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Azimuthal Anisotropies of Dimer Ions Ejected from Ion Bombarded Ni(001)

S. P. Holland, B. J. Garrison, and N. Winograd
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802
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The angular distributions of Ni^+ and Ni_2^+ ejected from Ni(001) by bombardment with 2-keV Ar^+ have been shown to exhibit large azimuthal anisotropies. The experimental results have been well reproduced by classical dynamical calculations of the ion impact event. For the dimers, the peak in the distribution arises from a unique ejection mechanism such that the atoms in the dimer are known to form from specific surface locations relative to the ion impact position.

The determination of the arrangement of atoms on solid surfaces is central to a complete description of their physical and chemical properties. Knowledge of the factors that influence the surface segregation of alloys[1] and that allow selective catalytic hydrogenation of hydrocarbons by bimetallic clusters[2] are examples of the need for this determination. The composition of cluster ions ejected during ion bombardment of solids has been suggested to be a measure of the original surface structure.[3-7] Since the clusters are believed to arise primarily from only the top atomic layer,[8] an analysis of the intensity of these species would provide considerable insight into arrangement of surface layer atoms. Recent calculations with classical dynamics show, however, that the clusters are formed by atoms which eject independently and combine in the near-surface region.[8-10] No direct relationship has been shown to exist between the constituent atoms of the cluster and their original spacings on the surface.

In this paper we present angle-resolved secondary-ion mass-spectrometric (SIMS) measurements of the dimers ejected from Ni(001) resulting from 2-keV Ar^+ bombardment at normal incidence. These measurements are the first to be recorded in the low-dose static mode,[3] where the structure of the (001) surface is not significantly altered by the primary ion beam. The results show that the Ni_2^+ intensity maximizes at the same azimuthal angle as the Ni^+ intensity. Of most interest, however, is that the results from the dynamics calculations for the neutral dimers are in excellent agreement with the experiments and predict that the dimers which contribute to the peak in the azimuthal scan are preferentially ejected by a single mechanism. For this situation, then, the constituent atoms in the ejected dimer are known to form from surface atoms with a specific location relative to the primary impact point.

The SIMS measurements were performed with a previously described apparatus.[11,12] Angular resolution is achieved by placing a cylindrical shield with two small apertures in front of the sample. One aperture collimates the normally incident primary ion beam. The other aperture selects a given polar angle for the ejected particles. This angle is constrained to be $\sim 45°$ by the current geometry of our apparatus. The calculated angular resolution, based on the size of the apertures and the distance of the sample from the shield, is estimated to be $\pm 5°$. The crystal can be rotated to obtain a full 360° azimuthal scan. The total ion flux during the experiment is kept below 10^{13} ions/cm^2 to avoid significantly altering the surface structure. A 45° electrostatic analyzer selects ejected ions with between ~ 10 and ~ 50 eV of kinetic energy. The Ni crystal was oriented by Laue backscattering to within 1° of the (001) face, then cut, mechanically polished, and acid etched. It was cleaned *in situ* by several cycles of exposure to oxygen, ion bombard-

ment, and annealing. The surface impurities were monitored by the O^-, C^-, and $C_2H_2^-$ peaks in the SIMS spectrum.

The calculations are performed for a microcrystallite of ~240 atoms.[10,13] The motion of the particles due to the bombardment of a normally incident Ar^+ ion at 1 keV of kinetic energy was followed by integrating Hamilton's equations of motion. The exact form and parameters of the potential are tabulated elsewhere.[14] The collision cascade is terminated when none of the particles remaining in the solid have sufficient energy to escape subsequently. After termination of the collision process, the final positions and momenta of the particles are analyzed for possible dimer formation[8] by calculating the relative kinetic energy, T_R, and the potential energy, V, for each pair of ejected atoms. If the total energy

$$E_{\text{tot}} = T_R + V$$

is less than zero, the pair of atoms is considered to be a dimer. Physically to be a dimer, two atoms must be near enough in space to experience attractive interactions and their motions must be nearly parallel so that the T_R is not too large. From the final momenta, the center-of-mass kinetic energy, $T_{\text{c.m.}}$, and center-of-mass ejection angles can be determined. A total of 1255 different impact points were calculated to obtain statistically reliable dimer angular distributions.

The angle-resolved SIMS spectra for Ni_2^+ and Ni^+ are shown in Fig. 1. Both azimuthal distributions peak in the ⟨100⟩ directions ($\varphi = 0°$) by use of the angles and directions illustrated in Fig. 2(a). The Ni_2^+ distribution is more anisotropic (anisotropy is defined as the ratio of maximum counts per second to minimum counts per second) than the Ni^+ distribution. It is difficult, however, to ascertain whether the full width at half maximum (FWHM) of this distribution is significantly smaller than for the monomer because of the presence of a diffuse background count. If the minimum count is subtracted from each curve, then the FWHM is ~40° for Ni^+ and ~30° for Ni_2^+. The difference determined by the above procedure is smaller than the apparent difference shown in Fig. 1. These results are in qualitative agreement with earlier studies on tungsten (110) in that the W_2^+ intensity maximized at similar ejection angles as the W^+ intensity.[15] Those experiments, however, were performed with 150-keV Ar^+ under heavy dose conditions and the actual surface structure and cleanliness was ill defined.

The shapes of these azimuthal plots can be well

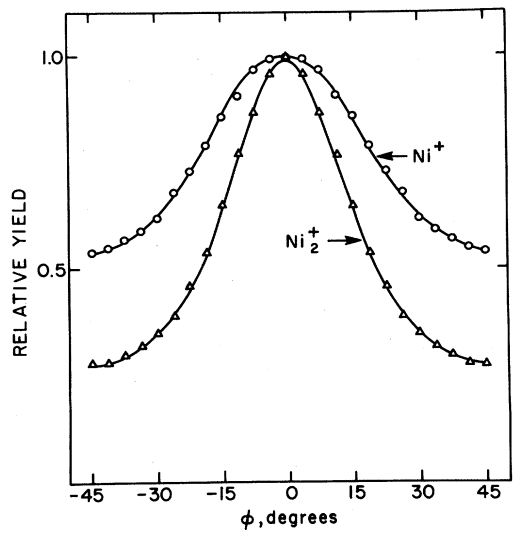

FIG. 1. Experimental angular distributions of Ni^+ and Ni_2^+ ejected from Ni(001) at a polar angle of 45° ± 5°. The center-of-mass kinetic energy of the particles is between 10 and 50 eV. Both curves are fourfold averages of the original data. The incident Ar^+ ion has 2 keV of kinetic energy and is at normal incidence. The solid is at room temperature. The peak counts are ~900 and ~500 counts/sec for the Ni^+ and Ni_2^+ distributions, respectively. The ⟨100⟩ azimuthal directions correspond to $\varphi = 0°$ [see Fig. 4(a)].

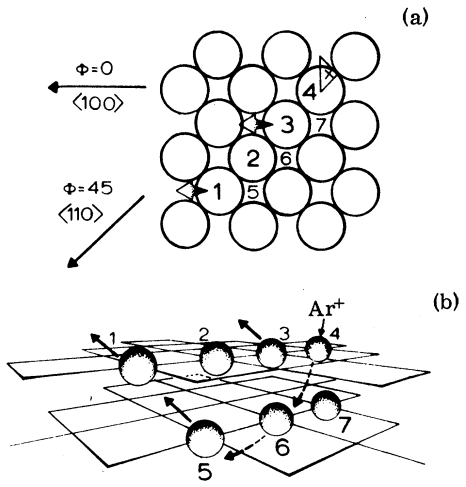

FIG. 2. (a) Ni(001). The numbers are labels used in the text. The × denotes the Ar^+-ion impact point for the mechanism shown in Fig. 4(b). (b) Mechanism of a dimer formation. See text for discussion. The thin grid lines are drawn between the nearest-neighbor Ni atoms in a given layer.

understood with use of a classical dynamical model to describe the nuclear motion subsequent to the ion impact event.[8,9] Although this procedure can only determine the motion of the neutral species, we believe that the trajectories of the high-energy (> 10 eV) particles should be nearly identical for both ions and neutrals.[16]

The calculated angular distribution of the Ni_2 dimers ejected from a Ni(001) face is shown in Fig. 3(a). The ejected particles are displayed on a flat-plate collector placed an arbitrary distance above the surface. There is a definite pattern reflecting the symmetry of the crystal face. As was the case for the monomer angular distributions,[16] by collecting only the particles which are ejected with higher kinetic energies (10 eV $\leq T_{c.m.} \leq$ 50 eV), the fourfold pattern is considerably enhanced [Fig. 3(b)]. The higher-energy particles generally leave early in the collision cascade when more surface structure is present and thus they reflect more of the surface symmetry. To compare with experiment, the azimuthal distribution at a polar angle of $45° \pm 5°$ is given in Fig. 4. Also shown is the calculated Ni-monomer distribution for the same angle and energy range.

The azimuthal direction of the ejected monomers is determined by the surface structure. The atoms can more easily escape through the fourfold holes in the surface, and the distribution peaks in the ⟨100⟩ directions.[12,14] For the identical reason the dimers have a maximum intensity of ejection along the ⟨100⟩ azimuths. The formation of a dimer, particularly one with relatively large center-of-mass kinetic energy, requires that the velocities of the constituent atoms be virtually parallel. This additional constraint selectively picks atoms which are most channeled by the surface and are thus most nearly moving parallel to the ⟨100⟩ directions.

The mechanisms which give rise to the peak in the Ni_2 distribution at a polar angle of 45° can be ascertained from the dynamics calculations. Approximately 70% of the dimers that contribute to the peak in the distribution of Fig. 4 were found to be ejected via similar mechanisms. This mechanism is shown schematically in Fig. 2. The Ar^+ ion strikes the target surface atom, No. 4, which moves under No. 3, ejecting it. Atom No. 3 is channeled through the fourfold hole in the surface and thus escapes in the ⟨100⟩ direction. Concurrently, atom No. 4 is moving towards the second layer pushing atoms No. 6 and No. 7 down. In the same manner in which atom No. 4 ejected atom No. 3, No. 6 pushes No. 5 up toward the first layer. Atom No. 1 is subsequently ejected by atom No. 5. Again No. 1 is channeled through the fourfold hole in the ⟨100⟩ direction. These two atoms, No. 1 and No. 3, are moving parallel to each other (typically $T_R \simeq 1$ eV, $T_{c.m.} \simeq 20$ eV, $V \simeq 1$ eV), are in close proximity and are thus susceptible to dimer formation. When ejected as monomers, these two atoms (No. 1 and No. 3) ex-

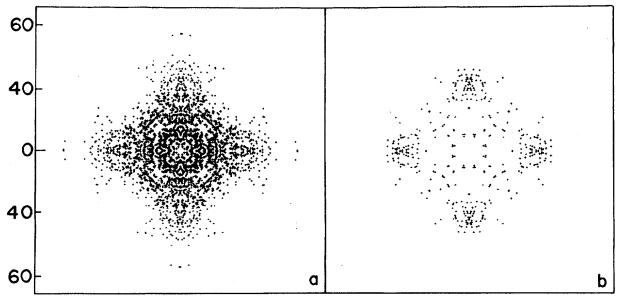

FIG. 3. Calculated angular distributions of Ni_2. The ejected particles are displayed on a flat-plate collector an arbitrary distance above the surface. The radial distance is the polar ejection angle in degrees as given by the scale on the left. The orientation of the crystal is the same as in Fig. 4(a). (a) Ni_2 dimers of all $T_{c.m.}$ are shown. (b) Only dimers of energy 10 eV $\leq T_{c.m.} \leq$ 50 eV, are shown.

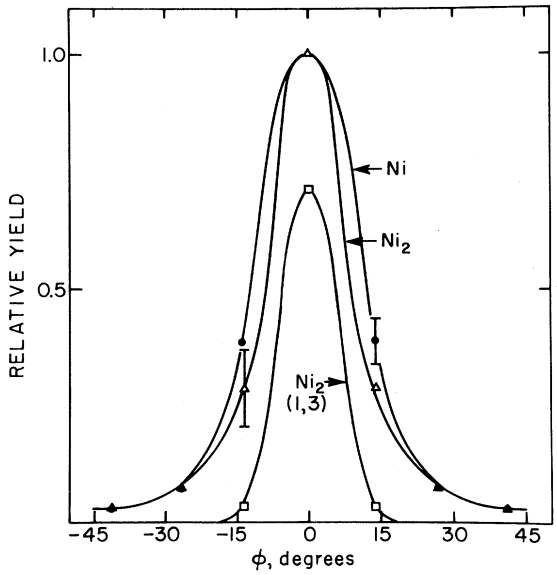

FIG. 4. Calculated angular distributions of Ni and Ni_2 at a polar angle of $45° \pm 5°$. The center-of-mass kinetic energy is between 10 and 50 eV. Also shown is the contribution to the Ni_2 distributions from dimers formed on atoms No. 1 and No. 3 of Fig. 3. The peak intensity is 110 and 12 particles for the Ni and Ni_2 distributions, respectively.

hibit the same azimuthal anisotropy; however, the are a relatively minor part (~10%) of the corresponding energy-selected monomer peak.

There is an important ramification of the prediction that the dimers that give rise to the maxima in the angular distribution are formed primarily from constituent atoms whose original relative location on the surface is known. If this result were extrapolated to alloy surfaces such as CuNi, the relative placement of the alloy components on the surface would be determined. Recent calculations indicate that other originating sites of ejected dimers can be preferentially enhanced by varying the angle of incidence of the primary Ar^+ ion.[17] It is hoped that information on the surface structure of alloys can be obtained from an analysis of the angular distributions of the multimers. Preliminary experiments and calculations of other clusters which form via a recombination mechanism also display angular anisotropies. These include such species as Ni_3, NiO, and NiCO. The ejection direction tends to be more toward the surface normal and thus is difficult to measure with the current experimental setup.

In conclusion the first angle-resolved SIMS experiment detecting Ni_2^+ clusters which eject from Ni(100) as a result of 2-keV Ar^+-ion bombardment has been presented. The dimers are more directed in space than the monomers. Classical dynamics calculations of the collision process predict angular distributions which are in semiquantitative agreement with the experiment. In addition, the calculations show that the constituent atoms that form the dimers in the peak of the angular distribution are ejected through a similar mechanism and thus the atoms had a specific relative location on the surface.

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