

SURFACE SCIENCE LETTERS

**THE DILEMMA IN DEFINING THE VELOCITY AND ANGLE
DEPENDENCE OF THE PROBABILITY OF ELECTRONIC EXCITATION
NEAR A SURFACE**

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A discussion of the difficulties in defining the velocity and angle dependence of the probability of electronic events (e.g. ionization) in SIMS, ESD and PSD experiments is given. To extract the essential physics of these processes the effect of different potential surfaces for each ejected species must be taken into account.

To understand the electronic events in secondary ion mass spectrometry (SIMS), electron stimulated desorption (ESD) and photon stimulated desorption (PSD), it is desirable to measure or calculate the velocity and angular distributions of the neutral, ionic and possibly excited state species that eject from the surface. If the measured intensity of one species, for example ionic, is defined as $I^+(v, \theta, \phi)$ and the neutral intensity as $I^0(v, \theta, \phi)$, then there is a temptation to define the ionization (or excitation) probability as [1,2]

$$R^+(v, \theta, \phi) = I^+(v, \theta, \phi) / I^0(v, \theta, \phi).$$

Here v is the measured velocity of the particle, θ is the polar angle as measured from the surface normal, and ϕ is the azimuthal angle.

The problem with this definition arises because the ions and neutrals depart the surface region with trajectories that are influenced by different potential energy surfaces. For a particle near the solid surface (i.e. the sample) two schematic potential curves that are appropriate for near-resonant charge exchange processes are shown in fig. 1. There is a curve crossing at a distance R^* from the surface. Assume that a particle reaches this point with energy E^* or corresponding velocity v^* . If the particle ejects along the neutral surface (lower one) the measured velocity will also be nearly v^* . However, if the particle is ionized, there is still a barrier of energy ΔE that must be overcome before the particle finally reaches the detector. An image charge in the solid is one possible source of this energy barrier.

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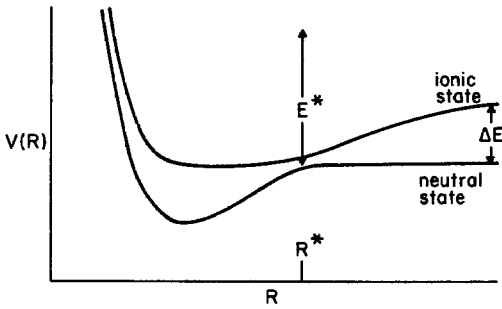


Fig. 1. Schematic potential energy curves for a particle a distance R from the surface. Adapted from ref. [14].

The easiest way to analyze the experimental data for the ionization probability is to determine the ratio of the ion to neutral yield as a function of the measured velocity. However, to compare neutral and ionic particles that had analogous histories of motion in the solid, one must compare neutral species that eject with velocity v^* and ions that eject with velocity v' where $(v')^2 \propto (v^*)^2 - 2\Delta E/m$. The appropriate ratio for ejection normal to the surface thus becomes

$$R^+(v^*) = I^+(v')/I^0(v^*),$$

or

$$R^+(E^*) = I^+(E^* - \Delta E)/I^0(E^*).$$

(The neutral particle may also have to surmount an additional potential barrier before escaping the solid and a further adjustment in its energy may be necessary.)

The manifestation of this correction on experimental results is naturally most important for the low energy ($< \approx 15\text{--}20$ eV) particles that eject in SIMS, ESD and PSD experiments and not for the high energy particles expected in ISS experiments. Typical values of ΔE are comparable to the ionization energy of the ejected species which is also comparable to the binding energy of the species to the solid.

The shifting of the energy is only one part of the correction that needs to be considered. The angles of particles ejecting on different potential surfaces will also be affected [3]. One way to imagine this effect is to think of an image force in a metal. The neutral particle ejects at one polar angle θ while the ion is attracted to the surface by its image and ejects at a more grazing polar angle. For example, if the neutral particle has 8 eV of kinetic energy and ejects at $\theta = 45^\circ$ and for the ion there is an image energy of 2 eV, then the ion will reach the detector with ≈ 6 eV of energy at $\theta = 55^\circ$. Experimentally these two conditions are easily resolvable. The dependence of the two potential surfaces

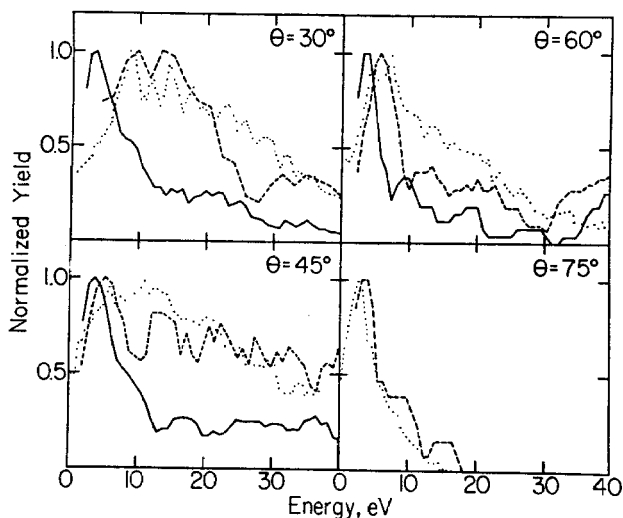


Fig. 2. Energy distributions for Ni ejected due to 1000 eV Ar^+ ion bombardment. Taken from ref. [4], fig. 6. The three curves in each panel are identified as follows: (—) calculated Ni distribution; (---) calculated Ni distribution with inclusion of a 3.6 eV image correction; (.....) experimental Ni^+ distribution.

on the azimuthal angle is not presently known, although there may well be different dependences for each state.

The magnitude of an image force distortion is shown in fig. 2 where the calculated energy distributions as a function of polar angle of Ni atoms ejected from an ion bombarded Ni{100} surface covered with a half monolayer of CO are given [4]. Also shown are the energy distributions corrected for a 3.6 eV image energy. These image corrected distributions should be comparable to ion as opposed to neutral distributions. It has been assumed here that R^+ is independent of v , θ and ϕ , yet the neutral and ion distributions are very different. Note that at $\theta = 75^\circ$ there are no neutral particles. The image force brings particles from other angles into the detector at 75° .

Another complication in interpreting the velocity dependence of the ionization probability at low energies (i.e. at energies less than the binding energy to the solid) is the non-constancy of the velocity during the ejection process. This effect has been pointed out by Lang [5] and Lin and Garrison [6]. The theoretically important velocity appears to be the velocity near the beginning of the ejection event and not the experimentally measured velocity determined at the detector.

One could ask, does the distinction in definition discussed above really matter? To examine this question, below is given a brief survey of current experimental attempts to extract the velocity dependence of the ionization probability in SIMS.

Most work has focussed toward measuring the energy distributions of secondary ions. Yu [2,7] found that the ionization probability has the following functional form,

$$R^+(v, \theta) \propto \exp(-A/av \cos \theta),$$

where A and a are two constants fit to experimental data. This is the expression originally proposed by Hagstrum [8] for higher energy ion scattering. Yu's experiments utilized the ejected O^- signal arising from bombarded vanadium and niobium oxide surfaces [7]. He also found a similar dependence for Ba atoms, ions, and excited species ejected from clean barium metal, barium fluoride and barium oxide [2]. Krauss and Gruen [9] found that

$$R^+ \propto E^m,$$

with m between 1.1 and 1.53 for positive ions ejected from clean and oxygen covered beryllium surfaces. In this work the authors were not able to measure the neutral distributions, but assumed that the neutral distribution followed Thompson's formula [10]. Lundquist [11] measured energy distributions of both Cu^0 and Cu^+ from clean copper surfaces. He found that

$$R^+ \propto E^n,$$

with $0.3 < n < 0.7$. These distributions were measured at a polar angle of 45° . Gibbs et al. [4] have compared measured Ni^+ ion distributions with image corrected calculated neutral distributions (shown in fig. 2) and found good agreement with the assumption that R^+ is independent of v and angle, i.e.,

$$R^+(v, \theta, \phi) \approx \text{constant}.$$

One must determine if these different dependences of R^+ on v , θ and maybe ϕ are due to *different physical processes* or simply *different manifestations* of potential surfaces (e.g. of binding energy and image force) on the definition of R^+ . In virtually all of the interpretations in these experiments there is at least one critical assumption. For example, in the Gibbs case the measured distributions were compared to calculated ones adjusted for the presence of an image force. A different substrate interaction potential does influence slightly the calculated polar distribution [12]. In the Krauss and Gruen experiments a Thompson distribution was assumed for the neutral particles. Recent experiments of Schick et al. [13] of measured neutral Rh and In energy distributions show that the peak position is strongly dependent on the polar angle and that it is not correct to assume that the E_b in Thompson's formula is the heat of sublimation. While Lundquist measured both the neutral and ion distributions, he did so at a polar angle of 45° . Undoubtedly, the ions have been deflected by an image charge in the metal. Only Yu's experiments of Ba distributions appear free from some of these interpretation problems, although the trajectory for each species should be influenced by a different potential energy surface. The specifics of the interaction potentials of each

ejected species with the solid are different in these experiments. Is it obvious, however, that $R^+(v, \theta, \phi)$ is different? It is possible that the true physics is being obscured?

At this stage the best suggestion, short of elaborate computer calculations that include the possibility of ejection on two or more surfaces [14,15], is to assume an additional planar surface binding energy for each of the species [3,4]. These values would be parameters along with the functional form for the process of interest. To ultimately understand the electronic events at surfaces an effort must be made to extract the *real* velocity and angle dependence of the ionization (neutralization) or excitation (de-excitation) process.

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References

- [1] R.F. Garrett, R.J. MacDonald and D.J. O'Connor, *Surface Sci.* 138 (1984) 432, and references therein.
- [2] M.L. Yu, D. Grischkowsky and A.C. Balant, *Phys. Rev. Letters* 48 (1982) 427; *Surface Sci.* 127 (1983) 315.
- [3] A complete discussion of the influence of the image force on polar distributions is given in Z. Miskovic, J. Vukanic and T.E. Madey, *Surface Sci.* 141 (1984) 285.
- [4] R.A. Gibbs, S.P. Holland, K.E. Foley, B.J. Garrison and N. Winograd, *J. Chem. Phys.* 76 (1982) 684.
- [5] N.D. Lang, *Phys. Rev.* B27 (1983) 2019;
M.L. Yu and N.D. Lang, *Phys. Rev. Letters* 50 (1983) 127.
- [6] J.H. Lin and B.J. Garrison, *J. Vacuum Sci. Technol.* A1 (1983) 1205.
- [7] M.L. Yu, *Phys. Rev. Letters* 47 (1981) 1325.
- [8] H.D. Hagstrum, *Phys. Rev.* 96 (1954) 336.
- [9] A.R. Krauss and D.M. Gruen, *Surface Sci.* 14 (1980) 14.
- [10] M.W. Thompson, *Phil. Mag.* 18 (1968) 361.
- [11] T.R. Lundquist, *J. Vacuum Sci. Technol.* 15 (1978) 684.
- [12] B.J. Garrison, unpublished results.
- [13] G.A. Schick, J.P. Baxter, J. Subbiah-Singh, P.A. Kobrin and N. Winograd, *J. Vacuum Sci. Technol.*, in press.
- [14] J.A. Olson and B.J. Garrison, *J. Chem. Phys.*, 83 (1985) 1392.
- [15] S. Sawada, A. Nitzan and H. Metiu, *Phys. Rev.* B32 (1985) 851;
S. Sawada and H. Metiu, *J. Chem. Phys.* 83 (1985) 3009.