Angle-Resolved SIMS—A New Technique for the Determination of Surface Structure

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One of the central problems in surface science is the experimental determination of surface structure. Recently we have theoretically predicted that the angular distributions of the particles that eject during ion bombardment are sensitive to the original site of the adsorbate [1]. Furthermore, we found that by analyzing only the higher energy particles (kinetic energy $\gtrsim$ 10 eV) strong enhancement of the angular anisotropies occurs. Although the molecular dynamics calculations employed to predict this effect were for neutral ejected species, the ejected ions should exhibit similar angular distributions. For example, the polar deflection of a 20 eV particle due to the image force will be less than 2° [1]. Hence we feel that SIMS would be a viable technique with which to measure the angular distributions of ejected particles.

For the initial experiments of angle-resolved SIMS we have chosen to investigate a c(2x2) coverage of oxygen on Cu(001) and clean Ni(001). The angle-resolved SIMS experiments were performed using a previously described apparatus [2]. Angle selection was accomplished by placing a cylindrical shield with two small apertures around the crystal [3]. One aperture collimates the normally incident primary ion and the other selects a given polar angle for the ejected particles. Although this configuration is simply constructed it allows only one polar angle to be investigated. To maximize the structural information as indicated by the theoretical calculations we have chosen a polar angle of 45°. The crystal can be rotated to obtain a full 360° azimuthal scan. We estimate the angular resolution to be 8-10°. The energy selector collects ions with between approximately 10 and 50 eV of kinetic energy. For all the experiments the primary ion was Ar^+ at normal incidence with between 900 and 1500 eV of energy. The total dose of ions was kept below 10^{13} ions/cm^2 to avoid significantly altering the surface structure.

For a c(2x2) coverage of oxygen on Cu(001), the azimuthal angular distributions at a polar angle of 45° of both Cu^+ and O^- exhibit large anisotropies, changing by more than a factor of two between minimum and maximum values. The interesting feature is that the Cu^+ maximizes in the <100> directions while the O^- maximizes in the <110> directions, 45° out of phase. Comparing these results with the calculations indicates that the oxygen is in a fourfold bridge site.

The effect of the height of the adsorbate above the surface plane on the angular distributions is shown in Fig.1. In all cases the oxygen is in a fourfold bridge site on Cu(001). The patterns all have the maximum intensity of the oxygen in the <110> directions, however, the polar angle of the

maximum intensity varies with height above the surface. The preliminary experimental results of oxygen on Cu(001) indicate that the adsorbate height is ∿1.2-1.5 Å above the surface. To be sure of the precise atomic position, however, SIMS measurements at other polar angles would be desirable.
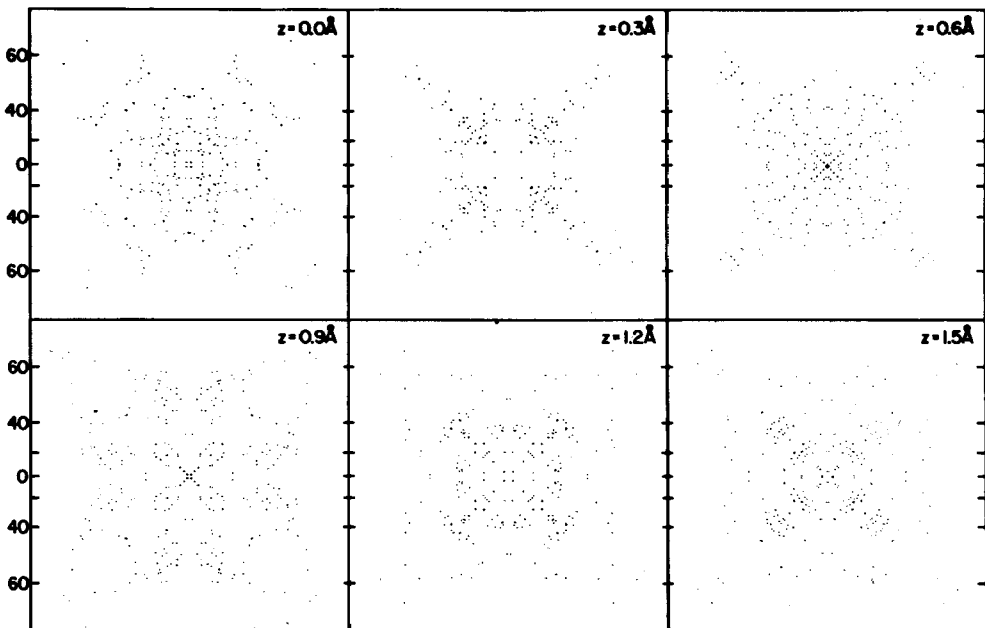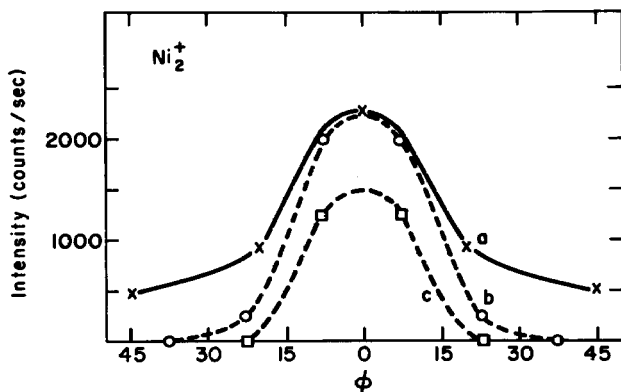

Fig.1 Calculated angular distributions of ejected oxygen atoms as a function of height (z) above the surface plane of Cu(001). In all cases the oxygen is in a fourfold bridge site at a c(2x2) coverage. Only the atoms with between 10 and 50 eV of kinetic energy are shown. The Ar$^+$ ion is at 600 eV for all these calculations. Each ejected atom is plotted on a flat-plate collector an arbitrary distance above the crystal. The numbers on the ordinate refer to the polar deflection angle given in degrees. The vertical and horizontal directions correspond to the <100> directions of the (001) face

The cluster ions also exhibit angular anisotropies. Shown in Fig.2 is the azimuthal angular distribution of Ni_2^+ from Ni(001) at a polar angle of 45°. The anisotropy is larger than a factor of 5, with the peak count rate being quite substantial (∿2000 cps) under "static" SIMS conditions. Also shown in Fig.2 is the calculated angular distribution of Ni_2. Excellent agreement is obtained.

For the angular distributions of the monomers we found that generally only one or two mechanisms of ejection were responsible for the majority of the anisotropy [1,4]. This appears to be true for the dimers as well. Shown in Fig.2 is the contribution to the theoretical curve for dimers that originated a distance of 4.98 Å apart on the surface. The mechanism that gives rise to this particular type of dimer causes the majority of the anisotropy. In fact, for 600 eV Ar$^+$ on Cu(001) this mechanism is responsible for *all* the dimers in this angle-energy regime. Recent calculations of oblique angle of

incidence of the primary Ar^+ ion have shown that other mechanisms of dimer formation and thus other originating sites can be preferentially enhanced [5]. By adjusting the experimental conditions, such as angle of incidence of the primary ion and energy and angle of detection of the ejected dimers, one can hopefully be able to obtain structural information of alloy surfaces.

Fig.2 Azimuthal angular distributions of Ni_2^+ from Ni(001) at a polar angle of 45±10°. a - experiment with the Ar^+ at 1500 eV. b - theoretical with the Ar^+ at 1000 eV. c - contribution to the theoretical curve from dimers which originated a distance of 4.98 Å apart on the surface. The nearest neighbor spacing in nickel is 2.49 Å. In all cases only the dimers with between 10 and 50 eV of total kinetic energy are shown

In conclusion, angle-resolved SIMS is being proposed as a powerful new method for the determination of surface structure. An example of adsorbate site and height determination has been given. In addition, the angular distributions of Ni_2^+ dimers have been measured for the first time.

Acknowledgements

References

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