different molecules in the target.\textsuperscript{12} The importance of this finding extends beyond merely elucidating the sputtering process; cross-linking is believed to be an important factor contributing to signal loss in C\textsubscript{60} SIMS depth profiling experiments of some organic polymers like polystyrene (PS).\textsuperscript{13} Interestingly, other polymers such as poly(methyl methacrylate) (PMMA) depth profile readily with C\textsubscript{60},\textsuperscript{13} which could be attributed to the ease with which small gas molecules are formed during the bombardment process, since volatile gas formation would facilitate the removal of target material.

Studying the chemical processes associated with such phenomena as cross-linking and small gas molecule formation using MD is difficult, since it requires the use of a many body reactive potential such as AIREBO, which are generally complex and thus computationally expensive. Cluster bombardment simulations using reactive potentials generally do not extend beyond much more than a few picoseconds and do not capture all of the dynamic effects of the bombardment process.\textsuperscript{8} For instance, a MD simulation of 5
keV C\textsubscript{60} bombardment of molecular benzene would require a sample size 350 Å wide by 200 Å deep to take into account all of the relevant dynamics, using the AIREBO potential with a serial computer code would require several years of CPU time for each trajectory.\textsuperscript{8,14} Performing full scale cluster bombardment simulations of molecular solids with many body reactive potentials has currently only been performed using the AIREBO potential with a parallel code\textsuperscript{15} as in Chapter 5. However, repetitive bombardment simulations that mimic the SIMS depth profiling experiment are as yet unachievable. Alternatively, several groups have used a coarse-grained representation to describe molecular solid targets for cluster bombardment MD simulations.\textsuperscript{14,16-21} Although a complete simulation can be performed, no chemistry is included other than C-C bond cleavage.

One solution to the computer time cost is provided by using a mixed resolution model, where the sample is partitioned so that the reactive potential is only used to describe the interactions of atoms that initially reside in the volume of the sample where all the reactions will take place. The remainder of the sample is described by coarse-grained (CG) beads that represent a segment of a molecule. Interactions between the CG beads and between CG beads and atoms are described using simpler pair potentials. This article will describe the requirements and set-up of a mixed resolution model for MD simulations of C\textsubscript{60} cluster bombardment of molecular benzene, describe how the pair potentials are tested and show a result from the initial testing.
3.2 Methods

Several requirements must be met when developing a full scale mixed resolution MD simulation of C\textsubscript{60} cluster bombardment of a molecular solid:

1. The dimensions of the target must be able to encompass all dynamic effects of the cluster bombardment.

2. An all atom (AA) description of the target is used for those atoms initially residing in the reaction zone; the volume of the target containing all the reacted atoms over the time period that reactions can occur.

3. The reactive potential that describes the interactions between atoms must be able to model the relevant reactions that will possibly occur during cluster bombardment with reasonable energetics.

4. The pair potentials used to describe the interactions between CG particles and between CG particles and atoms must be properly blended with the reactive potential so that the dynamics of the system are properly modeled between the AA and CG regions of the target.

Each of these points will be discussed in turn in this section as they apply to a target composed of molecular benzene, which will be the system used to develop the methodology for mixed resolution C\textsubscript{60} cluster bombardment of molecular solids.

The dimensions for the molecular benzene\textsuperscript{22} target are 350 Å wide by 200 Å deep and have been taken in accordance with previous calculations of the size crystal required for a 5 keV C\textsubscript{60} MD cluster bombardment simulation that includes all dynamic effects.\textsuperscript{8,14}

Ultimately for the simulations, only a cylindrical region of molecules described by the
AA potential is required as found in MD simulations of 20 keV C\textsubscript{60} bombardment of octane and octatetraene.\textsuperscript{8} The rest of the benzene crystal is composed of coarse-grained (CG) benzene molecules, where one CG bead represents a carbon of the benzene ring with its bonded hydrogen atom (Figure 3-1). For the testing of the mixing of the AA and CG regions we have chosen a system with six layers (21 Å) of AA benzene on a substrate of CG benzene, a cross sectional slice of which is shown in Figure 3-2a.

Figure 3-1. All atom (AA) representation of benzene (left), with carbon represented as light green spheres and hydrogen as silver spheres. The coarse-grained (CG) benzene representation is on the right with blue spheres representing a carbon and its bonded hydrogen atom as one bead.

For the initial testing of the mixed resolution model, the reactive AIREBO potential\textsuperscript{11} will be used since MD cluster bombardment simulations have been previously performed on solid benzene using this potential, and the results of which can be used to gauge the performance of the mixed resolution model. Eventually, it would be desirable to use the ReaxFF reactive potential\textsuperscript{23} due to its parameterization for C, H, and O,\textsuperscript{24} and ReaxFF's previous testing, in Chapter 2, showed the ability to form small gas molecules such as CO and CO\textsubscript{2} along with its ability to model cross-linking reactions with
reasonable energetics. These features of ReaxFF will be necessary if the mixed resolution model is to be eventually employed for investigating how cross-linking reactions and small gas molecule formation effect C$_{60}$ cluster bombardment of organic solids such as PS and PMMA.

Besides the reactive potential (initially AIREBO), pair potentials in the form of 12-6 Lennard-Jones (LJ) potentials are used to describe the interactions between CG particles and between CG particles and atoms (C and H). In addition, there are Morse potentials that describe intramolecular ortho-, meta- and para- nearest neighbor interactions in the CG benzene molecules. The parameters for these potentials were initially taken from previous simulations of C$_{60}$ cluster bombardment of CG benzene.$^{16}$ For the potentials between the AA and CG particles, we follow the prescription of Nielsen et al.$^{25}$ Namely, the interaction between the AA C-H moiety and the CG CH unit is described by the CG potential. The force on the AA C and H atoms is assigned by the mass fraction. That is, 12/13 of the force from the CH unit is assigned to the C atom and 1/13 of the force is on the H atom.

Since the interaction potentials are different for the AA and CG regions, the system as shown in Figure 3-2a contains an interface between the two materials. The C$_{60}$ bombardment process induces a pressure wave in the substrate. It is essential that this pressure wave does not reflect at the interface, thus inducing artificial motion. Thus we monitored how the pressure wave created by the impact of the C$_{60}$ cluster travels through the interface between the AA and CG regions of the benzene crystal. A sharp increase or decrease in the velocity of the pressure wave at the interface is an indicator that the potentials are not properly blended; there should be a smooth transition of the pressure
wave between AA and CG regions. Testing was done on a sample that is roughly half the size of that required for a full simulation, and the center of mass velocity is monitored as the pressure wave travels down into the sample from the impact point.

Figure 3-2. Time evolution of 1 keV C$_{60}$ cluster bombardment of mixed resolution model of solid benzene. Cross sectional images representing the system at (a) 0 fs, (b) 400 fs and (c) 800 fs where light green and silver spheres represent the AA region (top 6 layers) encompassing the reaction zone. Blue spheres represent the CG region (bottom 21 layers).
3.3 Results and Discussion

Contour plots of the vertical velocity as a function of time for various layers in the system are shown in Figure 3-3a-c for the AA, CG and mixed systems. The average center-of-mass (COM) vertical-velocities for benzene were calculated for a 9 by 15 Å rectangle containing four benzene molecules of each layer directly under the impact point. Red indicates the highest velocities in the positive or downward direction; black indicates the highest velocities in the negative or upward direction. The predominant shade of yellow indicates that the benzene atoms or CG beads are vibrating around their natural crystal coordinates. The vertical-axis of the plot is the number of the benzene layers with layer one being the topmost layer. The x-axis indicates the time in femtoseconds. The leftmost contour line represents the leading edge of the pressure wave, which has roughly reached layer six in the AA and mixed systems at ~170 fs (Figure 3-3a,c) and for the CG sample at ~160 fs (Figure 3-3b).

The first key observation is that the AA and CG potentials give very similar speeds for the pressure wave motion in the substrate. This is demonstrated by the leading edges of the pressure waves for both the AA and CG systems approximately reaching layer eleven at roughly ~400 fs as shown in Figure 3-3a, b. The blending scheme described above for the AA-CG interactions maintains similar speed of the pressure wave. If reflection of the pressure wave had occurred, then negative velocities (black or lightest shade of yellow region) would have appeared at about 170 fs for layers 1-6. As visual confirmation that no reflection has occurred, snapshots of the simulation at 400 fs and 800 fs are shown in Figure 3-2b,c.
Figure 3-3. Contour plot of the average COM vertical-velocity of benzene from MD 1 keV C\textsubscript{60} cluster bombardment simulations on pure AA benzene (a), pure CG benzene (b) and mixed system of benzene (c). Layer 1 on the y-axis is the topmost layer of the sample.
3.4 Conclusion

Previous MD simulations of C\textsubscript{60} cluster bombardment of molecular solids have primarily concentrated on physical phenomena associated with the sputtering process. To fully describe C\textsubscript{60} cluster bombardment of molecular solids, it is necessary to take into account chemical phenomena, which will require the use of a complex reactive many body potential. Full scale atomistic simulations using reactive potentials are computationally expensive and intractable for repetitive bombardment simulations. A solution to the high computational expense of atomistic reactive potentials is to employ a mixed resolution model for C\textsubscript{60} cluster bombardment. Such a model is implemented by partitioning the target into an AA region describing the reaction zone, and a CG region for the remaining volume of the sample. Interactions between CG beads and between CG beads and atoms are described by simple pair potentials, thus drastically reducing the cost of a full simulation. A mixed resolution model of solid benzene has been created to develop the methodology for blending a reactive potential with pair potentials. An indication of how well the potentials are blended can be gauged by how the pressure wave created by C\textsubscript{60} cluster bombardment travels through pure AA and CG benzene. Initial testing shows that this approach is very promising.
3.5 References


(13) Mahoney, C. M. *Mass spectrometry reviews* **2010**, *29*, 247-293.


Chapter 4
Applying a Mixed Resolution Model to the Investigation of Damage in Solid Benzene Resulting from Both Energetic Cluster and Atomic Bombardment

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4.1 Application of Mixed Resolution Model

The desire to utilize reactive potentials in molecular dynamics investigations of cluster bombardments of molecular solids has spurred efforts to reduce the computational time required for such simulations. One such effort has been the development and testing of a mixed resolution model for energetic cluster bombardment that was described in
Chapter 3. Chapter 4, in essence, gives a proof of principle for the mixed resolution model by applying it to a solid benzene system large enough to encompass the dynamics initiated by 15 keV cluster bombardment, an initial kinetic energy that is more in line with experimental SIMS conditions as compared to the 1 keV of kinetic energy imparted to the impacting clusters in the initial pressure wave tests in Chapter 3. Besides providing further testing of the mixed resolution model, these simulations compare the total sputtering yields and the amount and location of the chemical damage induced by the 15 keV impacts of three clusters with different properties as relates to their constituent atoms’ mass, velocity, kinetic energy and chemistry. These simulations provide an important comparison of C\textsubscript{60} and argon gas clusters on the same size scale and will be described in Section 4.2. Another study that involved in part the application of the mixed resolution model of solid benzene is described in Section 4.3 and relates the damage resulting from 15 keV C\textsubscript{60} bombardment of solid benzene with the damage caused by low energy Ar bombardment at an incident angle of 45°. The relationship between the damage incurred by the different projectiles will be used to elucidate the positive effects of cobombardment on molecular depth profiles.
4.2 Chemical Damage Resulting from 15 keV C$_{60}$, Ar$_{18}$ and Ar$_{60}$ Cluster Bombardment of Solid Benzene

4.2.1 Introduction

Continued efforts to extend the limits of depth profiling and three-dimensional (3D) imaging to a wide variety of biological and organic samples using secondary ion mass spectrometry (SIMS) with primary ion cluster sources has not only spurred research aimed at optimizing experimental parameters for such experiments but also has motivated investigations into understanding the fundamental dynamics and chemistry of the sputtering process.\textsuperscript{1} Since the realization that cluster ion beams have opened the door to depth profiling and 3D imaging,\textsuperscript{2} much of the theoretical studies have concentrated on the dynamics of the sputtering process.\textsuperscript{3-12} Through the use of molecular dynamics (MD) computer simulations, a microscopic view of how the cluster interacts with the substrate has been captured which in turn has yielded descriptions of elements of the sputtering process such as crater formation, the ejection process, how initial cluster parameters effect the sputtering process and how multiple impacts modify surface topology.\textsuperscript{1,13-20} Computational research done on the damage caused by cluster bombardment has used MD simulations to study impact induced mixing and molecular fragmentation; however, there have not been many studies using MD simulations to examine chemical damage that results from reactions during the cluster bombardment process. This is due to the computational difficulty in employing reactive force fields on the scale required for MD simulations of cluster bombardment of organic solids.\textsuperscript{21} The build-up of chemical damage from cluster bombardment in the form of cross-links (covalent bonds between substrate...
molecules or fragments) in organic solids is believed to be a major factor in signal loss during “unsuccessful” depth profiling experiments.\textsuperscript{22}

Even though there is a lack of theoretical work on chemical damage that occurs in cluster bombardment, experimentalists have looked at many ways to try to minimize chemical damage effects during depth profiling experiments such as changing the angle of incidence of the cluster ion beam, rotating the sample, using different temperatures and testing different cluster ion beam sources.\textsuperscript{22} One promising source in reducing chemical damage build-up in certain organic materials such as the polymer polystyrene during depth-profiling as compared with C\textsubscript{60} bombardment has been the use of argon gas cluster ion beams (Ar-GCIB).\textsuperscript{23} First introduced in SIMS research by Matsuo and co-workers,\textsuperscript{24} argon ion beams have been shown to both successfully reduce chemical damage accumulation and also to reduce the amount of low mass fragments that are usually generated during cluster bombardment.\textsuperscript{23,25} The reduced chemical damage and fragmentation found with argon clusters recently lead Rabbani and co-workers to compare depth-profiles of several polymer and biological samples with C\textsubscript{60} and four different argon gas clusters of increasing size: Ar\textsubscript{60}, Ar\textsubscript{200}, Ar\textsubscript{1000} and Ar\textsubscript{2000} at 20 keV with a 45° angle of incidence.\textsuperscript{26} The addition of a small gas cluster Ar\textsubscript{60} in the study was intriguing since most of the research with argon clusters has been done with large clusters. If C\textsubscript{60} and Ar\textsubscript{60} clusters with the same kinetic energy are compared, even though they have the same initial kinetic energy per particle, the argon atoms of Ar\textsubscript{60} are traveling at roughly half the velocity in the direction of impact as the carbon atoms of C\textsubscript{60}. However, argon is ~3 times more massive than carbon and thus a carbon atom impacts the surface with half the momentum of an argon atom at the same kinetic energy.
With these differences in the cluster properties between C\textsubscript{60} and Ar\textsubscript{60}, it was thought that a microscopic picture of the cluster bombardment of C\textsubscript{60} and Ar\textsubscript{60} was in order. Molecular dynamics simulations could be beneficial in understanding how the differences in the cluster properties of C\textsubscript{60} and Ar\textsubscript{60} relate to chemical damage. It was also decided that MD simulation of Ar\textsubscript{18} might assist in providing a better understanding of the similarities between C\textsubscript{60} and small argon cluster bombardment. Using both Ar\textsubscript{60} and Ar\textsubscript{18} to compare with C\textsubscript{60} would give both a comparison of an argon cluster with the same kinetic energy per particle as C\textsubscript{60} (Ar\textsubscript{60}) and a cluster with roughly the same total mass as C\textsubscript{60} and hence same velocity per particle (Ar\textsubscript{18}).

4.2.2 Computational Method

Molecular dynamics simulations of 15 keV cluster bombardment of solid benzene\textsuperscript{27} at normal incidence were carried out using three different clusters: C\textsubscript{60}, Ar\textsubscript{60} and Ar\textsubscript{18}. Ten trajectories for each type of cluster were run with a random impact point in the central unit cell on the surface of the benzene crystal and a random initial orientation of the clusters. The benzene crystal was in the shape of a hemisphere with the flat surface being the surface of impact. The benzene crystal's radius was 17 nm and consisted of 87,413 benzene molecules of which 6546 molecules were described by an atomistic representation. The remaining benzene molecules were coarse-grained, where a CH moiety of the benzene molecule was represented by one bead.\textsuperscript{28}

The application of both an atomistic and coarse-grained representation in the benzene/cluster system was done using a mixed resolution model for simulating cluster
bombardment. The mixed resolution uses the atomistic representation for those molecules that are in the reaction zone of the cluster impact. The interactions between these atoms are described using a computationally intensive reactive potential which for these simulations was the AIREBO potential.\textsuperscript{29} Molecules not in the reaction zone are coarse-grained in which case more than one atom is described by a single bead. The interactions between coarse-grained beads and both other coarse-grained beads and atoms are described by simpler pairwise interaction potentials. A more in depth description of the mixed resolution model for cluster bombardment of organic solids was provided in Chapter 3.

The utilization of the mixed resolution model for cluster bombardment reduces the computational time for a MD simulation dramatically compared to a simulation that would employ a reactive atomistic potential for the whole system. The simulations that were undertaken in this work would have taken on the order of 5 months for a single trajectory using the AIREBO potential to describe the interactions between all the atoms of the system whereas by employing the mixed resolution model a single trajectory took approximately 3 weeks.
4.2.3 Results and Discussion

The average total damaged molecular benzene equivalents remaining in the solid (calculated from the total mass of reacted benzene molecules left in the solid), and the total sputter yields for 10 trajectories for each of the clusters impacts of C$_{60}$, Ar$_{18}$ and Ar$_{60}$ at 15 keV and normal incidence are given in Table 4-1. Ar$_{60}$ has the least damage remaining in the solid. Ar$_{18}$ has the most damage and, C$_{60}$ has a value in between the two argon clusters. The trend in total damage remaining in the solid can be rationalized by relating the damage totals back to the initial properties of the clusters. Ar$_{18}$ has the greatest energy per particle and the greatest momentum per particle, and therefore its argon atoms have a greater chance of breaking bonds of the benzene molecules than either C$_{60}$ or Ar$_{60}$. Both Ar$_{60}$ and C$_{60}$ have the same kinetic energy per particle, and even though the argon atoms in Ar$_{60}$ are moving slower upon impact than the carbon atoms of C$_{60}$, they have almost twice the momentum of the carbon atoms. However, mass matching the C$_{60}$ carbon atoms with the molecular benzene carbon atoms allows for more efficient energy transfer for C$_{60}$ than for Ar$_{60}$, resulting in the creation of more damage than Ar$_{60}$.
Table 4-1. Average total sputter yields and average total chemical damage remaining in the benzene crystal surface for ten trajectories each of 15 keV C$_{60}$, Ar$_{18}$ and Ar$_{60}$. Ten impacts were calculated for each cluster.

<table>
<thead>
<tr>
<th>Cluster type</th>
<th>Total sputter yield</th>
<th>Damaged molecular benzene equivalents remaining in the solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$_{18}$</td>
<td>1180 ± 25</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>1230 ± 28</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>Ar$_{60}$</td>
<td>1340 ± 23</td>
<td>13 ± 1</td>
</tr>
</tbody>
</table>

Though the differences in total damaged molecular benzene remaining in the solid can be explained by the different properties of the clusters, it is important to realize that these differences are actually rather minor. The total molecular benzene damage remaining in the solid is at most two percent of the total sputter yields for the different clusters. The differences then should be considered minor when put in the context of using these clusters to depth-profile an organic solid composed of a small molecule such as benzene. Since C$_{60}$, Ar$_{18}$ and Ar$_{60}$ total sputter yields are much greater than the damage created in the solid, these three clusters should be good candidates for depth-profiling molecular solids similar to benzene according to the analytical model proposed by Cheng, Wucher and Winograd. Their model proposes that the best depth-profiles are produced when the total sputter yield greatly exceeds the damage volume remaining in the solid, which is the case here. The relationship between the total sputter yield and the damaged volume remaining in the solid has been viewed as a “clean-up” effect of cluster bombardment where the impacting cluster is able to remove the damage created by
previous impacts while still sputtering intact molecules for analysis due to the sputtered volume being greater than the damaged volume.

Figure 4-1. Chemical damage (red) resulting from 15 keV C$_{60}$ impact(s) remaining in crystal surface after 50 ps (2 nm slice). Undamaged molecular benzene is colored grey. The top frame is for one trajectory, and the bottom frame is an overlay of the chemical damage from 10 trajectories.
Figure 4-1 gives an indication of why this “clean-up” effect is possible. Figure 4-1 shows a 2 nm slice of the benzene crystal at 50 ps, showing the crater formed by the 15 keV impact of $C_{60}$. The damaged molecular benzene is colored red and undamaged molecular benzene is grey. The top frame has the damage from a single trajectory, and the bottom frame has the damage from 10 trajectories overlaid on one crater. From both frames it can be seen that the damage is confined to the near surface region of the crystal which would allow for efficient removal by a following impact in a multiple impact scenario. Another important observation from Figure 4-1 is that the damage from the 10 overlaid trajectories is confined to the crater without any apparent crater depth preference. Figure 4-2 is a view looking down from above on the crystal and crater that was formed from a 15 keV $C_{60}$ impact. The top frame of Figure 4-2 shows the chemical damage (red) for a single trajectory which illustrates how little damage is produced by a single hit. The bottom frame of Figure 4-2 has the chemical damage for 10 trajectories overlaid on a single crater for 15 keV $C_{60}$ cluster bombardment. The black circles represent approximately the boundaries of the crater wall. What may stand out first when observing the bottom frame of Figure 4-2 is how little chemical damage is located outside the crater to what is confined inside the crater, which clearly shows that the large majority of surface damage is contained by the crater. The other important observation from the bottom frame of Figure 4-2 is that the damage is approximately uniformly and randomly distributed around the crater. There is no apparent preferential accumulation of chemical damage in any area of the crater. These observations can also be extended to the chemical damage generated by Ar$_{18}$ and Ar$_{60}$ by examining Figure 4-3, which shows the
top view of the chemical damage for 10 trajectories from each of the clusters showing that the topography of the chemical damage is similar for all three clusters.

Figure 4-2. Top view of benzene crystal impacted by 15 keV C$_{60}$ after 50 ps, where the black circles indicate the approximate position of the crater wall. The top frame is the chemical damage (red) for one trajectory; the bottom frame is an overlay of the chemical damage from 10 trajectories. Grey represents undamaged molecular benzene.
4.2.4 Conclusion

The results for the total damaged molecular benzene left in the solid show that although there are differences in the initial properties of $\text{Ar}_{60}$, $\text{C}_{60}$ and $\text{Ar}_{18}$ that can explain the differences in trends among the results for the three clusters; the overall numbers are quite small when compared to the total sputtering yields, and in actual depth-profiling of a small organic solid like benzene would most not likely be relevant when considering experimental error. The topography of chemical damage remaining in the solid was shown to be in the near-surface region and approximately uniformly and randomly distributed about the crater with little damage occurring outside the crater. Both topographical factors of the damage would be beneficial for the “clean-up” effect that is believed to be essential for successful depth profiling.
4.3 MD Simulations Elucidate the Synergy of \( C_{60} \) and Low-Energy Ar Cobombardment for Molecular Depth Profiling

4.3.1 Introduction

In relation to SIMS molecular depth profiling, the importance of experimental conditions and the interaction of these conditions with the system being investigated are a pivotal part in determining if the depth profile is successful.\(^{22}\) However, even with the optimal experimental conditions, finding strategies to overcome unwanted chemical effects that can derail a depth profiling experiment are challenging. Recently, Shyue and coworkers have performed experiments that hint at the possibility of a method of overcoming the negative effects of chemical damage on depth profiles by the application of \( C_{60} \) and low-energy Ar ions in the cobombardment of the system.\(^{32-40}\) Possibly due to few research groups having both a \( C_{60} \) and low-energy Ar ion beam capabilities, currently only one research group has implemented this strategy of eroding samples.

The cobombardment experiments utilize X-ray photoelectron spectroscopy (XPS) for surface analysis after erosion by \( C_{60} \) and Ar bombardment; in some cases SIMS measurements have been conducted also.\(^{32,33}\) The cobombardment experimental set-up by Shyue and coworkers operates a 10 keV \( C_{60} \) source at a 70° polar angle of incidence with respect to the sample. The Ar source operates between 100 to 400 eV at a 45° polar angle of incidence and oriented 33° from the \( C_{60} \) beam. The orientations of the \( C_{60} \) and Ar sources with respect to the surface and each other can be seen in the schematic of Figure 4-4. The beam current for the Ar source is 30 times greater than the current for \( C_{60} \). Since it is necessary for the Ar source to operate at 200 eV or less for cobombardment to
positively affect the depth profile, higher energies result in the change in composition of the sample, as measured by XPS.³³

![Image](image.png)

Figure 4-4. Schematic of the cobombardment experiment showing the orientations of the C₆₀ and Ar sources with respect to each other and the surface.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Without 200 eV Ar</th>
<th>With 200 eV Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>1.58</td>
<td>1.94</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>2.52</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Table 4-2. Sputter rates in nm³ per incident ion for 10 keV C₆₀ bombardment of two polymers without and with 200 eV Ar cobombardment.³²
Experimental measurements of sputtering rates and surface roughness give the first clues to what is occurring in the cobombardment experiments. For poly(ethylene terephthalate) (PET), it was observed that cosputtering removes the high mass species from the mass spectrum and enhances the low mass species, which indicates that Ar is breaking the apart the polymer.\textsuperscript{32} The sputtering rates for cobombardment of the polymers PET and poly(methyl methacrylate) without and with 200 eV Ar cobombardment are listed in Table 4-2,\textsuperscript{32} which shows that there is a slight enhancement in sputtering with cobombardment for the Shyue group’s experimental configuration. Also, it was found in the latest study that cobombardment produces smoother surfaces than C\textsubscript{60} bombardment alone.\textsuperscript{32} However, quality depth profiles and the ejection of large species do not occur with low energy inert gas bombardment.\textsuperscript{32,41} Clearly from the experimental results for cobombardment, there is a synergistic effect occurring in the solid due to the cosputtering configuration. To discern the nature of this effect, molecular dynamics simulations of both C\textsubscript{60} cluster and low-energy Ar bombardment of solid benzene were performed.

4.3.2 Computational Details

The solid benzene system was chosen due to its practicality, a mixed resolution model for its use with C\textsubscript{60} had already been developed, and from the assumption that the effect of C\textsubscript{60} and Ar cobombardment is generic to hydrocarbon species. The potentials used to describe the interaction energies and forces between the particles along with the details of the mixed resolution model have been described in Chapter 3. Two different
benzene system sizes were used for Ar bombardment at a 45° angle of incidence, however both had rectangular prism shapes. For 100 and 200 eV Ar, the system had surface dimensions of 6.56 by 5.64 nm and a depth of 3.45 nm and consisted of 1080 molecules. The second benzene system for 300 and 400 eV Ar bombardment had surface dimensions of 8.03 by 6.59 nm and a depth of 4.14 nm and consisted of 1848 molecules. These systems used periodic boundary conditions in the horizontal directions and a 0.347 nm rigid layer at the bottom with a 0.736 nm stochastic layer above it. Fifty trajectories were run for each incident energy of Ar. Single trajectories were run for 10 keV C\textsubscript{60} bombardment at 0° and 70° angles of incidence due to the computational expense. The system was in the shape of hemisphere with a radius of 21.2 nm and was composed of 175,434 benzene molecules. The bottom of the hemisphere was surrounded by a 0.7 nm rigid layer with a 3.3 nm stochastic layer bordering the rigid layer internally. Ten trajectories were run for 15 keV C\textsubscript{60} bombardment of solid benzene using a mixed resolution model, and its system composition has been described above in Section 4.2.2.

### 4.3.3 Results and Discussion

One possible explanation for the improvement in depth profiling due to cobombardment is that the inclusion of the Ar beam is directly increasing the sputtering yield. The erosion dynamic model predicts, that for effective depth profiling, the total sputtering yield relative to the damage created should be large. However, the sputtering yield shown in Table 4-2 are from roughly 1 to 3 nm\textsuperscript{3} per incident ion, which are very small compared with the experimental yield for 40 keV C\textsubscript{60} bombardment of cholesterol.
at 73° angle of incidence that produces a yield two orders of magnitude larger.\textsuperscript{42} The total sputtering yield reported by You et al. is 20-30 % larger when the Ar beam is operating.\textsuperscript{32} Table 4-3 shows the total sputter yields for the MD simulations of bombardment of solid benzene. Even though the yields for the small molecular organic solid are larger compared to the experimental values for the polymers of Table 4-2, the yield for Ar bombardment is more than an order of magnitude lower than the yields produced by 10-15 keV C\textsubscript{60} bombardment. Therefore, the hypothesis that the Ar beam is increasing the sputtering yield to the point observed in the experiment is unlikely.

Table 4-3. The total sputtering yield $Y_{tot}$ in units of molecular equivalents of benzene, sputtered volume $V_s$, the average number of damaged molecules that remain in the bombarded solid $N_D$ and the ratio of sputtered to damaged molecules $Y_{tot}/N_D$ for Ar and C\textsubscript{60} projectiles bombarding a crystal of solid benzene.

<table>
<thead>
<tr>
<th>Projectile</th>
<th>$Y_{tot}$</th>
<th>$V_s$ (nm\textsuperscript{3})</th>
<th>$N_D$</th>
<th>$Y_{tot}/N_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 eV Ar</td>
<td>4.9 ± 0.3</td>
<td>0.6 ± 0.03</td>
<td>0.8 ± 0.2</td>
<td>6.1 ± 0.4</td>
</tr>
<tr>
<td>200 eV Ar</td>
<td>6.9 ± 0.6</td>
<td>0.8 ± 0.08</td>
<td>3.2 ± 0.3</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>300 eV Ar</td>
<td>9.1 ± 0.9</td>
<td>1.1 ± 0.1</td>
<td>5.0 ± 0.4</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>400 eV Ar</td>
<td>11.5 ± 1.4</td>
<td>1.4 ± 0.2</td>
<td>6.9 ± 0.4</td>
<td>1.7 ± 0.2</td>
</tr>
<tr>
<td>10 keV C\textsubscript{60} 0°</td>
<td>745</td>
<td>90</td>
<td>14</td>
<td>53</td>
</tr>
<tr>
<td>10 keV C\textsubscript{60} 70°</td>
<td>342</td>
<td>41</td>
<td>9</td>
<td>38</td>
</tr>
<tr>
<td>15 keV C\textsubscript{60} 0°</td>
<td>1242 ± 28</td>
<td>150 ± 3</td>
<td>88 ± 3</td>
<td>14.2 ± 0.6</td>
</tr>
</tbody>
</table>
The co-bombardment experiments also show that there is an initial loss of measured ion signal with projectile fluence and indicates that the chemical composition of the near surface region of the organic sample is being modified. Hydrogen removal has been shown by computer simulations to be the most efficient channel of particle emission.\textsuperscript{43} Dehydrogenation of surface molecules can lead to a network of cross-linked molecules, a carbonized overlayer, or both, which will result in a severe reduction in sputtering yield, which is what is observed.\textsuperscript{22,43} The experimental researchers propose that the Ar beam could break up the damage induced by the C\textsubscript{60} beam.\textsuperscript{32} This would require that the additional damage caused by the Ar beam not extend beyond that already created by the C\textsubscript{60} beam. The depth of damage for the 15 keV C\textsubscript{60}, 200 and 300 eV Ar are shown in Figure 4-5; the damage for C\textsubscript{60} bombardment is defined as the average number of fragments located at a given depth measured from the wall of the final crater, Figure 4-5 inset. Due to only having a single trajectory for 10 keV C\textsubscript{60} bombardment at 70\textdegree angle of incidence; 15 keV C\textsubscript{60} at normal incidence is used as an upper limit for the damage produced. For 200 eV Ar the damage is confined to the top 2 nm of the sample as is with the vast majority produced by 15 keV C\textsubscript{60} at normal incidence; however, 300 eV Ar causes significant damage below 2 nm. The data in Figure 4-5 is represented graphically in Figure 4-6, where cross-sections of 15 keV C\textsubscript{60} crater, 200 eV and 300 eV Ar damage are aligned so that the crater bottom lines up with the surfaces of the Ar samples. This presentation makes it clear that bombardment by 200 eV Ar confines the damage to the altered layer of the C\textsubscript{60} bombardment; whereas, damage by 300 eV Ar extends into pristine sample.
Figure 4-5. Depth dependence of the average number of fragments created by 15 keV C\textsubscript{60} at normal incidence and by 200 and 300 eV Ar at 45° impact angle. The depth d is measured as the distance from the walls of the final crater for the 15 keV C\textsubscript{60} trajectory, as shown in the inset, and from the top of the initial surface for the Ar trajectories.
Figure 4-6. Location of the molecular fragments (red and enlarged) created by a) 15 keV $\text{C}_{60}$ bombardment of solid benzene at a normal incidence and b) 200 and c) 300 eV Ar at 45° impact angle. The trajectories are selected to represent average damage. Only the molecules located in a slice 5 nm wide, centered at the point of projectile impact, are shown. In addition, for non-damaged molecules, only the C atoms are shown. The snapshots are aligned so that the surfaces of Ar bombarded samples correspond to the bottom of the crater induced by $\text{C}_{60}$ impact to easily compare the damage induced by these two projectiles. The scale bar refers to all the images.
One last possibility for why co-bombardment by C$_{60}$ and 200 eV Ar improves the depth profiles of organic solids as compared to C$_{60}$ bombardment stems from the elongated valleys and ridges parallel to the beam direction that are created on the sample surface during high-fluence simulations of C$_{60}$ impacts at 70° incidence on Ag. By performing sample rotation during cluster bombardment simulations, the elongated valleys and ridges do not form, the surface becomes smoother and the sputtering yield increases by ~10%, which is comparable to the co-bombardment experimental yield increases of 18-23%, and the surface roughness decreases. Therefore, it appears as though the 200 eV Ar beam oriented at 33° with respect to the C$_{60}$ beam is breaking up the ridges in the surface formed by the C$_{60}$ beam. Since the Ar beam is kept at 200 eV the damage is restricted to the same region as that produced by the C$_{60}$ beam. Also, the smoothing of the surface would increase the yield slightly in turn increasing the depth profiling ability. From the logic presented here for the enhancement of depth profiles due to co-bombardment, that the favorable synergy would persist with a decrease in incident angle closer to the surface normal or that the enhancement would take place for beam conditions with much higher yields. A change in the beam conditions of C$_{60}$ may give the same or greater depth profiling enhancement as co-bombardment with low-energy Ar ions.

4.3.4 Conclusion

MD simulation have been used to explain how co-bombardment by 10 keV C$_{60}$ at 70° angle of incidence and low-energy Ar at 45° angle of incidence and oriented 33° to
each other, improve depth profiling capabilities. MD simulations demonstrate that the sputtering enhancement is due to a decrease in surface morphology caused by the breaking up of ridges by the low-energy Ar beam. The surface ridges having been formed due to the primary beam conditions. The breaking up of the ridges creates a smoother surface and increases the sputtering yield. The enhancement due to cobombardment is believed to be only effective for the specific \( C_{60} \) beam conditions employed in the cobombardment experiments.

4.4 References

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Chapter 5

Dynamics Displayed by Energetic C$_{60}$ Bombardment of Metal Overlayers on an Organic Substrate

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5.1 Introduction

Three dimensional characterizations of materials with depth resolutions down to the nanometer level can be obtained using time-of-flight secondary ion mass spectrometry (tof-SIMS). Depth profiles can be produced by bombarding the surface with cluster ions in continuously so that successive layers of the material are removed and analyzed by the tof-SIMS instrument. Due to dynamic and chemical effects of the cluster ions’ interaction with the surface, not all materials are easily or successfully depth profiled.$^{1-4}$ Samples that contain metal-organic interfaces are one type of material that has been shown to be particularly problematic.$^2$ Metal layers are important components in organic electronic devices. The most prominent example is the metal cathode in organic light emitting diodes (OLED).$^5$ However, metal layers have also been applied in
developing organic bistable devices for rewritable memory cells, and in the construction of metal-organic microcavities, which could be used to develop electrically driven organic solid-state lasers. The difficulty of depth profiling through metal-organic interfaces was shown by Cheng and Winograd for depth profiles of both aluminum overlayers on a peptide-doped trehalose film and Ag overlayers on a pure trehalose film using a $C_{60}^+$ ion beam. In the depth profiles, the secondary ion signal for the metal species was shown to persist well below the metal-organic interface. The observed effects on the depth profiles were attributed to the possible mixing and chemical damage resulting from ion cluster bombardment. Recently, tof-SIMS has been used successfully to depth profile through OLED and OLED like devices using large gas cluster ion beams with the caveat of having first removed the outer metal cathode or that a metal cathode was not included in the construction of the OLED. The necessity to remove the metal cathode is added evidence suggesting that there are complications when depth profiling through the metal-organic interfaces. Understanding the microscopic origin of these difficulties and finding practical solutions are, therefore, important.

Molecular dynamics (MD) simulations have been instrumental in developing our current understanding of the mesoscopic processes that occur during cluster bombardment of both inorganic and organic solids. Therefore, their application to the study of cluster bombardment of metal-organic interfaces is natural and should enable elucidation of the reasons for the difficulties of depth profiling through such systems. Recently, MD simulations performed by Restrepo et al. have been used to explain the enhanced sputtering yields observed in SIMS experiments on organic surfaces coated with metallic nanoparticles; a technique referred to as metal-assisted SIMS (MetA-
The systems that the authors studied were composed of ~2.5 nm gold nanoparticles (Au-NP) deposited on top of both crystalline and amorphous polyethylene (PE) surfaces or embedded in the amorphous PE. These studies show the complexity and diversity of actions that occur in systems with interfaces between metallic structures composed of heavy atoms and softer and lighter organic materials.

The objective of this Chapter is to describe the dynamics of energetic $C_{60}$ cluster bombardment of metal overlayers deposited on an organic substrate. To accomplish this goal, MD simulations of 15 keV $C_{60}$ bombardment at normal incidence of silver (Ag) metal overlayers with a thickness varying from 0 nm (a bare octatetraene crystal) up to 4.7 nm on a crystalline octatetraene substrate have been performed. The results are used to provide insight into phenomena being responsible for the difficulties associated with depth profiling through metal-organic interfaces.

### 5.2 Description of the Calculation

MD simulations were employed to investigate the dynamics of cluster bombardment of metal-organic interfaces. Ag{111} and a trans,trans-1,3,5,7-octatetraene crystal ($C_8H_{10}$) were chosen for the metal overlayer and underlying organic solid due to previous familiarity with using these systems in MD simulations. Systems with metal overlayers varying from 4.7 nm thickness down to the bare octatetraene solid in roughly 0.94 nm (4 atomic layers) decrements were utilized to mimic the various stages of transition through a metal-organic interface during depth profiling. The crystalline octatetraene solid has a monoclinic structure with a density of 1 g/cm$^3$, which is much
smaller than a density of 10.5 g/cm$^3$ for fcc Ag sample. There is also a significant difference in cohesive energies between these materials. Octatetraene and silver have cohesive energies of 0.52 and 2.95 eV, respectively. The CrystalMaker program was used to generate the octatetraene structure, which was then energy minimized. Thirty-five layers of Ag{111} were positioned above the organic surface and the system was allowed to quench. The resulting system was then cropped into hemispheres with the appropriate radius to confine 15 keV of the primary kinetic energy for the intended metal overlayer thickness. As a result, the radius of the hemispherical samples changed from 16.5 nm for a thickest metal overlayer to 20.5 nm for the bare molecular crystal. Corresponding samples have from 709,011 to 1,854,312 atoms. Excluding the surface, the outer shell of the hemispherical systems were contained by a rigid boundary of 1.3 nm, which was bordered by a stochastic region with a width of 2.6 nm that was used to prevent reflection of the pressure waves generated by the cluster impacts.

Several interatomic potentials were used to model the relevant interactions that occur during the bombardment process. The reactive AIREBO potential was used for interactions between the hydrocarbon atoms comprising both the molecules of the octatetraene solid and the C$_{60}$ cluster. The Ag-Ag interactions were described by the molecular dynamics/Monte Carlo corrected effective medium (MD/MC-CEM) potential. Because a potential that would describe chemistry between the Ag and the organic molecules does not exist, interactions between Ag and organic atoms were described using two-body Lennard-Jones (LJ) potentials splined with Moliere potentials for the repulsive walls. The parallel sputtering code implementing the message passing interface strategy (MPI) was used to perform calculations. The details of this approach
can be found elsewhere.\textsuperscript{34} We used 16 processors per simulation, and the elapsed time per trajectory ranged from 1 to 6 weeks. We used a variable time step fifth-order Gear predictor-corrector integrator,\textsuperscript{34} and the time step ranged from hundredths of femtoseconds, during the initial impact of the cluster when the forces are changing most rapidly, to a little over one femtosecond at the end of the trajectory. Simulations were terminated when molecular sputtering from the organic solid had ceased, which usually took from 50 to 90 ps. Since the goal is to understand the general dynamics of the bombardment of a metal/organic system and not to obtain detailed quantitative results, we have calculated only one trajectory per set of initial conditions.

The simulations described here stretch the use of empirical interaction potentials. As we have noted previously,\textsuperscript{11,34-37} if one does not have a perfect set of interaction potentials, then that limits the interpretations that can be made from the computer simulations. Briefly, the reactive REBO potential has been described quantitatively for small molecules and fragments by Brenner et al.\textsuperscript{38,39} The energetics and geometry of small molecules such as octatetraene are well-described; however, the quantitative descriptions of activation barriers for reactions other than direct bond cleavage are not calibrated and there is no reason to suspect that the reaction barriers are good. The long-range portion of the AIREBO potential\textsuperscript{31} has been described by its authors. The binding energy of the octatetraene crystal is experimentally unknown. The experimental octatetraene structure is stable using the AIREBO potential. The interaction between the Ag surface and atoms with the organic molecules and fragments is a complete approximation because, unfortunately, there is not a good many-body description for the system. The LJ potential used describes a weak interaction between particles. In
summary, then, the system described in the simulations is a molecular solid bound weakly to a metal overlayer. The results that we can describe well are those related to physical processes such as changes in ejection mechanisms and how the changes in mechanisms change the sputtering yields and kinetic energy distributions. There is limited ability to describe specifics of chemical reactions. Moreover, we view this system as a generic molecular solid with a generic metal overlayer and do not attach significance to the octatetraene and Ag chemistry.

The empirical potentials generally used assume that the system stays in the ground electronic state. Consequently, all bond cleavage reactions go to neutral species and not ionized states. Also, as discussed previously the impact of the cluster can create a very dense region in molecular solids. This environment cannot be described by a single electronic state. Thus, the initial reactions in the systems in which the cluster deposits considerable energy in the organic material should be considered approximate.

5.3 Results and Discussion

Distinctive dynamics are elucidated by MD computer simulations for the energetic cluster bombardment of systems composed of metal overlayers on an organic substrate as compared to the energetic cluster impacts on systems such as inorganic solids, molecular organic solids, molecular organic overlayers on metal substrates and metal nanoparticles deposited on organic polymer substrates. Important factors responsible for these distinctive dynamics include the large disparity in the cohesive energy of the tightly bound metal atoms in the overlayer and the loosely bound organic
molecules of the substrate, and the much greater compressibility of the organic material compared to the metal overlayer. The resulting dynamics due to keV cluster bombardment depends on the metal overlayer thickness as shown in Figure 5-1.

The MD studies performed on single component systems have shown that the basic dynamics initiated by C\textsubscript{60} impact involve projectile stimulated mesoscopic motion that pushes material hemispherically away from the impact point. The lateral movement of relocated material is later converted into vertical fluid-like motion of atoms along the walls of the forming crater. The downward motion of material causes the material below the impact point to compress. This compressed material eventually relaxes and causes an upward movement of atoms to fill in the bottom of the crater.\textsuperscript{19,21,26,49,50} The final result of all these actions is the formation of the azimuthally isotropic crater surrounded by the almost circular rim. Atoms or molecules with sufficient kinetic energy can escape the surface and be ejected. MD studies identify two processes leading to particle emission. High energy particles are emitted from the forming corona of the crater soon after the projectile impact by a fluid flow type process, while low energy particles are ejected later from the volume of the crater by an effusive like motion.\textsuperscript{49} Although, these basic motions are also observed for these metal-organic overlayer systems as shown in Figure 5-1 there are also important differences. The snapshots for each system of Figure 5-1 are taken at the moment when the metal overlayer is penetrated by the C\textsubscript{60} cluster (left), when a plume of ejecting organic molecules and fragments initiates (middle) and when the final surface topography is formed (right). First, for the 3.8 nm film (Figure 5-1a-c), the main change from the pure metal system is that the soft organic material allows the metal layer to push into it creating a small but temporary hole. Some of the organic molecules
expand into the hole (Figure 5-1b) and eject, while some ultimately adsorb to the top metal surface. In this case, almost all impacting energy is absorbed in the metal overlayer (see caption to Figure 5-2). The trend continues for the 2.8 nm film (Figure 5-1d-f) except that now the thickness of metal layer is not sufficient to absorb all the incident energy, integrity of the layer is compromised, a permanent hole in the overlayer is created and chunks of metal are deposited in the organic material. Organic molecules eject through the hole and organic material coats the metal surface as shown in Figure 5-1f. The final configuration includes one large metal cluster and several metal atoms deposited in the organic layer. For the 0.9 nm film (Figure 5-1g-i) the C\textsubscript{60} blasts into the organic substrate depositing many metal particles into the organic material. Much of the cluster energy is deposited in the organic layer. If there were no overlayer, the organic molecules would begin to flow off the surface by the fluid flow along the walls of the forming crater\textsuperscript{28,49} The metal overlayer, however, prevents this type of ejection. The upward motion of the molecules is blocked by the overhanging metal layer and the pressure exerted by the organic molecules trying to escape puts the thin metal layer into a cantilever type motion. The existence of the hard metal overlayer limits the diameter of the crater opening as compared to the bare organic solid making it more difficult for the molecules to eject. The final topography of the system depicted in Figure 5-1i is of a crater 4 nm deep with the metal overlayer overhanging the crater walls of the organic region. Even though a few metal clusters were sputtered with the upward expansion of solid, the majority of these clusters remain implanted in the organic region (Figure 5-1i).
Figure 5-1. Cross-sectional snapshots of 15 keV 0° C₆₀ bombardment of octatetraene crystalline solids (red) with varying thicknesses of Ag overlayers (gray, thicknesses listed on left). Frames are taken from 1.5 nm slices of the central part of the systems. Columns from left to right show different stages of the bombardment process. From the initial opening of a hole in the Ag overlayers, followed by a plume of ejected organic material and finally the resulting topography from the C₆₀ impact.

5.3.1 Energy Deposition

How the C₆₀ energy is deposited illustrates the mechanisms of damage formation and sputtering. Snapshots of the kinetic energy distribution taken at 400 fs, a time when the energy has reached the interface for all layer thicknesses, are shown in Figures 5-2a-d. The atoms are colored by their kinetic energies with grey atoms indicating energies less than 0.1 eV and atoms with from 0.1 eV to 20 eV of kinetic energy colored from
yellow to reddish orange. Particles with greater than 20 eV are red. The discussion below focusses on the red atoms. The caption gives the total kinetic energy deposited in both the metal overlayer and the organic substrate for the given systems.

Figure 5-2. 1.5 nm cross-sections of C\(_{60}\) cluster impacts of Ag/octatetraene systems at 400 fs colored according to an atom’s kinetic energy (yellow to red: 0.1 to 20 eV, grey < 0.1 eV where dark grey are Ag atoms and light grey are C and H atoms). The kinetic energy totals for the Ag and octatetraene regions for each of the different systems shown are a) 9.6 keV and 0.4 keV, b) 10.6 keV and 0.8 keV, c) 8.0 keV and 2.6 keV d) 3.6 keV and 5.5 keV respectively.

The starting point for understanding the change in the energy deposition as a function of metal layer thickness is for the thickest layer as shown in Figure 5-2a. The energy that goes into the metal substrate is distributed among many Ag atoms as the hard metal material is relatively uncompressible. In this case, almost 96% of deposited energy is confined to the metal overlayer. When the metal overlayer is thinner (Figure 5-2b, c), the energy deposition occurs both in the metal and organic layers. There are two consequences of this change. First, there is energy directly deposited in the organic layer
that goes towards ejecting molecules or remains trapped in the organic substrate leading to material mixing. Second, metal atoms move downward at the interface and are deposited in the organic material. Solid metal samples, on the other hand, confine the energy deposition to a depth of about 4 nm, the introduction of a metal organic interface allows the energy as well as metal particles to go as deep as 8 nm below the surface as seen in Figure 5-1 and discussed below. The change in the mechanism of energy transfer as the metal overlayer becomes thinner affects the amount and spread of metal implantation in the organic substrate as well as the velocities of the sputtered organic molecules.

### 5.3.2 Kinetic Energies of Sputtered Substrate Molecules

A change in the mechanisms of ejection stimulated by cluster impacts on systems with metal overlayers with respect to cluster impacts on pure organic solids is reflected in the kinetic energy (KE) distributions of sputtered substrate molecules shown in Figure 5-3. The KE distribution for the molecular solid is characterized by an initial rise from 0 eV to a peak at about 0.4 eV followed by a decay at higher energies. One could expect that molecules ejected from metal covered systems would have a lower kinetic energy as a large portion of the primary energy is absorbed in the metal overlayer. The distributions of the kinetic energy of sputtered molecules from the systems with metal overlayers, however, are shifted to higher KE as compared to bare organic solid. In fact, there are very few molecules sputtered with kinetic energy below 1 eV, while over 40% of the molecules sputtered from the pure organic solid have kinetic energies less than 1 eV. As
it was already mentioned, in bare organic solids molecules with high kinetic energy are ejected relatively soon after projectile impact from the corona of the forming crater by a fluid flow process, while low energy molecules are emitted later from the volume of the crater by effusion.\textsuperscript{28,49} Our data indicate that low energy emission is hindered due to existence of thick metal channel with relatively narrow diameter that is formed in the punctured metal overlayer. Animations of the cluster bombardment also show that the fluid flow mechanism leading to emission of high energy molecules from the corona of the crater is absent due to blocking of the molecular flow by the dense metal overlayer composed with heavy atoms bounded with high cohesive energy. This observation indicates that high energy molecules must be ejected by some other mechanism not present during sputtering of pure organic systems.

This mechanism of emission can be identified from the available animations of the cluster impacts that show that the hole produced in the metal overlayer as well as the bending of this layer into the organic material by the impacting cluster causes a jetting effect in the upward flow of substrate molecules from a pressurized volume located below. As a result of the jetting, the organic molecules experience an increase in velocity as they eject into vacuum. This jetting effect may become more pronounced as the metal overlayer thickness increases since the cross-sectional area of the hole is decreasing and a higher pressure is needed to squeeze the molecules out. This is indeed observed for the 0.8, 1.9 and 2.8 nm overlayers. However, as the layer becomes too thick it absorbs most of the primary energy and at certain moment, the delivered energy is too small to enhance sufficient pressure and the process of jetting disappears. Such is the case for the overlayer
3.8 nm as indicated by the kinetic energy distribution shift to lower kinetic energies as compared to thinner metal overlayers.

Figure 5-3. Kinetic energies of sputtered octatetraene molecules, signal normalized to the signal for the octatetraene solid (solid line) with no Ag overlayer. Dashed lines represent the kinetic energies for the sputtered octatetraene molecules from the systems with Ag overlayers.
5.3.3 Sputtering Times for the Molecular Substrate

Molecular octatetraene sputtering times are shown in Figure 5-4a-c for systems with metal overlayer thicknesses of 1.9 nm, 0.9 nm and for the bare organic solid. First, by examining the length of the period of sputter times, we can see the effects of the energy trapping by the metal overlayer that was mentioned above. Both of the metal overlayer systems have sputtering occurring at later times than occur for the system without the metal overlayer. The trapping of energy in the organic substrate by the metal overlayers enables molecules to effuse from the holes over a longer period of time relative to the organic solid; the difference in times is however inconsequential in respect to experimental detection times. The energy trapping effect becomes more pronounced as the metal overlayer becomes thinner due to the increase in energy deposited to the organic substrate as the metal overlayer thickness decreases, and the increase in the cantilevering effect of the metal overlayer storing and then re-depositing energy to the organic substrate. The re-distribution of energy from the cantilevered metal overlayer to the organic substrate can be seen influencing the molecular sputtering in Figure 5-4a,b by the smaller secondary peaks that correspond with the cantilevered metal overlayer colliding with the organic substrate, which can be seen at 42 ps for the 1.9 nm metal overlayer system and at 54 ps for the 0.9 nm metal overlayer system.

The metal overlayers appear to increase the minimum time for sputtering to occur as compared to C_{60} impacting the organic solid, which has a minimum sputter time of 700 fs (Figure 5-4c). This apparent difference is because the artificial surface for deciding if a molecule is ejected is about 2.5 nm above the actual surface. For the overlayer systems,
the ejecting organic molecules have to traverse a longer distance to reach the point where they are declared ejected in the simulations.

Figure 5-4. Sputtering times shown for octatetraene molecules for the 1.9 nm and 0.9 nm Ag overlayer systems (a) and (b) and for the bare octatetraene solid (c).
5.3.4 Sputtering Yields

The creation of holes in the metal overlayer due to the cluster bombardment followed by the jetting of the organic molecules from the organic substrate means that the sputtering yield of molecules initiates at a metal layer coverage of 3.8 nm as shown in Figure 5-5 and steadily increases as the metal thickness decreases. For the organic solid (i.e. no metal overlayer), the yield is 4.5 times larger than for the 0.9 nm overlayer which indicates that even a thin overlayer has a pronounced influence on molecular emission. The metal overlayers thus suppress the molecular yield. As discussed above, the most prominent mechanism of emission with the metal overlayer is jetting motion; whereas, the emission from an uncovered surface is through fluid flow and effusion.\textsuperscript{28,49}

![Figure 5-5. Total sputtering yield of octatetraene molecules versus metal overlayer thickness.](image)
The sputter yield trend with respect to Ag overlayer thickness from Figure 5-5 is in line with the experimental results found by Cheng and Winograd for depth profiles of a 15 nm Ag overlayer on a 650 nm thick film of trehalose sugar using a 20 keV C$_{60}^+$ primary ion beam at 40° angle of incidence.$^{2,51}$ The depth profiles show the rise of the trehalose signal starting at roughly halfway through the erosion of the Ag film and continuing to rise through the Ag/trehalose interface. Early onset of the trehalose signal indicates the penetration of the Ag overlayer and escape of trehalose well before the interface has been reached. The formation of holes in the Ag overlayers shown in Figure 5-1 depicts how this is possible. Also, the increase in the sputtered molecules with decreasing Ag overlayer thickness, shown in Figure 5-5, agrees with the increase in the trehalose signal as it approaches the Ag/trehalose interface. Of course, the trehalose depth profile shows the penetration of a much thicker Ag overlayer than was used in the simulations; however, the experimental C$_{60}^+$ beam was at a higher kinetic energy, and the Ag surface had already been eroded, which would have resulted in a roughened surface that could have regions much thinner than the ~7.5 nm Ag penetration that the depth profile would imply.

### 5.3.5 Mixing by Metal Cluster Implantation of the Organic Substrate

The energetic cluster impact leads not only to ejection of Ag particles but also causes implantation of the metal atoms into the organic substrate. The results of the implantation of metal clusters in the organic substrate for three different metal overlayer thicknesses are shown in Figure 5-6. A top view of the horizontal spread of the metal
clusters is presented in the top of the figure, and a side view showing the depth of the implanted clusters is shown in the bottom of the figure with the red line indicating the original surface height and the blue line indicating the initial interface between the metal overlayer and the organic substrate. The images in both the top and bottom of Figure 5-6 clearly show that as the metal overlayer thickness decreases, the size of the implanted clusters is reduced and the lateral and vertical spread in the implanted clusters increases. As can be seen by the darker orange and red metal atoms in Figure 5-2c, d, the kinetic energies of the metal clusters, that break free of the metal overlayer, increase as the metal overlayer thickness decreases. The increase in KE of the metal cluster and the decrease of the average cluster size translate into the faster clusters and thus is the cause of the increase in the spread of the metal clusters as the overlayer thickness decreases.
Figure 5-6. Images showing the amount, size and distribution of Ag clusters implanted in the octatetraene substrate of the solid for a given metal overlayer thickness. Top row of images show a view looking down on the sample from the direction of C$_{60}$ cluster impact. Bottom row are the side views. The red line indicates the original surface height and the blue line represents the Ag/octatetraene interface, the solid black line is the depth at 8 nm. Ag atoms are depth cued so that light grey atoms are closest to the viewer and dark grey the farthest away.
Experimental depth profiles of a 15 nm Ag overlayer on a 650 nm thick trehalose film shows that the Ag signal monotonically decreases, yet persists, through the extent of the trehalose film thickness. The implantation of metal clusters shown in Figure 5-6 demonstrates why initially, after reaching the Ag/trehalose interface, the Ag signal is being detected since the metal clusters have been implanted roughly 8 nm deep in the substrate and would have to be sputtered after the Ag overlayer has been removed. However, the persistence of the Ag signal through 650 nm of trehalose implies that the C₆₀ cluster’s ability to clean up the damage incurred by penetrating the metal overlayer is being impaired. The larger size metal clusters produced by cluster impacts on thicker overlayers, as seen in Figure 5-6, could fragment on subsequent cluster impacts resulting in metal clusters driven deeper into the substrate. Also, smaller metal clusters could undergo interlayer mixing within the organic substrate during multiple cluster bombardment. It is plausible that the combination of these phenomena could result in the continuation of signal from the metal overlayer through the organic substrate that was seen in the depth profiling experiment.

5.3.6 Depth Profiling through Metal-Organic Interfaces

The calculations presented herein yield perspective into why depth profiling through a metal organic interface such as found in an OLED is challenging. Molecular dynamics simulations of repetitive bombardment of a Ag surface along with a model to extrapolate the MD results to actual depth profiles have allowed us to identify two key features important for good depth profiles.
First, the information depth or depth from which particles are sputtered should be small. The information depth has two components, the inherent depth from which material is sputtered convoluted with the peak to valley height associated with the rms roughness. At this point we cannot compare rms roughness of this system with the metal Ag system for which we have performed repetitive bombardment simulations, thus we stick to comparing the depth from which particles sputter. For Ag, the typical sputter depth is ~2.5 nm as shown in Figure 5-1c. The crater depth for the pure organic material is also about 2 nm. If we take the 2.8 nm film of Figure 5-1d-f as our example overlayer since it is just slightly thicker than the pure material information or sputter depths, we can see from Figure 5-1e that organic molecules from 3-4 nm below the surface are ejecting. Thus, the information depth for the organic molecules is greater in the metal-organic interface region for the flat surface of either pure organic or pure metal.

Second, the amount of material displacement due to the cluster’s impact should be small for good depth profiles. For the metal system, the displacements for a single impact are dominated by up and down motions of 1 nm although there is some contribution of 2 nm movements up and down. From Figures 5-1f and 5-1i, organic molecules can have upward displacements of 1-3 nm due to the jetting effect. From Figure 5-6, metal atoms can have downward displacements of 3-6 nm. These particles will collide with organic molecules causing additional relocation. As a result, the average material relocation is significantly increased when the metal organic interface is reached.

The snapshots of the systems taken after bombardment suggest the presence of an additional complexity for depth profiling through a metal organic interface, namely, a changing environment. The pictorial information shown in Figures 5-1 and 5-6 clearly
show that subsequent impacts will see not only a different surface topography but also a
different environment, one with holes in the metal overlayer, metal atoms and clusters of
metal atoms in the organic layer and organic molecules on top of the metal overlayer.
The MD simulations of Restrepo et al.,$^{23-25}$ show very clearly that the microscopic nature
of the impact environment with nanoparticles in an organic matrix can have a significant
influence on the dynamics. In addition, depending on the particular combination of
species, the physical mixing of metal atoms with intact molecules and fragments of
molecules could induce chemical changes in the system and, consequently, may
significantly modify the ejection yield of secondary ions as was observed in MetA-SIMS
experiments.$^{56-63}$

The larger information depth, the larger displacements and the altered physical
and chemical environment provide a glimpse into why depth profiling through a metal-
organic interface is challenging. The real issue, however, is whether the insight obtained
from these simulations aid in designing a better strategy for depth profiling through a
metal-organic interface. First, any layer with a low cohesive energy (large volatility)
below a layer with large cohesive energy will present a challenge because holes can open
in the overlayer and energy can get trapped in the underlayer forming separated, highly
pressurized volumes that extend deep into the solid from where molecules will be
released in a jetting motion. The next challenge is to prevent the metal atoms from
implanting in the organic substrate. The ease with which the metal atoms implant is in
part due to the mass mismatch between the metal atoms and the carbon and hydrogen
atoms in the organic material. The light elements have difficulty in efficiently stopping
the heavier atoms. The other challenge is that, at least in the case considered here, the
organic material is much more compressible than the metal overlayer. Any cluster that can sputter the metal will also push it into the organic layer. These factors arise from the inherent system properties and cannot be altered experimentally.

5.4 Varying the Impacting Cluster Initial Conditions

Several preliminary cluster bombardment simulations were performed on the metal-organic interface systems with the goal of finding beam conditions that would minimize the adverse effects of cluster bombardment previously discussed. The initial conditions were adjusted with respect to the clusters incident energy and angle of incidence for both C\textsubscript{60} and Ar\textsubscript{872}. By altering these initial conditions, the amount and area over which the clusters’ energy was deposited were varied. Both reducing the kinetic energy of the impacting atoms, either by reducing the cluster’s incident KE or by spreading the energy over more atoms by employing a larger cluster size, and by increasing the angle of incidence of the impacting cluster, results in a decrease in the amount of energy deposited to the surface by the impacting cluster.\textsuperscript{15,64} The goal being to minimize the depth of energy deposition primarily to the metal overlayer region while, in conjunction with this restraint, maximizing the amount of energy deposited in the metal overlayer. It was thought that the combination of these effects would reduce the amount of metal clusters deposited in the organic substrate, reduce the amount of sputtered substrate molecules, while still maintaining a sufficient metal atom sputter yield to remove the metal overlayer. The initial conditions used for the impacting clusters were as follows: 15 keV Ar\textsubscript{872} at normal incidence, 15 keV C\textsubscript{60} at 45°, 60° and 75° angles of
incidences, \( \text{C}_6\text{O}_\text{60} \) at 60° angle of incidence with incident energies from 1 to 10 keV, and \( \text{Ar}_{\text{872}} \) at 60° angle of incidence with from 10 to 40 keV incident energies.

For impacting cluster conditions that were able to produce significant sputtering of metal atoms (all \( \text{C}_6\text{O}_\text{60} \) impacts except for 1 keV, 60° and 15 keV 75°, 15 keV \( \text{Ar}_{\text{872}} \), normal incidence and \( \text{Ar}_{\text{872}} \), 60° with incident energies of 25 keV and above), varying degrees of metal implantation and ejection of underlying organic molecules occurred. Cluster conditions that did not produce any molecular ejections had almost no sputtering of metal atoms. For instance \( \text{Ar}_{\text{872}} \) at 60° angle of incidence, the sputtering of metal atoms did not occur until 25 keV; however, for 15 keV and above, holes were formed in the metal overlayer from which molecules ejected. These results showed that finding a set of initial conditions for the impacting clusters that are optimal for removing the metal overlayer will be difficult to find, if not extremely unlikely, without some alternate strategy to assist in the sputtering process, at least for systems similar to the Ag on octatetraene presented here.

### 5.5 Conclusion

The dynamics associated with 15 keV \( \text{C}_{\text{60}} \) cluster bombardment of metal-organic interfaces consisting of Ag overlayers on an octatetraene organic solid were investigated using MD simulations. The impacting clusters were shown to create holes in the metal overlayer through which the underlying organic molecules can sputter in a jetting motion. For metal overlayers thinner than 3 nm, metal atoms and clusters were implanted in the underlying organic solid. The larger information depth, the larger displacements and the
altered physical and chemical environment are the main reasons for the poor ability to
depth profiling through a metal-organic interface. Although the simulations provide a
picture of the issues associated with depth profiling through a metal-organic interface,
they do not provide a magic solution that will be under the experimentalist’s control. We
did perform test simulations with other beam conditions, for instance with Ar$_{872}$ clusters
as the projectile. These simulations did not find a good solution.

5.6 References

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Chapter 6

Conclusion and Future Direction

6.1 Conclusion

Molecular dynamics simulations of cluster bombardment have been extended to systems that are of current importance to the SIMS community. Incorporation of chemistry on length and time scales that capture the dynamics associated with cluster bombardment in a computationally tractable manner provides a basis for the study of organic solids in which chemical effects are of paramount importance in SIMS experiments. MD simulations also have been used to elucidate phenomena related to the difficulties associated with SIMS experiments of materials that include metal-organic interfaces, such as organic electronic devices.

6.1.1 MD Model to Incorporate Reactions in Cluster Bombardment Simulations

A mixed resolution model has been developed for the cluster bombardment of solid benzene. The model partitions the impacted system into an atomistic region capable of modeling the chemical reactions that occur in the bombardment process and a surrounding region of coarse-grained (CG) particles representing the CH moiety in a benzene molecule. The atoms are initially confined to a known reaction volume, while the surrounding CG particles allow the model to capture the full dynamics of the cluster bombardment process in a realistic simulation time frame. Testing on an initial small benzene system demonstrated the smooth transition of the cluster induced pressure wave
through the atomistic/CG interface, which demonstrated the ability of the model’s interaction potentials between the two sets of particles to capture the mesoscopic motion in the benzene solid resulting from the cluster impact. Proof of principle simulations of the bombardment of solid benzene by \( C_{60} \), \( Ar_{18} \) and \( Ar_{60} \) demonstrated that the mixed resolution model was computationally efficient and provided an interesting result related to experiment. Namely, that bombardment with Ar clusters that have similar masses or similar number of constituent particles results in total sputter yields and total damage close to that produced by \( C_{60} \) bombardment; differences that should not be noticeable on the experimental scale. The results from the \( C_{60} \) bombardment of solid benzene were also used to elucidate the relationship between \( C_{60} \) and Ar in cobombardment experiments. The results showed that the sputter yield enhancements produced by including a monoatomic Ar beam in conjunction with \( C_{60} \) during depth profiling was from the poor experimental beam conditions used and that similar results could be attained by using just the \( C_{60} \) source with optimal beam conditions.

Also, with respect to the mixed resolution model, test simulations of the ReaxFF force field were performed and demonstrated that it is capable of modeling the reactions believed to effect the removal or accumulation of chemical damage in SIMS depth profiling experiments of the organic polymers poly( methyl methacrylate) (PMMA) and polystyrene (PS). Therefore, ReaxFF could be employed in a mixed resolution models of PMMA and PS for cluster bombardment simulations to investigate chemical processes caused by the cluster impact.
6.1.2 MD Metal-Organic Interfaces

MD simulations of the cluster bombardment of metal overlayers on an organic substrate have presented a microscopic view that uncovers the dynamics involved in the physical processes associated with the difficulties in SIMS experiments on materials with metal-organic interfaces. The simulations demonstrate that, at a certain overlayer thickness and below, the cluster impacts produce holes in the overlayer that can be transient in nature. Due to energy being deposited to the substrate, organic molecules can eject through the holes in the metal overlayers; however, the rigidness of the metal overlayers prevents the fluid flow mechanism of ejection that occurs during bombardment of bare organic substrates, thus the sputter yields are reduced. Also, the fact that the information depth for cluster bombardment of the metal solid is less than the thickness of the metal overlayer that resulted in the formation of a transient hole illustrates why early ejection of the organic substrate is observed in depth profiling experiments of metal-organic interfaces. Finally, the simulations revealed that metal clusters from the metal overlayer were implanted in the organic substrate. Due to their depth, many of these metal clusters would still be present after another cluster impact. Considering that multiple cluster impacts would most likely drive some of the clusters deeper into the substrate, the simulation clearly demonstrate the cause for the persistence of the metal overlayer signal after the metal-organic interface has been reached. The microscopic view of the dynamics involved in the cluster bombardment of metal overlayers on an organic substrate give experimentalists a clearer picture of the difficulties associated with depth profiling through such materials.
6.2 Future Directions

The goals of this dissertation have been tied to broadening the application of MD simulations to systems that are currently important to SIMS researchers such as organic solids that have possible chemical effects during SIMS experiments and substrates with metal-organic interfaces that are difficult to depth profile. The work presented in this dissertation has laid the basis for including chemical reactions in cluster bombardment simulations of SIMS and has produced insights into the processes that occur during cluster bombardment of metal-organic interfaces that make these materials difficult for SIMS. However, much work still needs to be done with regards to both of these areas.

The increasing use of parallel programming in cluster bombardment simulations has at present made the use of the mixed resolution model in cluster bombardment simulations unnecessary. However, the desire for simulations to reflect experimental conditions has increased the importance of repetitive bombardment simulations. So far these simulations have been restricted to substrates composed of metals, silicon and coarse-grained organic materials.\textsuperscript{1-6} This is due to the computational cost of performing simulations of organic materials with a reactive potential. Even with the use of parallel code, the simulation time for cluster bombardment of an organic solid is on the order of 3 weeks;\textsuperscript{7} to achieve repetitive bombardment fluences similar to experiment, the simulation time needs to be on the order of hours to complete in a reasonable time frame. The mixed resolution model could assist in reaching such short simulation times in combination with the implementation of a parallel code.
The successful testing of ReaxFF with respect to modeling reactions related to cluster bombardment of PMMA and PS has led to the testing of ReaxFF in cluster bombardment simulations of small organic solids. The use of ReaxFF has the potential of opening the door to cluster bombardment simulations of a wide array of substrates such as polymers and organometallic compounds used in OLED’s and could be used to simulate the chemical effects that occur in bombardment of metal-organic interfaces. ReaxFF offers such possibilities as a result of its ability to be parameterized for different elements. A long term goal would be to use ReaxFF in repetitive bombardment simulations that could mimic SIMS depth profiling through multi-layered materials such as OLED’s.

Further MD investigations of metal-organic interfaces should concentrate on organic substrates with embedded metal clusters to examine the clean-up ability of cluster impacts on the underlying bombarded organic substrate in a metal-organic interface system and the dynamics related to metal cluster fragmentation and further implantation. Also, repetitive bombardment simulations of a metal-organic interface should be undertaken to investigate the effects of surface roughening on SIMS experiments.

With the possibilities laid out in this section, it is clear that MD simulations of cluster bombardment will continue to play an important role in uncovering the chemical and physical phenomena associated with SIMS experiments. The work in this dissertation has provided an important basis for future MD simulations that will continue the collaboration between theory and experiment in SIMS research.
6.3 References


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