Molecular Dynamics Simulations of Organic SIMS with Cu_n (n=1-3) Clusters

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Molecular dynamics simulations have been performed to study the effect of cluster size on the emission yield and damage cross section in organic SIMS. A model system composed of a monolayer of biphenyl molecules on a Cu(001) substrate was bombarded with Cu_n (n=1-3) projectiles at kinetic energies of 0.100 keV per atom. The yield increases with cluster size, but a nonlinear enhancement in yield is not observed. The yield-to-damage ratio, on the other hand, increases with the use of clusters, indicating that clusters have the potential to improve the sensitivity of SIMS.

INTRODUCTION

Secondary ion mass spectrometry (SIMS) experiments, which have measured the secondary ion emission resulting from the keV bombardment of solids with monoatomic and polyatomic ions, have raised some interesting issues about the processes for energy deposition leading to the ejection of particles from the solid (1-5). In many cases, polyatomic projectiles produce a big enhancement in the secondary ion yield compared to monoatomic projectiles. The yield is defined to have a nonlinear dependence on the number of atoms in the primary projectile when the yield from a polyatomic projectile containing n atoms with total energy E is more than n times greater than the yield from a monoatomic projectile with energy E/n (2a,b). Experiments show that the degree of enhancement will depend strongly on the kinetic energy, mass, size and composition of the primary cluster as well as the characteristics of the target and matrix or substrate. The greatest enhancements in yields are with molecular ions and molecular fragments (2,3) and with multi-layer targets rather than monolayer films (2d).

There are potential problems with the use of polyatomic projectiles that may overshadow their advantages. In conjunction with producing a larger emission yield, experiments by Van Stipdonk, et. al. show that polyatomic projectiles may also increase the damage cross section on the surface and produce a greater number of molecular fragments (2d). However, experiments by Appelhans, et al. (1a) and Groenewald, et. al. (1b) show both an increase in yield and a smaller damage cross section with polyatomic projectiles. The ultimate test to whether polyatomic projectiles may improve the sensitivity of SIMS is in how they increase the emission yield of intact molecules in comparison to the total damage cross section.

Therefore, the key issue is whether there is a more efficient way to deposit energy with keV projectiles that results in a greater number of ejected intact molecules while minimizing surface damage. In order to address this issue, we have perfomed molecular dynamics simulations of the bombardment of organic films with atomic and cluster projectiles. From the simulations, the emission yield and the yield-to-damage ratio is calculated as a function of cluster size. Although a nonlinear enhancement is not observed with the cluster projectiles, the yield-to-damage ratio increases with cluster size.

METHODS

The classical method of molecular dynamics simulations is used to study the system of interest and the details of this method are described extensively elsewhere (6). The model system, shown in Figure 1, is composed of a monolayer of twenty biphenyl molecules on a Cu(001) microcrystallite consisting of nine layers of 286 atoms. The positions of the biphenyl molecules are determined by allowing the adsorbates to equilibrate on the surface at 0 K. A symmetrically equivalent impact zone is defined on the surface and a set of 150 impact points is evenly distributed over the impact zone. The emission yield with each projectile is calculated by averaging over a set of trajectories, where each trajectory has a different aiming point on the surface.

Potentials developed by DePristo's MD/CEM approach (7) are used for the Cu-Cu interactions. Brenner's hydrocarbon potential is used for the C-C, C-H and H-H interactions (8). The Brenner potential was not developed to describe the repulsive region in which hard collisions occur, and therefore, a Molière pairwise potential is used in the repulsive region of the potential (9). A linear interpolation scheme used by Taylor and Garrison

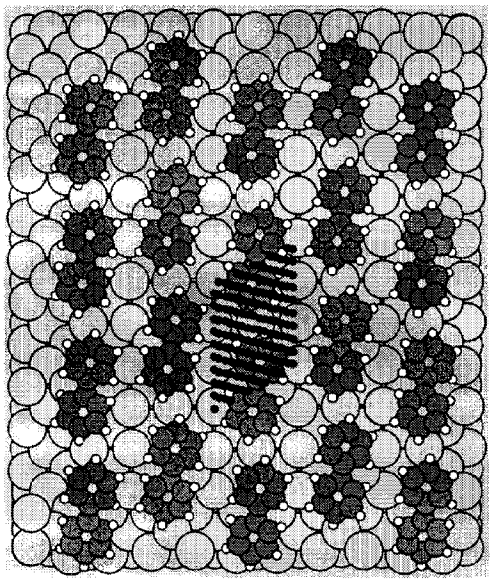

FIGURE 1. Top view of the model system composed of a monolayer of twenty biphenyl molecules on a Cu(001) substrate. The black dots represent the 150 impact points of the bombarding particle.

connects the repulsive and many-body attractive potentials and is described in detail elsewhere (10). A Lennard-Jones potential is used to describe the pairwise Cu-C and Cu-H interactions between the biphenyl molecules and the copper surface, resulting in a binding energy of 2.4 eV (11). A Molière pairwise potential is used in the repulsive region of the potential for these interactions and is connected to the Lennard-Jones potential with a cubic spline polynomial function.

The emission yield is calculated as the number of stable, whole biphenyl molecules ejected from the surface. In order to determine the energy cutoff for stable molecules, simulations were run over a time period of 2 ps for biphenyl molecules with a range of internal energies. From the results of these simulations, it was determined that molecules with internal energies greater than 10 eV are unstable and will fragment before reaching the detector. The total number of damaged molecules is estimated as a sum of the number of ejected, unstable whole molecules and the number of fragmented molecules. From visual inspection of the surface after the bombardment process takes place, the molecules left on the surface intact appear to be undamaged.

RESULTS AND DISCUSSION

The numerical results from the simulations with the Cu_n (n=1-3) projectiles are shown in Table 1. The degree of nonlinear enhancement can be quantified by the enhancement factor. Mathematically, the enhancement factor is defined as $\frac{Y_n(E)}{nY_1(E/n)}$, where $Y_n(E)$ is the yield for the homonuclear cluster at energy E and $Y_1(E/n)$ is the yield for the atomic projectiles at the same velocity (2a,b). An enhancement factor of one indicates that the yield increases linearly with the number of atoms in the cluster. For example, the yield with the Cu_2 cluster at 0.200 keV is simply twice the yield with the Cu atom at 0.100 keV. Table 1 also shows the number of damaged molecules and the ratio of yield to the number of damaged molecules. The yield-to-damage ratio increases with the use of clusters and increases with cluster size.

In Figures 2 and 3, the spatial arrangement of the yield of ejected stable biphenyl molecules and the yield of damaged molecules is shown with the Cu and Cu_3 projectiles, respectively. In these figures, each circle or cone represents one of the twenty biphenyl molecules on the surface. The dark circles represent biphenyl molecules that are not affected by the bombardment. Molecules that are either ejected or damaged are represented by light colored cones. The height of the cone corresponds to the yield of ejected, stable molecules in Fig. 2a and 3a and to the yield of damaged molecules in Fig. 2b and 3b. The impact zone of the incoming projectile encloses the middle two biphenyl molecules.

In Fig. 2a and 2b, the results with the Cu projectile are shown. The Cu projectile leads to the ejection of the two molecules in the impact zone and the immediate neighboring molecules, affecting a total area of 200 $Å^2$. The group of small cones in Fig. 2a represents the number of biphenyl molecules that are ejected intact with internal energies less than 10 eV. In Fig. 2b, the two high cones represent the number of biphenyl molecules in the impact zone that are damaged by the incoming projectile. The incoming projectile damages only a few of the surrounding molecules.

The results with the Cu_3 projectile are shown in Fig. 3a and 3b. Interestingly, the affected area around the impact zone does not increase greatly compared to the area with the Cu projectile. However, a greater proportion of the molecules surrounding the impact zone are ejected intact.

TABLE 1. Yield, Damage, Yield-to-Damage Ratio and Enhancement Factors with Cu_n (n=1-3) clusters

Bombarding Particle	Incident Kinetic Energy (keV)	Yield	Enhancement Factor compared to Cu	Damage	Yield-to-Damage Ratio
Cu	0.100	31	NA	91	0.34
Cu_2	0.200	71	1.1	131	0.54
Cu_3	0.300	97	1.0	164	0.59

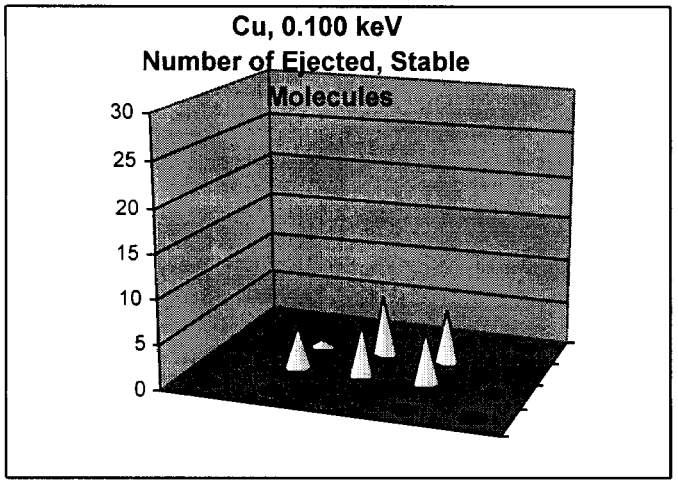

Figure 2a. Spatial arrangement of the yield of ejected stable biphenyl molecules with the Cu projectile.

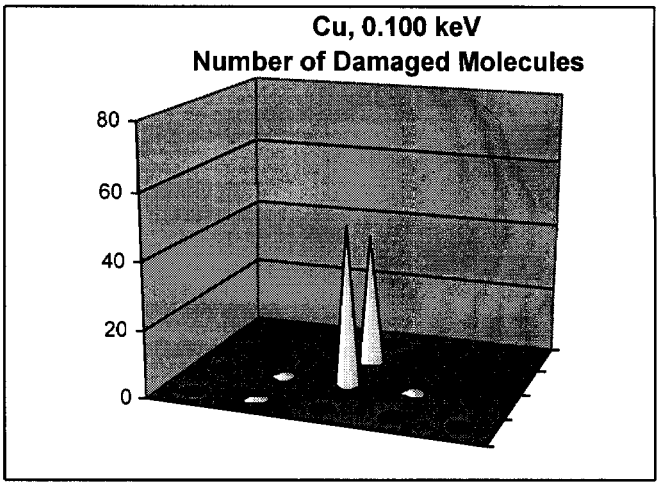

Figure 2b. Spatial arrangement of the yield of damaged biphenyl molecules with the Cu projectile.

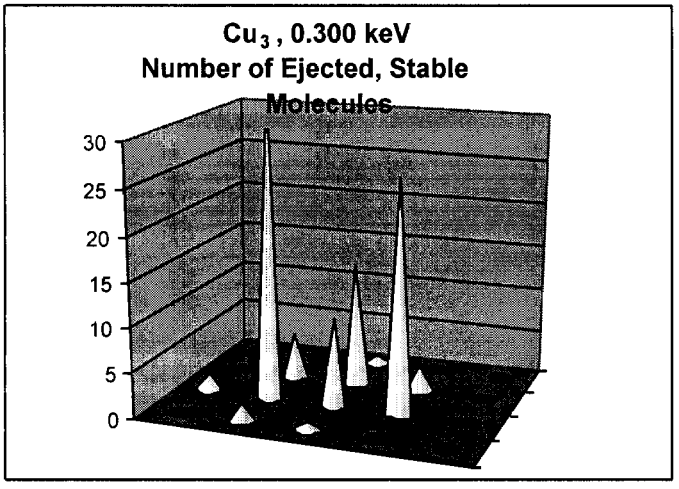

Figure 3a. Spatial arrangement of the yield of ejected stable biphenyl molecules with the Cu_3 projectile.

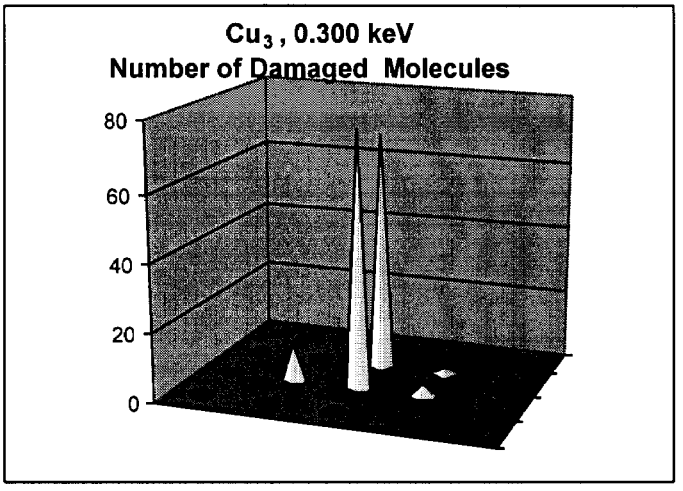

Figure 3b. Spatial arrangement of the yield of damaged biphenyl molecules with the Cu_3 projectile.

In Fig. 3b, the two high cones represent the large number of biphenyl molecules in the impact zone that are damaged. The number of surrounding molecules that are damaged is only a little greater than the number with the Cu projectile. Consequently, the yield-to-damage ratio is larger with the Cu_3 projectile. Previous simulations identified a collaborative mechanism with cluster projectiles (12), in which the cluster atoms initiate adjacent collision cascades that work together to eject the intact molecule from the surface. The collaborative mechanism will lead to a greater proportion of ejected intact molecules, and therefore, to an increase in the yield-to-damage ratio.

CONCLUSIONS

Molecular dynamics simulations of the bombardment of a monolayer of biphenyl molecules on a copper substrate with Cu_n (n=1-3) projectiles have been performed. From the simulations, the yield of ejected, stable molecules and the yield-to-damage ratio has been

determined. The greatest contribution to the yield comes from the ejection of molecules immediately surrounding the impact zone. The two molecules in the impact zone are the primary damaged molecules and only a very small amount of the surrounding molecules are damaged.

The yield of ejected, stable molecules increases linearly with cluster size, but a nonlinear enhancement is not observed. However, the yield-to-damage ratio does increase with polyatomic projectiles. With the cluster projectiles, adjacent collision cascades can collaborate to eject the intact molecule from the surface, which leads to an increase in the yield-to-damage ratio.

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REFERENCES

1. a) Appelhans, A.D., and Delmore, J.E. *Anal. Chem.* **61**, 1087-1093 (1989). b) Groenewold, G.S., Gianotto, A.K., Olson, J.E., Appelhans, A.D., Ingram, J.C., Delmore, J.E., and Shaw, A.D. *Int. J. Mass. Spectrom. Ion Processes* **174**, 129-142 (1998).
2. a) Blain, M.G., Della-Negra, S., Joret, H., LeBeyec, Y., and Schweikert, E.A. *Phys. Rev. Lett.* **63**, 1625-1628 (1989). b) Benguerba, M., Brunelle, A., Della-Negra, S., Depauw, J., Joret, H., Le Beyec, Y., Blain, M.G., Schweikert, E.A., Ben Assayag, G., and Sudraud, P. *Nucl. Instr. and Meth. B* **62**, 8-22 (1991). c) Van Stipdonk, M.J., Harris, R.D., and Schweikert, E.A., *Rapid Commun. Mass Spectrom.*, **10**, 1987-1991 (1996). d) Harris, R.D., Van Stipdonk, M.J. and Schweikert, E.A., *Int. J. Mass. Spectrom. Ion Processes* **174**, 167-177 (1998).
3. a) Boussofiane-Baudin, K., Bolbach, G., Brunelle, A., Della-Negra, S., Hakansson, P., and Le Beyec, Y. *Nucl. Instr. and Meth.B* **88**, 160-163 (1994). b) Le Beyec, *Int. J. Mass. Spectrom. Ion Processes* **174**, 101-117 (1998).
4. Kotter, F., Benninghoven, A. *Appl. Surf. Sci.* **133**, 47-57 (1998).
5. a) Mahoney, J.F., Parilis, E.S. and Lee, T.D. *Nucl. Instr. and Meth. B* **88**, 154-159 (1994).
6. a) Garrison, B.J. and Winograd, N. *Science*, **216**, 805-812 (1982). b) Garrison, B.J., *Chem. Soc. Rev.*, **21**, 155-162 (1992). c) Bernardo, D.N., Bhatia, R., and Garrison, B.J. *Comp. Phys. Comm.* **80**, 259-273 (1994).
7. a) Stave, M.S., Sanders, D.E., Raeker, T.J., and DePristo, A.E. *J. Chem. Phys.* **93**, 4413-4426 (1990). b) Raeker, T.J. and DePristo, A.E. *Int. Rev. Phys. Chem.* **10**, 1-54 (1991)., c) Kelchner, C.L., Halstead, D.M., Perkins, L.S., Wallace, N.M. and DePristo, *Surf. Sci.* **310** 425-435 (1994).
8. a) Brenner, D.W. *Phys. Rev. B* **42**, 9458-9471 (1990). b) Brenner, D.W., Harrison, J.A., White, C.T., Colton, R.J. *Thin Solid Films* **206**, 220-223 (1991).
9. O'Connor, D.J. and MacDonald, R.J., *Radiat. Eff.*, **34**, 247-250 (1997).
10. Taylor, R.S. and Garrison, B.J. *Langmuir* **11**, 1220-1228, (1995).
11. Allen, M.P. and Tildesley, D.J. *Computer Simulations in Liquids*, Great Britain: Oxford University Press, 1987, pp. 9-11.
12. a) Zaric, R., Pearson, B., Krantzman, K.D. and Garrison, B.J., *Int. J. Mass Spectrom. Ion Processes,* **174**, 155-166 (1998). b) Zaric, R., Pearson, B., Krantzman, K.D. and Garrison, B.J. in Lareau, R. and Gillen, G, (Eds.) *Secondary Ion Mass Spectrometry, SIMS XI*, New York: John Wiley and Sons, 1998, pp. 601-604.