Ejection of molecular clusters from ion-bombarded surfaces

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We have modeled, using classical dynamics, the dissipation of momentum of a 600-eV Ar$^+$ ion as it bombards a metal single crystal. The model correctly predicts relative sputtering yields, secondary particle energy distributions, and angular distributions. In addition, it also gives considerable insight into the mechanism of molecular cluster formation. For the three low index faces of copper, for example, the observed dimers, trimers, and higher multimers form over the surface but within interaction range of the solid. The clusters show rearrangement of their constituent atoms from their original surface positions, but do arise from a localized region of radius ~5 Å. We have also examined oxygen atoms and CO molecules adsorbed on copper and nickel, respectively. For the chemisorbed O atoms, the clusters Cu$_2$, CuO, O$_2$, Cu$_3$, Cu$_2$O, CuO$_2$, and O$_3$ have all been observed to form over the surface, analogous to the clean metal case. For CO, however, most of the ejection occurs molecularly due to the strong carbon–oxygen bond (~11 eV). The formation of NiCO and Ni$_2$CO clusters occurs over the surface.

I. INTRODUCTION

During the ion bombardment of a solid, many types of clusters are ejected. For adsorbates on clean metals, these vary from pure metal clusters M_n where n can be as large as 12, to metal atoms attached to adsorbed species, e.g., CuO or NiCO, to large organic molecules that were originally adsorbed on the surface of the solid which eject retaining their molecular formula. Different experiments are used to detect the clusters including secondary ion mass spectrometry (SIMS),[1] time of flight measurements,[2] and sputtered neutrals mass spectrometry (SNMS).[3]

The observation of these clusters leads to speculation regarding the mechanism of their formation, and the information they contain about the original surface structure. For example, our model predicts that the pure metal clusters show considerable rearrangement of atoms from their original surface positions.[4] However, it is highly improbable that large organic molecules completely break up and then reform in the identical configuration. Obviously there must be more than one mechanism of cluster formation.

The absolute yield of a cluster depends on many physical properties. For example, the stability of a cluster will affect the total yield. Both the binding energy to a surface and the coverage of an adsorbate are influencing factors. In addition both experimentally[5] and theoretically[4] the surface morphology is found to cause large differences in multimer yields between different crystal faces of an fcc crystal.

In this paper we will discuss the qualitative and quantitative factors involved in cluster formation which occurs during ion bombardment of solids. Clean and oxygen covered copper single crystals are considered. In addition we present the first calculations of the ion bombardment process of a simple organic molecule, CO, adsorbed on a Ni(100) surface.

II. DESCRIPTION OF THE CALCULATION

The dynamics of the ion bombardment process are followed by integrating Hamilton's equations of motion for the ion-solid system. We approximate the infinite solid by a micro-crystallite of ~250 atoms (4 layers of ~60 atoms/layer).[6] Additional atoms can be placed on the surface to model an adsorbate system.[7] In all the studies presented here, the incident energy is 600 eV at normal incidence to the surface. The interaction potential for all the particles is represented by a sum of pair potentials. The metal–metal pair potential has been chosen to reproduce the elastic constants and binding energy of the bulk. The adsorbate-metal pair potentials are chosen to give an experimentally reasonable heat of adsorption. The ion-metal and ion-adsorbate potentials are represented by purely repulsive interactions. The tabulated parameters are given elsewhere.[7]

Each individual collision cascade, representing a unique impact point on the surface, is terminated when no particles have sufficient kinetic energy to eject. After termination the particles that have ejected are then analyzed for possible multimer formation.[8]

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. The potential energy between any pair of atoms i and j, V_{ij}, is calculated using a Morse potential[9] with constants derived from spectroscopic measurements. If the total energy of the dimer

$$E_{tot}^{dimer} = T_R^{dimer} + V_{ij} \qquad (1)$$

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, $E_{tot}^{cluster}$ where

$$E_{tot}^{cluster} = T_R^{cluster} + \sum_{i=1}^{n-1} \sum_{j<i}^{n} V_{ij}, \qquad (2)$$

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 $E_{tot}^{cluster}$ for the atoms in the linkages is less than zero then the atoms are considered to be a cluster.

Since very little is known regarding potential surfaces for most clusters, we have chosen to use the gas phase dimer potential in evaluating V_{ij} in both Eqs. (1) and (2). A prediction concerning the exact number of clusters formed during ion bombardment of single crystals will clearly depend on our choice of potential. We have found, however, that relative yields on different crystal faces are insensitive to large variations in the well depth.[4]

There are other possible definitions of what constitutes a cluster. Our 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.

As a model for organic molecule ejection we have studied CO adsorption on Ni(100) by placing the CO molecule in an upright position on the surface and in various symmetry sites. The carbon end is down as is thought to be observed experimentally. Carbon monoxide has a very strong bond in the gas phase (11.1 eV). We have assumed that this bond strength remains unchanged and that the diatomic is bound by ~1.5 eV to the metal substrate.[10]

III. RESULTS AND DISCUSSION

A. Mechanisms

Our calculations allow us to follow the motion of all the particles during the ion bombardment process. From the analyses of the atomic trajectories we find two mechanisms of cluster formation. For clean metals and atomic adsorbates on metals the clusters establish their identity in the near surface region. For adsorbates like CO, the CO can molecularly eject.

A manifestation of the clean metal mechanism is that the clusters show considerable rearrangement and do not necessarily reflect their original positions on the surface. Since there are no molecular units in a metal, one would not expect the clusters to necessarily eject intact. No one atom has a strong bonding preference to *one* of its neighbors; the interactions are spread among all its neighbors. The components of the clusters do originate, however, from a fairly localized region of the surface, an area of radius ~5 Å.[4] The constituent atoms must originate close enough together so that they are within interacting range of each other. We have found cases in our

calculations where as many as 5–7 atoms form a cluster in this manner.[8]

Clusters originating from an atomic adsorbate on a metal single crystal form in a manner similar to the clean metal clusters. Although the adsorbate, oxygen in our studies,[7] may be preferentially bonded to one-metal atom, this metal atom has several metal neighbors. Thus, our model predicts that clusters like CuO will form by each atom ejecting and coming together in the near surface region. In our calculations on oxygen atom adsorbates on a copper crystal all possible dimers and trimers have been observed as well as many of the tetramers, pentamers, and hexamers.[7]

For CO adsorption on Ni(100) our calculations predict predominantly *molecular* CO ejection. Approximately 80% of the carbons and oxygens that eject are still bound in their *original* molecules. The carbon and oxygen, in contrast to the atoms in a metal, do have a strong bonding preference for each other, thus they remain together as they eject. Since the ejecting CO generally is struck on one end rather than at the center, it often has internal energy in the form of vibrations or rotations.

The remaining ejected carbons and oxygens undergo *dissociative ejection*. These result from a CO being struck vigorously by another atom or molecule, thus breaking the CO bond. This low yield of atomic carbon and oxygen is observed experimentally in SIMS studies of CO on nickel.[11,12]

Our calculations show that metal-molecule clusters like NiCO form via a combination of both mechanisms. The CO molecularly ejects and then combines with the Ni in the near surface region to form NiCO. Ni_2CO can form via interactions with two Ni atoms and a CO molecule above the surface. These same species have been observed experimentally.[11,12]

In summary, we propose two mechanisms of cluster formation. First for pure metal and metal oxide clusters, the atoms come together within interaction range of the surface and establish their identity as the molecular cluster. These clusters do not reflect their exact original positions on the surface. Second for CO or by extrapolation to larger organic molecules, the compound can remain intact as it ejects. Clusters like NiCO are formed via both mechanisms. These results would lead one to speculate that the $(H_2O)_n$ clusters that have been observed[13] from ion bombardment of ice are formed by the H_2O units ejecting intact and combining with other water molecules in the near surface region.

B. Quantitative aspects

Many factors influence the absolute yield of a cluster. Some of these are morphological, depending only on the relative placement of the atoms, and thus can be generalized from one system to another. Other factors depend on the specific physical properties of the system that is under study.

In our calculations on the low-index faces of copper, we found that the dimer yield for the (111) face is four times larger than the (100) face. Similarly the trimer yield is three times higher for the (111) face. The yields for the (110) face in both cases are lower.[4] These trends reflect the crystal face that is being bombarded and should be extendable to any fcc crystal.

TABLE I. Effect of site symmetry and coverage on the O_2 yield.

Site/Coverage	$p(2 \times 2)$	$c(2 \times 2)$
A-top	0.02	0.03
Fourfold bridge	0.02	0.16
Twofold bridge	0.02	0.25

Similarly the site symmetry and coverage of an adsorbate influences the yields. The O_2 yields for O atoms adsorbed on Cu (100) in different sites and for $p(2 \times 2)$ and $c(2 \times 2)$ coverages, 0.25 and 0.50 monolayer, respectively, are shown in Table I. The first feature in this table is that virtually no O_2 molecules are formed for a $p(2 \times 2)$ coverage. As discussed in the previous section, the clusters form from atoms that were originally in a localized region of the surface. The density of O atoms on the surface is too low to observe O_2 molecules being ejected. For the $c(2 \times 2)$ coverage the yield goes up, although the amount it increases is very dependent on the site symmetry. The two-fold bridge site produces the most O_2 molecules while for the A-top site the yield is very small. Again these are trends that we would expect to hold true for any adsorbate.

The fact that the O atom density must be reasonably large to observe O_2 emission has been used in the analysis of SIMS data of oxygen on Pb.[14] In this study both the O_2^- to O^- ratio and the PbO_2^- to PbO^- ratio were reasonably constant versus oxygen exposure. Even at low coverages of oxygen atoms, O_2^- and PbO_2^- clusters were being detected. This implies a nucleation mechanism for the adsorption of the oxygen. If the oxygen were adsorbing randomly, one would expect the O_2^- to O^- ratio to significantly increase with increasing oxygen exposure.

If the relative yields for oxygen adsorbed in different site positions are due to atomic placement then the CO yields for different sites should follow similar trends. Shown in Table II are the CO yields for CO adsorbed in an A-top and twofold bridge configuration on Ni(100). Also given are the O and O_2 yields for atomic oxygen adsorbed in the same sites on Cu(100). Since the binding energies are different for the O atom and the CO, the results are normalized to the A-top site yields. For CO, the ratio of the twofold bridge yield to the A-top yield is ~1.7. This is most comparable to the O atom yield ratio (~1.6) rather than the O_2 ratio (~8.1). Since the mechanisms of O_2 ejection and CO ejection are not similar, one should not expect similar trends in the yields. To make a more quantitative comparison between the two systems, the total yield of carbons (or oxygens) including both molecular and dissociative ejection pathways should be compared to the oxygen atom ejection from the atomic adsorbate case. From Table II, the ratio of carbon total yields (1.6) for the two sites is in excellent agreement with the O atom ratio (1.6). The yields for different sites then depend almost entirely on the placement of the adsorbates.

No matter how favorable the surface morphology is for cluster formation, the clusters will not be observed if they are not thermodynamically stable. One measure of the stability of dimers is the well depth D_e of their mutual interaction potential. The yield of CuO dimers as a function of their gas phase well depth D_e is shown in Fig. 1. The yield increases

approximately linearly with D_e for $D_e \lesssim 4$ eV and then plateaus. The leveling off is due to a finite number of slow moving atoms that can form clusters. If the initial energy of the incident ion were increased so that the total number of atoms available to form clusters were increased, then the linear region would be extended to larger well depths. Note that even at $D_e = 0.1$ eV there are two pairs of atoms with extremely small relative kinetic energy so that two bound dimers are observed.

The binding energy E_b of an adsorbate to the surface also influences the yield of clusters. The effect of E_b on the CuO dimer yield is shown in Fig. 2. In all cases the qualitative trend is the same, the number of CuO dimers decreases with increasing binding energy of the oxygen to the surface. Our calculations show that the O atom yield also decreases with increasing binding energy,[7] thus the CuO yield reflects the total number of oxygens available for bonding. For all the calculations shown in Fig. 2, the Cu yield is nearly constant. If the CuO molecules were ejecting intact, one would expect the opposite trend—the more strongly bound the oxygen is to the copper the more CuO dimers that should be found ejecting. This figure again demonstrates the sensitivity of the cluster yields to both site position and coverage.

IV. CONCLUSIONS

Our calculations have shown that there are two basic mechanisms for cluster formation during the ion bombardment process. For systems that are basically atomic in nature, for example clean metals or atomic adsorbates on metals, we find that all the clusters form by the constituent atoms eject-
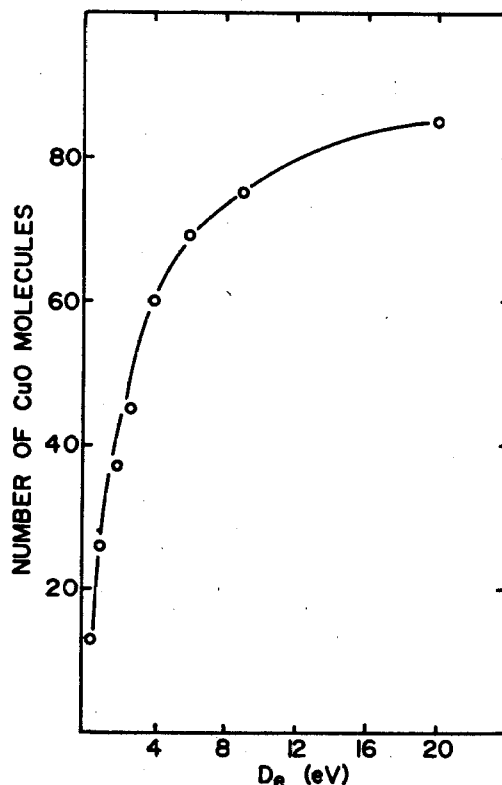

FIG. 1. CuO yield vs gas phase well depth D_e. The oxygen atoms were placed in a 2-fold bridge configuration in a $c(2 \times 2)$ coverage with a binding energy $E_b = 0.75$ eV. A total of 110 trajectories were calculated.
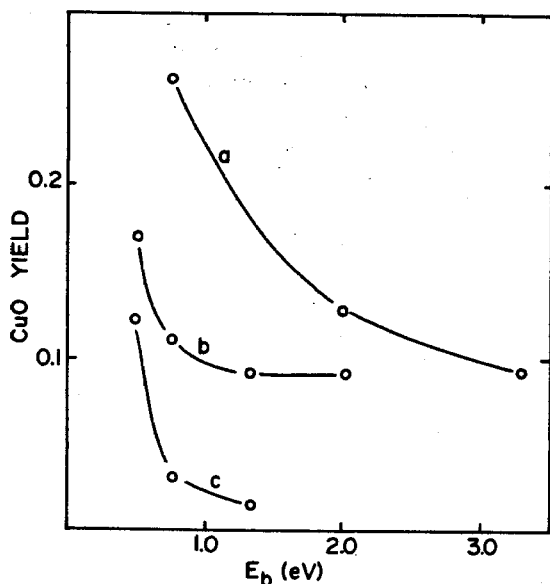
FIG. 2. CuO yield vs binding energy E_b. Curve a is for the $c(2 \times 2)$ fourfold bridge configuration, curve b is for the $c(2 \times 2)$ A-top configuration, and curve c is for the $p(2 \times 2)$ A-top configuration. A well depth D_e of 2.7 eV is used to determine the yields.

TABLE II. Adsorbate yields for a $c(2 \times 2)$ coverage.

Species/Site	A-top	two-fold bridge	
CO^a	1.0	1.7	$(1.7)^b$
C^a	1.4	2.2	$(1.6)^b$
O			
O^c	4.4	7.2	$(1.6)^b$
O_2^c	0.03	0.25	$(8.1)^b$

[a] The CO calculations were performed with the CO adsorbed on a Ni(100) crystal with a CO binding energy of 1.5 eV. The C atom and O atom yields include the molecular CO and the dissociated molecules. The O and C yields are within 4% of being equal.

[b] Normalized to the A-top yield.

[c] The O calculations were performed with the O atoms on a Cu(100) crystal with a binding energy of 0.75 eV.

ing, and then establishing the identity of the cluster in the near surface region. The original surface positions of the constituent atoms are fairly localized, thus the clusters reflect some of the surface structure.

For systems that have a definite molecular identity, e.g. CO adsorbates, our calculations show that molecular ejection is not only feasible but 80% of the CO's eject molecularly. Clusters like NiCO and Ni$_2$CO form via a combination of both mechanisms.

Many factors influence the absolute yield of the clusters. Atom placement, as reflected in the crystal face, adsorbate site symmetry or adsorbate coverage, has a strong influence on cluster yields. The yields also depend on the stability of the cluster and the binding energy of the cluster to the surface. These affects are very much system dependent.

ACKNOWLEDGMENTS

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