

Charge transfer at surfaces: A model for ionization in SIMS

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A microscopic model is presented to describe the probability of charge transfer for the desorption of ions from surfaces. Results from this model study provide a theoretical basis for understanding the ionization process in SIMS and ESD experiments. Predictions of the model that have a direct bearing on the interpretation of experimental data are emphasized in this study. We examine the effect of angle of ejection, both polar and azimuthal, and the nonconstant velocity during desorption due to a surface binding energy on the ionization probability.

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I. INTRODUCTION

The desorption of energetic particles from solids is a key feature of many experimental techniques for analyzing surface composition and structure. These techniques include secondary ion mass spectrometry (SIMS), fast atom bombardment mass spectrometry (FABMS), ²⁵²Cf plasma desorption mass spectrometry (PDMS), electron-stimulated desorption (ESD), and ion scattering spectrometry (ISS). One common feature of all these experimental procedures is that ions are generally measured whereas the predominant species that desorb are often neutral.¹⁻⁵ Unfortunately, the ion fraction is very sensitive to the details of the electronic structure of the surface. Thus, it is difficult to use these techniques for quantitative measurements of the abundance of surface species.

To make precise determinations, either of the quantitative composition of elements on the surface or of exact bonding geometries, the mechanism of desorption, both for the nuclear and electronic motion, needs to be understood in detail. Although considerable effort has been expended in trying to understand the nuclear motion of the desorbing particles,⁶ relatively little is understood about the basic processes involved in the ionization or neutralization, particularly at the microscopic level. Our goal is to develop a model for the charge transfer processes which occur in the surface region that takes into account the details of the local electronic structure of the system at the time of desorption as well as the nuclear motion of the atoms.

In this study a model is presented that incorporates the electronic motion into a well-developed scheme of following the nuclear motion of the atoms.^{7,8} The details of the electronic structure of the system are included through atomic orbitals and a time dependent coupling matrix element or hopping integral. The predictions of this model for the values of the ionization probability R^+ as a function of some of the model parameters have been examined previously.⁷ This original study indicates that the model is a physically reasonable one for examining the ionization process. In this study we examine predictions of the model that have a direct bearing on the interpretation of experimental results. We find that the ionization process is more strongly coupled to the perpendicular component of the velocity of the ejected atom than the total velocity. The model predicts relatively little

dependence of R^+ on the azimuthal angle of desorption. For velocities which correspond to kinetic energies that are comparable to surface binding energies, the value of R^+ correlates better with the velocity of the particle as it first begins to move rather than the final velocity which is measured.

II. MODEL

The ionization process for ejected adatoms is modeled using a classical path method. The Hamiltonian is separated into a part for the motion of the atomic nuclei in the system (adatom, metal substrate atoms); and a part for the electronic motion. The nuclear motion is presumed to be correctly described by classical mechanics. The details of the model for the electronic motion are described in detail elsewhere⁷ and will only be briefly summarized here. In this prescription the electronic levels of the system are described explicitly. The wave functions in the solid are expressed as a linear combination of atomic orbitals. First order differential equations can be derived for the time dependent expansion coefficients. These equations are then numerically integrated along with Hamilton's equations for the nuclear motion to determine the final ionization probability. The hopping integral that couples the atomic levels is assumed to be exponential in form as

$$V[r(t)] = V_0 e^{-\lambda[r(t) - r^e]}$$

where $r(t)$ is the time dependent distance between pairs of atoms, V_0 is the coupling strength, λ is the range of the interaction, and r^e is the equilibrium separation between atoms.

In this paper we investigate an ensemble of atoms consisting of a single adatom adsorbed on a collection of metal atoms. The desorption is induced by giving the adatom an arbitrary velocity away from the surface. Both the adatom and substrate atoms have atomic orbitals that electronically interact. The arrangement of metal atoms and the adsorbate atom is shown in Fig. 1. The adsorbate atom is placed in a fourfold-bridged site 1.0 Å above the surface. The parameters used in the model for the nuclear motion are given in Ref. 7. The coupling strength V_0 is set equal to 0.20 eV for both the metal-metal and metal-adsorbate interactions. The coupling range λ is fixed at a value of 2.3 Å⁻¹. Each metal atom that electronically interacts has two atomic levels of

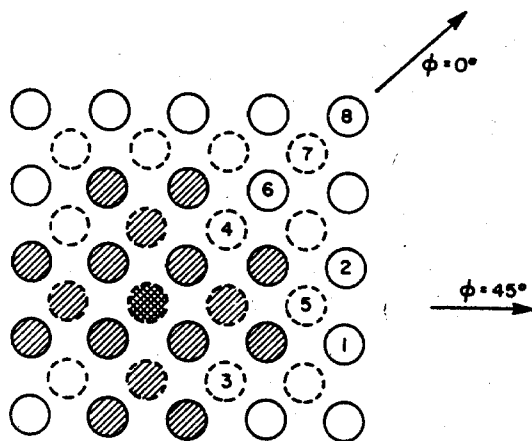


FIG. 1. Cu(001) face. The solid circles represent the first layer atoms and the broken circles represent the second layer atoms. The hatched circles are the metal atoms that constitute zone G of Ref. 7. The numbers from 1 to 8 designate atoms which are included in different zones used in this study. The adsorbate atom is originally located in a fourfold bridge site 1 Å above the surface and is denoted by the cross-hatched circle.

energies -5.0 and -5.5 eV. The adsorbate atom has one level of energy -6.0 eV.

III. RESULTS AND DISCUSSION

The values of the ionization probability R^+ have been examined for velocities of the desorbing adatom between $10^{5.5}$ and 10^8 cm/s. Shown in Fig. 2 is a typical dependence of the values of R^+ on velocity v of the ejected adatom for desorption normal to the surface ($\theta = 0^\circ$). For high velocities the value of R^+ approaches the initial charge of the adsorbate atom (sudden limit). For velocities of interest for the SIMS process R^+ is approximately proportional to v^n where n is between 2 and 4. A velocity of 10^6 cm/s corresponds to a kinetic energy of 8 eV for a particle of mass 16 amu (oxygen). The minimum in the curve at $v \approx 10^{6.3}$ cm/s results from a

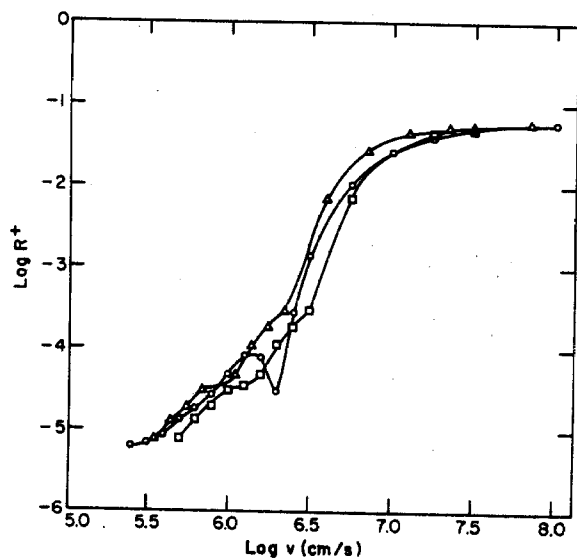


FIG. 2. $\text{Log } R^+$ vs $\text{log } v$ for various polar angles \circ - $\theta = 0^\circ$; \square - $\theta = 45^\circ, \phi = 45^\circ$; \triangle - $\theta = 45^\circ, \phi = 45^\circ, v = v_1$.

resonance effect due to the discrete nature of the energy spectrum.⁷ The effect of altering both the polar angle θ and azimuthal angle ϕ on the predicted values of R^+ is examined below. Finally, we discuss the effect of a nonconstant velocity caused by a surface binding energy on the predicted values of R^+ .

A. Convergence of R^+

In our previous studies we found that for the adatom desorbed in a direction normal to the surface that 9–17 metal atoms, each with two electronic levels, were needed so that the infinite system was reasonably approximated. For motion of the adatom that is not perpendicular to the surface we must redetermine the number of atoms that are necessary to include in the calculation. For the normal desorption case $\theta = 0^\circ$ we have included 17 metal atoms shown in Fig. 1 in the calculation. This group of atoms is referred to as zone G in Ref. 7. For a polar angle of 45° we have tested the effect of including additional atoms in the electronic zone in the azimuthal direction that the adatom desorbs on the predicted values of R^+ .

The convergence of the values of R^+ as a function of number of atoms in the electronic zone is shown in Fig. 3(a) for desorption angles of $\theta = 45^\circ$ and $\phi = 45^\circ$. Inclusion of atoms 3 and 4 with the atoms in zone G is sufficient to converge the predicted values of R^+ . Additional testing that included atoms 1 and 2 did not result in further changes in the values of R^+ . For exit angles of $\theta = 45^\circ$ and $\phi = 0^\circ$, inclusion of atoms 4 and 6 [Fig. 3(b)] is sufficient to converge the predict-

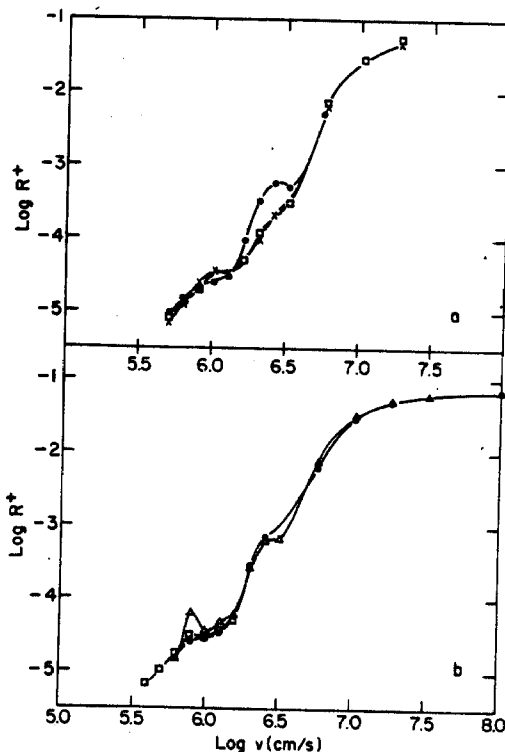


FIG. 3. $\text{Log } R^+$ vs $\text{log } v$ for various groups (a) $\theta = 45^\circ, \phi = 45^\circ$; \bullet - zone G; \times - zone G plus atoms 3 and 4 of Fig. 1; \square - zone G plus atoms 3, 4, and 5 of Fig. 1. (b) $\theta = 45^\circ, \phi = 0^\circ$; \triangle - zone G; \bullet - zone G plus atoms 4 and 6 of Fig. 1; \square - zone G plus atoms 4, 6, and 7 of Fig. 1.

ed values of R^+ . No testing was performed to see if atoms away from the direction of desorption could be omitted.

B. R^+ vs v_{\perp}

Since the model presented here is three dimensional we are in a position to test whether the assumption in most analytic models that the ionization probability depends only on the perpendicular component of velocity is valid.⁹ Shown in Fig. 2 are the calculated values of R^+ for desorption of the adatom normal to the surface and at a polar angle of 45° in the $\phi = 45^\circ$ azimuthal direction. The values of R^+ for $\theta = 45^\circ$ are plotted as a function of both the total velocity v and the perpendicular component v_{\perp} . If the two points due to the resonance at $10^{6.2}$ and $10^{6.3}$ cm/s in the $\theta = 0^\circ$ curve are ignored, then for velocities less than $\sim 10^{6.5}$ cm/s the values of R^+ vs v_{\perp} for $\theta = 45^\circ$ agree well with those for $\theta = 0^\circ$. As stated above, for high velocities the sudden limit is applicable and the value of R^+ is the initial charge on the atom. In this regime the parallel component of velocity is important for determining the time period in which the adatom interacts with the substrate. In this case the shorter the time period the higher the ionization probability. Thus, for velocities greater than $\sim 10^{6.5}$ cm/s the value of R^+ as a function of v_{\perp} for $\theta = 45^\circ$ is larger than the $\theta = 0^\circ$ value. The resonance effect does not appear in the $\theta = 45^\circ$ results indicating that more than just the magnitude of the velocity is important in the ionization process. Recent SIMS experiments by Yu¹⁰ where O^- is desorbed from niobium and vanadium surfaces have shown that the O^- intensity correlates well with v_{\perp} for velocities between 1×10^6 and 3×10^6 cm/s in qualitative agreement with the results presented here.

C. R^+ vs the azimuthal angle ϕ

The analysis of the angular distributions of particles ejected from single crystals has been shown to be useful for providing direct information of the bonding site of atoms and small molecules on surfaces. Anisotropic angular distributions are observed in SIMS,^{3,11} ESD,⁴ and ISS¹² experiments. Often it is not obvious whether the electronic processes or the preferred channeling of the nuclei in certain directions is responsible for the anisotropy. Generally, in the interpretation of SIMS and ESD experiments, it is assumed that the ionization probability is independent of azimuthal angle. Madey and Yates have observed isotropic azimuthal H^+ distributions in ESD experiments of H_2O adsorbed on Ru(001).⁴ In this case it appears that the reneutralization process is independent of the azimuthal angle. ISS experiments by several workers, however, indicate that the neutralization process operative for ion scattering is dependent on the azimuthal angle. Woodruff and Godfrey have proposed a structure dependent neutralization probability for this process.¹² As shown in Fig. 4 we find from our model that the ionization probability is mostly independent of the azimuthal angle for the two symmetry directions $\phi = 0^\circ$ and $\phi = 45^\circ$. There is a divergence of values, however, at $v \approx 10^{6.4}$ cm/s. We do not believe that this difference is due to incomplete convergence of the values of R^+ with respect to the number of atoms in the model, since the lack of convergence

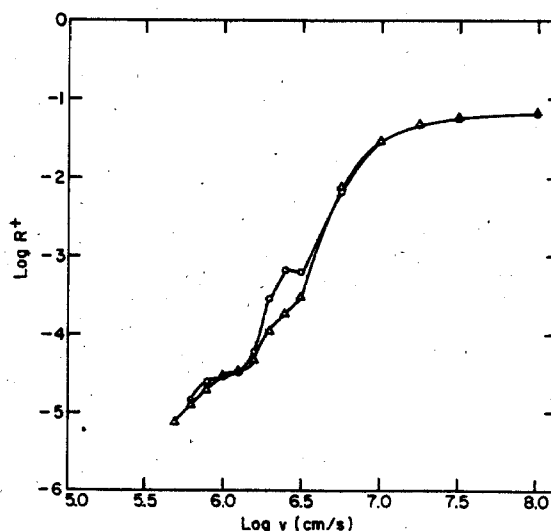


FIG. 4. $\text{Log } R^+$ vs $\text{log } v$ for different azimuthal angles and $\theta = 45^\circ$. \circ - $\phi = 0^\circ$; \triangle - $\phi = 45^\circ$.

should most significantly affect the slowest particles. It is possible that a resonance effect is operative for desorption in one azimuthal direction and not the other.

D. The effect of binding energy on R^+

All atoms that are part of a solid experience attractive forces. The kinetic energy of an atom in the solid during the process of desorption must be greater than the final kinetic energy as it leaves the surface, because some energy is transferred to overcome the binding energy E_b . This means that the atom has a nonconstant velocity as it interacts with other atoms during the desorption process. The final experimentally measured velocity is less than the maximum velocity that the particle had at some point during its motion. For particles whose final energy is of the same order of magnitude as the binding energy this nonconstant velocity should have an effect. In the results presented in Figs. 2-4 we have used a binding energy of 0.8 eV. For a particle of mass 16 amu, this corresponds to a velocity of $10^{5.5}$ cm/s.

The influence of binding energy or nonconstant velocity on the interpretation of the velocity dependence of R^+ is shown in Fig. 5. In the upper two panels R^+ is plotted versus the initial velocity v_{in} of the adatom for binding energies of 0.0, 0.8, and 1.6 eV and for desorption at $\theta = 0^\circ$ [Fig. 5(a)] and $\theta = 45^\circ$, $\phi = 45^\circ$ [Fig. 5(c)]. The lower two panels display R^+ vs v_f , where v_f is the final measurable velocity. Especially for $\theta = 0^\circ$ the value of the ionization probability correlates much better with the initial velocity [Fig. 5(a)] than the final velocity [Fig. 5(b)]. For very low final velocities, the initial velocity is almost totally that needed to escape the binding potential. Since R^+ correlates with v_{in} , the values of R^+ should be relatively constant as the velocity of the desorbed species decreases [Fig. 5(b)]. This is in qualitative agreement with the results of experiments by Yu where the O^- intensity was relatively independent of the final velocity in the low velocity regime.¹⁰

The correlation of R^+ to v_{in} for $\theta = 45^\circ$ is less obvious. One possible reason for the lack of agreement between the

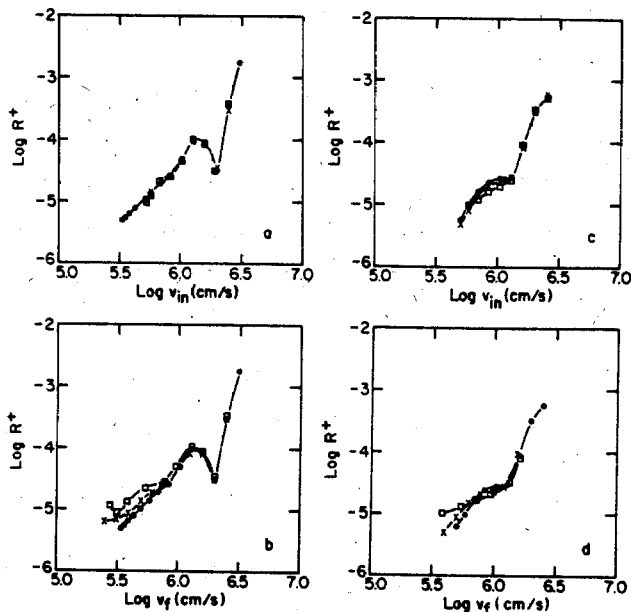


FIG. 5. $\text{Log } R^+ \text{ vs } \log v$ for different binding energies E_b . \bullet $E_b = 0.0 \text{ eV}$; \times $E_b = 0.8 \text{ eV}$; \square $E_b = 1.6 \text{ eV}$; (a) $\theta = 0^\circ$, $v = v_{in}$; (b) $\theta = 0^\circ$, $v = v_f$; (c) $\theta = 45^\circ$, $v = v_{in}$; (d) $\theta = 45^\circ$, $v = v_f$.

curves in Fig. 5(c) is that the binding energy affects most strongly the perpendicular velocity component and not the parallel component. Thus, as v_{\perp} changes so does the polar angle. The final measurable polar angle, 45° in this case, is more grazing than the angle at the start of the atom's motion. This ambiguity in determining the appropriate velocity and angle for correlating with the ionization phenomena will be present for all species desorbed at low velocities.

IV. SUMMARY

We have presented a microscopic model that describes the charge transfer process that occurs as atoms desorb from a surface. The model is especially attractive for application to ion bombardment experiments since the local electronic structure at the time of desorption rather than the original band structure of the quiescent surface is taken into account. We find for velocities of the desorbed atom that are appropriate for SIMS and ESD experiments that the ionization probability R^+ is more dependent on the perpendicular component of velocity than on the parallel component. The results show that the velocity of the atom during the desorption process is more important in controlling the ionization process than the final measurable velocity. For the very low final velocities, the velocity during the desorption is that needed to overcome the surface binding energy. In this re-

gime R^+ is almost independent of the final velocity. These results are in qualitative agreement with recent SIMS experiments by Yu.¹⁰

Note added in proof. Dr. A. R. Krauss kindly pointed out at the AVS Meeting two references where there is experimental evidence for a power law dependence of R^+ on velocity. In A. R. Krauss and D. M. Gruen, *Surface Science* **92**, 14 (1980), the authors find for beryllium ions ejected that R^+ is proportional to v^n , where $n = 2-3$. They also observe a binding energy effect at low velocities. T. R. Lundquist [*Surface Science* **90**, 548 (1979)] measured ion and neutral atom energy distributions of Cu and Ni and found that R^+ is approximately linear in velocity. Both of these works are in qualitative agreement with the conclusions presented here.

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