EVIDENCE FOR A RECOMBINATION MECHANISM OF CLUSTER EMISSION FROM ION BOMBARDED METAL SURFACES

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Classical dynamical calculations of the momentum dissipation of 600–20 000 eV Ar^+ in clean metal single crystals indicate that the experimentally observed cluster species form by a recombination mechanism in the near surface region. The dependence of cluster yields on primary ion energy has been computed and matches well the shape of the experimental curve for Ni_3^+/Ni_2^+. The results suggest that a simple power law based on the yield of monomers is not sufficient to predict accurate cluster yields.

Molecular cluster ions are frequently observed to be emitted from a variety of samples exposed to 500–30 000 eV ion bombardment [1]. The mechanism of formation of these cluster ions is important if they are to be utilized to determine the structure of solid surfaces [2]. Two basic approaches have been proposed to explain how these species evolve. One possibility involves the direct ejection of contiguous surface atoms by concerted motion of the atoms in the cluster [2,3]. A second mechanism is that the clusters establish their identity over the solid and are not necessarily formed from contiguous surface atoms [4,8].

We have recently been examining the ion impact event theoretically using a classical dynamical method to determine the positions and momenta of all the particles in a 240 atom model microcrystallite [6]. In a series of articles devoted to cluster formation [7–11], we have found that the recombination mechanism dominated the process when the cluster does not have a special molecular identity in the solid. This situation would exist for example, for the clusters observed from clean metals and from metal surfaces covered with atomic adsorbates. It would not apply, however, to molecular adsorbates. For CO on Ni (100), our calculations show that ~ 80% of the CO molecules eject intact, but that NiCO clusters form by a recombination of Ni and CO above the surface [11,12]. It has been suggested [3] that a consequence of the recombination mechanism is that the intensity of clusters of n atoms, I_n, should increase as the nth power of the yield Y of ejected monomers,

$$I_n \propto Y^n , \qquad (1)$$

where $n \leqslant 3$.

In this letter, we examine the predictions of our model as compared to the intuitive predictions of eq. (1). Of particular interest is the evaluation of the notion that if the dimer or trimer yields do not follow eq. (1), then the recombination mechanism must be incorrect.

To accomplish this goal, we have calculated the dependence of cluster yields on the primary ion kinetic energy over the range of 600 eV to 20 keV. This variation should significantly alter the momentum deposition process and the resulting sputterring yield so that the cluster yield should vary in a predictable fashion. The calculations are performed for the primary ion at normal incidence to the (111) face of the microcrystal-

lite. To compute the forces, we have used pair potentials appropriate for the Cu–Cu and Ar–Cu interactions [6]. However, the results should be directly comparable to any fcc metal if ratios of yields are considered [9]. The detailed calculational procedures and the method have been described previously [6,8]. To insure that the microcrystallite is large enough to contain all the processes that lead to the ejection of atoms, we have expanded its size to 90 atoms/layer with 4 layers. This expansion is only necessary if the primary ion kinetic energy is greater than 1000 eV. We find that 4 layers are sufficient to describe all the ejection processes.

The calculated results for the Cu_2/Cu ratio and the Cu_3/Cu ratio as a function of the primary ion energy are shown in fig. 1. Of special interest is that the Cu_2/Cu ratio is not grossly different from the monomer yield curve, except at the lowest energies. The Cu_2/Cu ratio at 600 eV and at 3000 eV are equal, even though the Cu yield has nearly doubled. On the other hand, the Cu_3/Cu ratio deviates considerably from the square of the yield curve and is in significant disagreement with eq. (1).

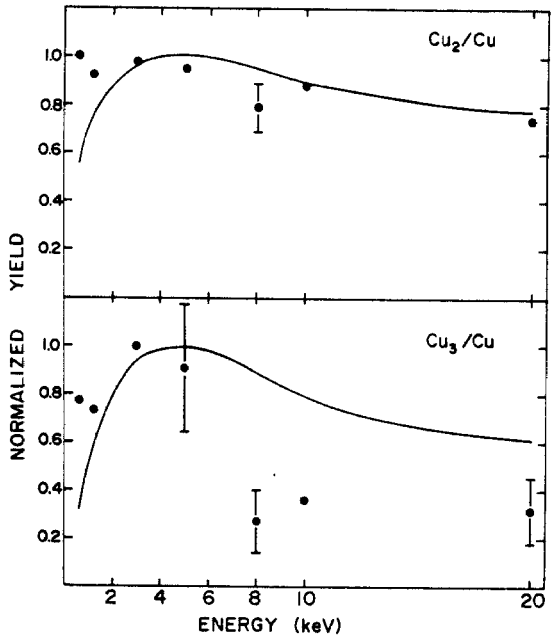

Fig. 1. Computed yields for Cu, Cu_2/Cu and Cu_3/Cu versus primary ion kinetic energy. For the top panel, the solid line is the normalized Y for Cu where the points are the computed values for Cu_2/Cu. For the bottom panel, the solid line is the normalized Y^2 and the points are the computed values for Cu_3/Cu. The calculation was performed for Ar^+ at normal incidence to the (111) face. The error bars show a conservative measure of the standard deviation, based on the square root of the number of clusters found. The error bars on the curves for Y and Y^2 are less than 5% of the normalized values. All curves are normalized to their peak value.

It is possible to gain some insight as to why eq. (1) is an oversimplification of the description of the cluster formation process by an analysis of the individual trajectory events. Of most significance to cluster formation is the distribution of the number of ejected atoms resulting from the single ion impacts. This distribution is shown in fig. 2 for 20 keV and 1.2 keV primary ions. These kinetic energies are particularly appropriate since the monomer yields are calculated to be identical. The important point is that there are more high yield impact points at 1.2 keV than at 20 keV. At 1.2 keV, the most probable number of ejected particles is 10, while at 20 keV the most probable number is only 6. As we have shown previously, it is the number of ejected atoms on any given impact which should form clusters following eq. (1) [9]. This result explains why the Cu_3/Cu ratio is three times higher at 1.2 keV than at 20 keV even though the monomer yields are the same. Our conclusion is that the monomer yield is an average macroscopic quantity and is not sufficient for a description of the probability of finding particles near each other above the surface during a given impact event.

It would be of direct interest to test these concepts

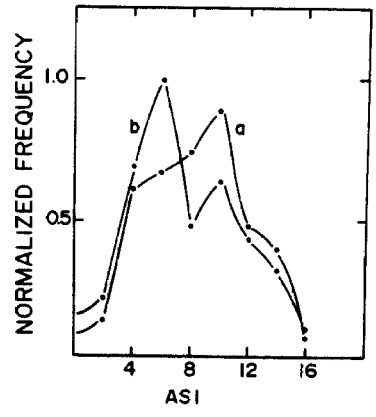

Fig. 2. Computed frequencies for the number of atoms sputtered per incident ion (ASI). (a) is for 1.2 keV Ar^+ and (b) is for 20 keV Ar^+. The highest frequency in curve a corresponds to 34 trajectories.

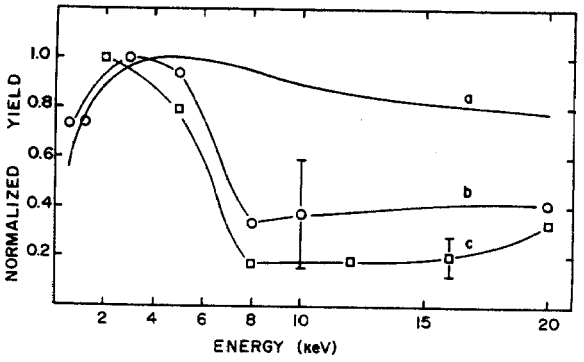

Fig. 3. Normalized cluster yields versus primary ion energy. (a) is the Cu yield curve and is identical to that shown in fig. 1. (b) is the computed Cu_3/Cu_2 ratio. (c) is the experimentally measured Ni_3^+/Ni_2^+ ratio for Ar^+ bombardment of a clean Ni(111) crystal. All curves are normalized to their peak value.

on experimentally measured cluster intensities. To date, a small amount of data is available for the formation of ionic clusters as determined by secondary ion mass spectrometry (SIMS). These ionic yields have been successfully compared to the calculations of neutral species if ratios of the yields are compared. For example, calculated yields for Cu_2/Cu agreed with measured values for Ni_2^+/Ni^+ when the yields were compared between the three low index crystal planes [9]. This ratioing procedure apparently minimized sufficiently the influence of the details of the interaction potential and ionization probabilities.

In fig. 3, we compare the calculated values of the Cu_3/Cu_2 ratio to experimentally obtained values for Ni_3^+/Ni_2^+ from a clean Ni(111) crystal surface. This ratio was chosen since it has been suggested [3] that the monomer yields are anisotropic while the dimer and trimer yields are generally isotropic [‡1]. The Ni surfaces were prepared and cleaned as indicated previously [13] and were always examined with a dose of Ar^+ of less than 10^{14} ions/cm^2 before re-annealing the surface at 1000 K. The agreement between these measurements and the calculations is strikingly good. In addition, both of these curves deviate significantly from the calculated monomer yield curve.

In conclusion, we believe that when the cluster species does not have a special molecular identity in the solid that it forms by a recombination mechanism above the surface plane. As related to this conclusion, we have shown that the intuitive application of eq. (1) to test this mechanism is a good zero order approximation, but can lead to difficulty if detailed calculations are made. For example, we believe recent results presented for Si_n^+ clusters [3] are in no way inconsistent with the recombination mechanism and certainly do not prove that the clusters form by an intact ejection process. Finally, we have presented some preliminary experimental results which are in excellent agreement with the quantitative predictions of our recombination model.

‡1 Recent measurements from our laboratory indicate that this assumption may not be valid.

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References

[1] R.E. Honig, J. Appl. Phys. 29 (1958) 549.
[2] See, e.g.: A. Benninghoven, Surf. Sci. 53 (1975) 596.
[3] K. Wittmaack, Phys. Lett. 69A (1979) 322.
[4] G.P. Können, A. Tip and A.E. deVries, Radiat Eff. 26 (1975) 26.
[5] W. Gerhard and H. Oechsner, Z. Phys. B22 (1975) 41.
[6] D.E. Harrison Jr., P.W. Kelly, B.J. Garrison and N. Winograd, Surf. Sci. 76 (1978) 311.
[7] D.E. Harrison Jr. and C.B. Delaplain, J. Appl. Phys. 47 (1976) 2252.
[8] B.J. Garrison, N. Winograd and D.E. Harrison Jr., J. Chem. Phys. 69 (1978) 1440.
[9] N. Winograd, D.E. Harrison Jr. and B.J. Garrison, Surf. Sci. 78 (1978) 467.
[10] B.J. Garrison, N. Winograd and D.E. Harrison Jr., Phys. Rev. B18 (1978) 6000.
[11] B.J. Garrison, N. Winograd and D.E. Harrison Jr., J. Vac. Sci. Tech. 16 (1979) 789.
[12] N. Winograd, B.J. Garrison and D.E. Harrison Jr., Phys. Rev. B, submitted.
[13] T. Fleisch, N. Winograd and W.N. Delgass, Surf. Sci. 78 (1978) 141.