Formation of small metal clusters by ion bombardment of single crystal surfaces

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The mechanism for the formation of small metal clusters ejected from an ion bombarded metal surface is examined in detail. The analysis is performed by classical trajectory methods which determine the positions and momenta of all particles in a model microcrystallite as a function of time. The calculation utilizes pair potentials for Cu derived from elastic constants of the solid and is performed for 600 eV Ar^+ ion at normal incidence to the crystal. The results show that cluster species do not leave the surface as intact parts of the solid but form in a region above the surface. A trajectory for Cu_5 formation is traced in detail showing a typical mechanism which is valid for Cu_n formation where $n \leq 7$.

During recent years there has been considerable interest in the preparation and characterization of metal particles which consist of only a few constituent atoms. This interest arises primarily because metal clusters seem to have unusual potential as catalysts[1-3] and because they represent an unexplored state of matter; a state in between that of a metal and that of a gas. Several experimental techniques have been devised to attempt to synthesize clusters of atoms of a given size,[4-7] although to date this has been a difficult experimental problem. The structural and band properties for some of these cases have been calculated using electronic structure techniques.[8-11]

An intriguing approach to producing metal clusters involves the ion bombardment of metal surfaces. The formation of secondary metal cluster ions containing 12 or more atoms has been observed to occur quite readily upon bombardment of solids with primary ions of kinetic energy on the order of 100 keV.[12] Cluster ions containing up to five or more atoms also have been observed utilizing ion beams whose energy was lower than 1 keV and whose total current was so low that each impact event could be considered as an isolated process.[13-14] The relative intensity of the multimers has been found to correlate with the crystal orientation of the metal surface;[15] and with the electronic properties and thermodynamic stability of a particular sized cluster[13,16].

In this paper, we examine the mechanism for cluster formation by ion bombardment of metal surfaces. The analysis is performed computationally by classical trajectory methods which determine the positions and momenta of all particles in a model microcrystallite as a function of time. The results indicate that the cluster species do not leave the surface as intact parts of the solid but form in a region above the surface. We find this mechanism to be valid not only for dimer and trimer formations as reported earlier,[17,18] but find it is a valid mechanism for the synthesis of clusters containing up to seven atoms.

DESCRIPTION OF THE CALCULATION

The ejection of particles which results when an energetic ion strikes a solid is modeled using classical dynamics. The positions and momenta of the primary ion and all the lattice atoms are developed in time during the trajectory or collision cascade. The cascade is terminated when the momentum has dissipated through the microcrystallite and no more atoms can be ejected. The final positions and momenta are used to determine yields, the energy distribution, possible multimer formation, and the angular distribution of ejected atoms.

The integration scheme,[19,20] the bulk solid potential[17,20] and the ion-solid potential have been described previously.[17] All trajectories reported in this work are performed using 600 eV Ar^+ at normal incidence to a Cu(111) surface. The microcrystallite size is identical to that reported previously[21] containing four layers with 65 atoms in each layer. Although this crystal size fails to contain the trajectory completely, considerable testing using 600 eV Ar^+ at normal incidence has shown that the number of ejected particles and the basic collision sequences are not altered by further increasing the surface area or the depth of the crystallite. For any situations where edge atoms are involved in cluster formation the impact point is shifted to a symmetrically equivalent point where the cluster forms from atoms not on the edge. To sample a representative area of the surface, 108 trajectories were performed over a triangular zone in the center of the crystal which possesses irreducible surface symmetry.[21]

To check for the formation of multimers, we first compute the relative kinetic energy, T_R, plus potential energy, V, for all pairs of ejected atoms after the trajectory has been stopped. The potential energy between any pair of atoms i and j, V_{ij}, is calculated using a Morse potential[22] with constants $r_e = 2.22$ Å, $D_e = 2.05$ eV, and $\beta = 1.41$ Å^{-1} as derived from spectroscopic measurements.[23] If the total energy of the dimer

$$E_{\text{tot}}^{\text{dimer}} = T_R^{\text{dimer}} + V_{ij} \tag{1}$$

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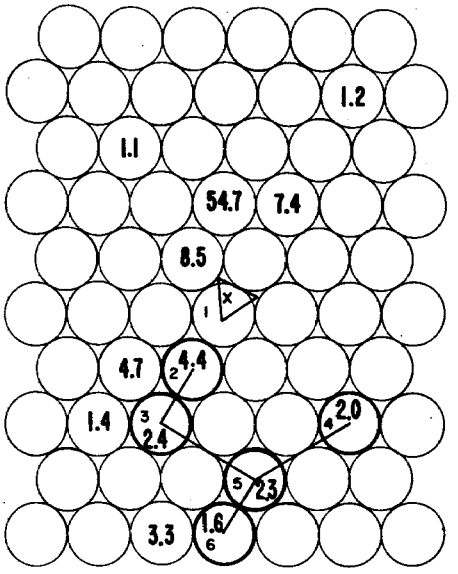

FIG. 1. Schematic representation of the (111) surface used in the trajectory calculation. The triangle in the center of the figure is the representative impact area and x shows the approximate impact point used in this work. The boldface numbers give the kinetic energy in eV of all the ejected atoms while the smaller numbers refer to the label of a particular atom. The darker atoms form a bound pentamer with linked bonds given by the straight lines.

is negative, then the tested dimer is considered to be bound. For many high yield impact points several bound dimers are formed above the surface. From these, we check for the possibility of linked or overlapping dimers. If this condition is found, $E_{\text{tot}}^{\text{cluster}}$

$$E_{\text{tot}}^{\text{cluster}} = T_R^{\text{cluster}} + \sum_{i=1}^{n-1} \sum_{j>i}^{n} V_{ij}, \tag{2}$$

with n being the number of atoms in the cluster, is recalculated for all of the atoms in the linkage to evaluate the possibility of forming a multimer. As in the dimer analysis, if $E_{\text{tot}}^{\text{cluster}}$ for the atoms in the linkages is less than zero then the atoms are considered to be a cluster.

Our choice of potential used to test for multimers is directed by the nature of the solid pair potentials since they account for many body interactions but do not have the proper dissociation limits. For example, Cu_2 has a gas phase well depth of 2.05 eV[23] whereas the bulk pair potential has a well depth of only 0.48 eV. Since the tested interactions occur above the solid, then, the dimer pair potential is more appropriate to use in the definition of a cluster than the solid pair potential. A prediction concerning the exact number of dimers formed during ion bombardment of single crystals will clearly depend on our choice of potential. We have found, however, that relative yields found on different crystal faces[18] are insensitive to large variations in the well depth.

We have applied a similar scheme to define the formation of larger clusters. Since exact potential surfaces are not available for Cu_n, $n \geq 3$, gas phase Cu_2 potentials have been arbitrarily chosen to evaluate $E_{\text{tot}}^{\text{cluster}}$ in Eq. (2). In the specific case of the pentamer (5-atom cluster) reported here, well depths greater than 0.75 eV still result in $E_{\text{tot}}^{\text{cluster}} < 0$. Since the equilibrium separation and Morse parameters are nearly identical for the bulk and gas phase potentials we have not attempted to vary these quantities. Thus, the proposed mechanisms for cluster formation are valid over a wide range of conditions and do not depend on a specific choice of the interaction potential.

Other procedures exist for checking for the possibility of multimer formation. For example, the total energy for every combination of ejected particles could be computed, with those having negative energies being considered a cluster. We have carried out this procedure for several trajectories and have found many multimers, with some containing as many as 12 atoms. This approach is unrealistic since one or more of the atoms may be only weakly interacting with the remaining cluster and therefore highly susceptible to dissociation. Using the requirement that each atom in the multimer be bound to another atom may be an overly stringent requirement for cluster stability but the fact that we do find these species using this scheme shows that they are in a favorable spacial position with low enough relative kinetic energy to experience binding interactions.

RESULTS AND DISCUSSION

We have surveyed the surface of a Cu(111) surface for 600 eV Ar^+ bombardment at normal incidence using over 100 different impact points. From the results of these studies a variety of mechanisms have been elucidated for the deposition of the momentum of the primary ion.[21] For example, when the target atom is impacted head on, it is driven into the solid and no particle ejection is observed. For certain impact points away from this condition, however, tremendous motion is observed throughout the crystallite producing as many as 13 ejected atoms. The calculated yield, then, of 6.4 ejected atoms/incident ion[21] represents an average of all 100 trajectories with considerable variation observed over the entire impact zone. It is these high yield regions that have special interest since it is these regions that give rise to the greatest probability of multimer formation.

The high yield impact point of interest in this work is denoted by the x as shown in Fig. 1. Its symmetry is such that most of the momentum is transmitted down the two diagonal rows of atoms causing the ejection of eight separate atoms in these rows. The mechanism for ejection of the atoms in the lower right corner of the crystallite surface will be discussed later. Because of the unique action displayed at this impact point, an additional 50 trajectories were computed in a small region consisting of an area of 10^{-4} Å^2 (0.05% of the area of the impact triangle) centered about the point of interest. The same 13 atoms are observed to be ejected in this area.

The energy distribution for the ejected particles in this high yield zone is plotted in Fig. 2 using the kinetic

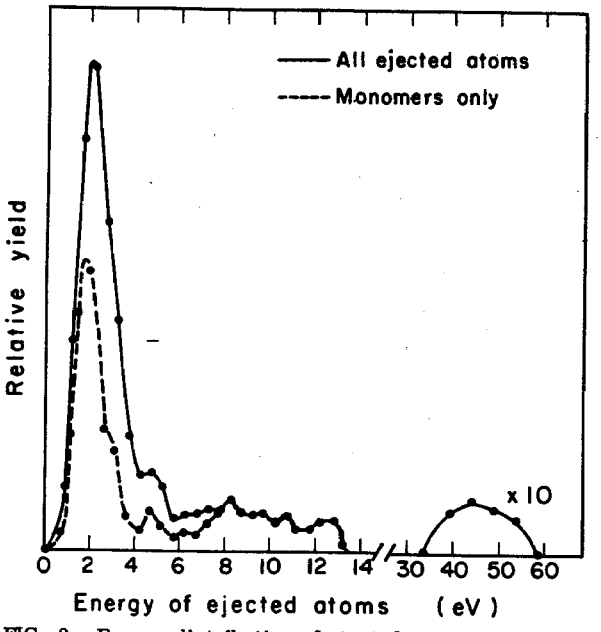

FIG. 2. Energy distribution of ejected atoms.

energy for the ejected atoms found in the additional 50 trajectories. The general shape of the curve is typical of the energy distribution for ejected atoms found by classical trajectory methods[21] as well as by experimental measurements.[24] The structure in the curve appearing near 44 eV and 12 eV arises from the two atoms near the target atom as shown in Fig. 1. These atoms leave the surface early in the collision cascade without interacting with the other slower moving ejected atoms. The broadening of the energy distribution curve about these energy values is due to small changes in the impact point which slightly alter the atomic motion for each of the examined trajectories. Note also that the majority of particles are moving with kinetic energy of less than 4 eV. Although the kinetic energy of an atom in a cluster is not a well defined quantity it does approximately represent the average energy of the atom. Also shown in Fig. 2 is the energy distribution of the monomers from these same 50 trajectories. The high energy parts of these curves are identical as the multimers generally form from the slower moving atoms. Thus, if these particles are in the same region of space as they leave the surface they are ripe for multimer formation.

Using the described procedure for testing for bound multimers we find a stable cluster of the five darker atoms (pentamer) shown in Fig. 1. At the impact point of greatest stability, the pentamer is bound by 2.4 eV. In addition to being able to move the impact point over 10^{-4} Å^2 we can also change the kinetic energy of the Ar^+ ion by more than ±20 eV and still maintain a pentamer bound by more than 1.0 eV.

One of the atoms in the pentamer (atom 6) originates on the edge of the microcrystallite. To verify that the pentamer formation is not an anomaly due to the edge of the finite microcrystallite, we moved the impact point to an equivalent (by symmetry) point on the surface. The new target atom (two rows higher) is identified by an energy of 54.7 eV in Fig. 1. An identical pentamer formed, verifying that edge effects do not alter this mechanism.

A careful examination of the atomic motion which gives rise to the formation of this particular pentamer provides a remarkable example of the complexity involved in the propagation of a collision cascade. In Fig. 3, we show a schematic representation of this trajectory. A considerable portion of the crystallite is not shown in the figure and only 14 of the most strongly involved atoms are displayed, simply to avoid graphical confusion. Three distinct, but interacting, collision sequences can be traced as a function of time. The first event involves the movement of the target atom 1 between the first and second layer causing immediate ejection of atom 2 and 3 while forcing atoms 7 and 8 into the lower layers of the crystallite. The second chain is then initiated as atom 7 moves through the third layer, reflects from atom 14 in the fourth layer pushing atom 12 into atom 9 which ejects atom 4. Note that this focused collision sequence involves four atoms and four layers of the crystal presenting a unique example of what some workers have referred to as a "focuson".[25] The last series of collisions originates with atom 8 reflecting from atom 13 in the third layer inducing the motion of atoms 10 and 11 which in turn eject atoms 5 and 6. The Ar^+ ion moves off to the left and does not significantly interact with the pentamer forming cascade.

We emphasize at this point that although it is possible to conceptually separate the three collision sequences, in fact all processes are interacting in a concerted manner. For example, although atom 2 is ejected first after 0.06 psec, atoms 3 and 5 leave the surface after

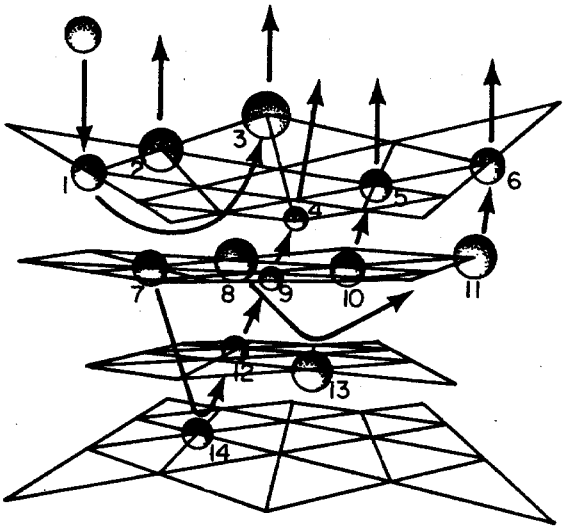

FIG. 3. Schematic representation of the pentamer formation. Only the atoms involved in the ejection of the indicated atoms are drawn. Other atoms are located at the intersection of the grid lines but are not shown. The actual size of the crystallite used in the calculation is considerably larger but is not shown for graphical clarity. The sizes of the atoms are arbitrary to allow maximum viewing through the crystal. The arrows indicate the approximate direction of motion of each atom during the trajectory. The numbers near the atoms are simply used as labels (see text).

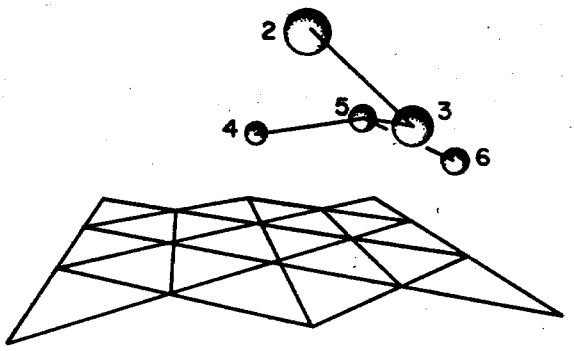

FIG. 4. Pentamer formation. The positions of the atoms are shown relative to the (111) surface given in Fig. 3. The atom labels are the same as those given in Fig. 1 and Fig. 3. The straight lines indicate the bound dimers. The crystal has been rotated counterclockwise by 15° from Fig. 3 to improve the viewing angle.

0.12 psec, while atoms 4 and 6 eject after 0.17 psec. The positions of the atoms, after 0.17 psec, are shown in Fig. 4. Thus, in this rather unique trajectory, five atoms with virtually zero relative kinetic energy find themselves in a localized region of space at roughly the same time.

The general mechanism for cluster formation from ion bombarded surfaces is critical to any basic understanding of the process and needs to be carefully analyzed. Our proposed scheme is best illustrated by a dimer formation mechanism. If two atoms eject from the solid and become noninteracting (i.e. $E_{\text{tot}}^{\text{dimer}} > 0$) then the only way that they can form a bound dimer is if one of them collides with a third body that can take away some of the excess kinetic energy. This event is highly unlikely in our model unless the third body is the solid since the experimental conditions are such that gas phase collisions are virtually impossible between two or more bodies. In the ion bombardment process, the dimer (and by extension a larger multimer) must form while the atoms are within interaction range of the solid, in our case ~4 Å.

The positions of the atoms at the end of the trajectory as shown in Fig. 4 will clearly be a critical function of the impact point and the kinetic energy of the primary ion. In the survey of impact points around the most stable pentamer, a variety of other metal cluster species are also apparent. A stable tetramer arises if atom 2, the most energetic of all the cluster atoms, happens to receive a slightly harder kick from the target atom. Under these circumstances it travels too far away from the other atoms to interact significantly. The loss of atom 4 from the pentamer is also observed due to the incredibly complex sequence leading to its ejection. There are many neighboring impact regions that give rise, in a similar fashion, to stable trimers and, of course, dimers. We also find an extremely small zone that gives rise to a septimer bound by 2.8 eV. Since the percentage of the surface area for which this cluster appears bound approaches zero, we have not focused our attention on this species. An entire range of cluster sizes, however, can certainly be found using this general approach.

The fact that we report bound metal clusters above the surface of an ion-bombarded metal does not, of course, guarantee that these clusters will reach the detector. For example, atoms 3 and 5 bound by energy 0.1 eV form the weakest bond in the cluster, making it most susceptible to dissociation through vibrational coupling with the other atoms. The point is, however, that we believe experimentally observed cluster ions must originate from a structure similar to the one shown in Fig. 4 even if it does slightly alter its size before reaching the detector.

CONCLUSIONS

The main purpose of this work has been to demonstrate the feasibility of forming metal clusters from ion bombarded solids via a recombination mechanism over the solid surface. Although this mechanism has been suggested to explain dimer and trimer formation it has not been at all clear that recombination of larger clusters is statistically feasible. We find, however, that for very specific high yield impact points that large numbers of atoms with near-zero relative kinetic energy can be sufficiently close together in space to experience binding interactions.

We believe these results have significance to a number of current experimental studies which investigate the properties of metal clusters. For example, it is clear that the pentamer shown in Fig. 1 does not originate from contiguous atomic sites on a surface. On the other hand all of the ejected atoms are produced either directly or indirectly from the target atom 1. As a result, the cluster does contain atoms from a highly localized region and should reflect in some degree the surface morphology. Although the calculations are yet to be performed, we believe similar conclusions can be made concerning molecular ions observed from reacted metal surfaces.

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[1] J. H. Sinfelt, J. Catal. 29, 308 (1973).
[2] M. Boudart, Proceedings of the Welch Foundation Conference on Chemical Research. XIV: Solid State Chemistry (R. A. Welch Foundation, Houston, TX 1971), p. 229.
[3] R. C. Baetzold, J. Appl. Phys. 47, 3799 (1976).
[4] J. H. Sinfelt, Science 195, 641 (1977).
[5] J. F. Hamilton and P. C. Logel, Thin Solid Films 23, 89 (1974).

[6]K. S. Kim and N. Winograd, Chem. Phys. Lett. 30, 91 (1975).
[7]D. M. Kolb, D. Leutloff, and W. Schulze, J. Chem. Phys. 66, 2806 (1977).
[8]M. G. Mason, L. J. Gerenser and S.-T. Lee, Phys. Rev. Lett. 39, 288 (1977).
[9]A. B. Anderson, J. Chem. Phys. 66, 5108 (1977).
[10]C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 62, 4815 (1975).
[11]R. C. Baetzold, J. Chem. Phys. 55, 4363 (1971).
[12]G. Staudenmier, Radiat. Effects 13, 87 (1972).
[13]A. Shepard, R. W. Hewitt, W. E. Baitinger, G. J. Slusser, N. Winograd, G. L. Ott, and W. N. Delgass, in "Quantitative Surface Analysis of Materials," edited by N. S. McIntyre (ASTM Special Tech. Publ. 643, 1978).
[14]A. Benninghoven, Surf. Sci. 53, 596 (1975).
[15]M. Barber, R. Bordoli, J. Wolstenholme, and J. C. Vickerman, *Proceedings of the* III *International Conference on Solid Surfaces* (Vienna, Austria, September, 1977).
[16]P. Joyces, J. Phys. Chem. Solids 32, 1269 (1971).
[17]D. E. Harrison, Jr. and C. B. Delaplain, J. Appl. Phys, 47, 2252 (1976).
[18]N. Winograd, D. E. Harrison, Jr., and B. J. Garrison, Surf. Sci. (in press).
[19]D. E. Harrison, Jr., N. S. Levy, J. P. Johnson, III, and H. M. Effron, J. Appl. Phys. 39, 3742 (1968).
[20]D. E. Harrison, Jr., W. L. Moore, Jr., and H. T. Holcombe, Rad. Effects 17, 167 (1973).
[21]D. E. Harrison, Jr., P. W. Kelly, B. J. Garrison and N. Winograd, Surf. Sci. (in press).
[22]G. Hertzberg, *Molecular Spectra in Molecular Structure* I. *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
[23]B. Rosen, *International Tables of Selected Constants* (Pergamon, New York, 1970).
[24]R. V. Stuart and G. K. Wehner, J. Appl. Phys. 35, 1819 (1964).
[25]G. Carter and J. S. Colligen, *Ion Bombardment of Solids* (American Elsevier, New York, 1968), pp. 225 *et. seg.*