Trapping of Ions at Metal Surfaces

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The surface trapping probability $S(E_i)$ of Na^+ on Cu(001) has been measured for incident energies E_i between 5 and 600 eV via resonant ion neutralization for both 45° and 8° incidence. For 8° incidence, $S(E_i)$ decreases with increasing energy. For 45° incidence, however, $S(E_i)$ decreases to zero at approximately 25 eV, and then *increases* with increasing energy up to 125 eV. We explain this behavior in terms of the changing surface corrugation seen by an ion as its energy increases. [S0031-9007(97)02941-4]

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The trapping of energetic particles at crystalline surfaces is a critical step in a number of thin film deposition methods, including sputter deposition, pulsed laser deposition, and direct ion beam deposition. These techniques involve particle energies from a few eV to a few hundred eV, an energy range where surface trapping, near-surface implanting, and deep implantation can all occur. Whether the trapping is predominately a surface or subsurface phenomenon can greatly affect the properties of a deposited film, as shown by Lifshitz *et al.* for C^+ beam deposition on Si(001) [1]. Therefore, understanding how trapping mechanisms vary with incident beam energy and direction can suggest appropriate deposition conditions for growing films with particular structural, tribological, and electronic properties.

The variation of trapping probabilities with energy is a basic concern of gas-surface dynamics as well. At very low incident energies E_i, the surface trapping probability $S(E_i)$ is determined by energy accommodation, i.e., the incident atom must transfer enough energy to the surface for it to be unable to escape the surface binding potential. This energy transfer can occur via surface recoil (phonon excitation) or electronic excitations. For alkali ions and metal surfaces, acceleration by the image force guarantees a hard collision with efficient energy transfer by recoil even for the lowest incident energies. We therefore expect $S(E_i)$ to be large at low energies. As the energy increases, however, the ion needs to shed a larger fraction of its energy in order to trap. It often cannot, and S decreases. Hurkmans *et al.* [2] studied 0.5 to 30 eV K and Na incident on W(110), and clearly saw a monotonic decrease in the $S(E_i)$ with increasing E_i; it approached zero well below 30 eV. $S(E_i)$ can decrease with E_i for another reason: at some energy, surface penetration becomes possible, and subsurface implantation begins to dominate the trapping probability. Marton *et al.* [3] and Choi *et al.* [4], who bombarded graphite with 10 to 600 eV noble gas ions, studied the energy dependence of the subsurface implantation probability, which increased with incident energy. However, none of these three studies could follow the trapping probability through the transition from surface to subsurface trapping: the former because of the low incident energies used, the latter two because noble gases do not surface trap at room temperature. In particular, these studies could shed no light on the behavior of $S(E)$ above its first low energy minimum.

Is there any way to arrest or even reverse the decline in $S(E_i)$ with E_i at fixed incidence angle? Yes. If the corrugation of the ion-surface interaction potential increases with increasing energy, then more violent, larger-angle collisions, with a larger associated fractional energy loss, become possible. If these collisions are sufficiently violent, *and* surface penetration is not yet possible, incident ions may again become able to transfer enough energy to trap on the surface. A clear signature of this would be a nonmonotonic energy dependence of $S(E_i)$.

The experiments described in this Letter provide the first evidence for a nonmonotonic $S(E_i)$ in this energy range. We have determined the surface trapping probability of 5 to 600 eV Na^+ on Cu(001), incident along the $\langle 100 \rangle$ azimuth at 8° and 45° from normal. We find that, for 45° incidence, $S(E_i)$ decreases with energy from 5 to 25 eV, but then *increases* again until approximately 125 eV. Combining these experimental results with scattering simulations, we explain this behavior in terms of the occurrence of a new collision type above 25 eV, made possible by the increased corrugation of the ion-surface interaction potential, well before subsurface implantation becomes possible.

For alkali ions incident on metals, $S(E_i)$ can be measured in a novel manner, which takes advantage of resonant ion neutralization [5]. By monitoring the charge state fraction of the *scattered* Na, we can determine the amount of *trapped* Na on the surface. This technique is quite surface sensitive; subsurface alkalis are much less effective at lowering the work function, and therefore contribute less to the neutralization [6].

The basis of the technique is the following. The scattered ion intensity at a particular final energy E_f and direction $\hat{\Omega}_f$ is related to the incident beam current density $\vec{J}(\vec{r})$, the coverage θ of trapped sodium, and the positive ion survival probability P^+ as

$$I(E_f,\hat{\Omega}_f,t)=\frac{d\sigma}{d\hat{\Omega}}\,\delta\Omega\int J_n(\vec{r})P^+(\theta(\vec{r},t))\,dA\,, \tag{1}$$

where $d\sigma/d\hat{\Omega}$ is the (energy- and geometry-dependent) scattering cross section, $\hat{n}$ is the surface normal, $J_n(\vec{r})=\vec{J}\cdot\hat{n}$, $\vec{r}$ is a macroscopic surface coordinate, t is the time, and the integral is taken over the illuminated surface. We have suppressed the dependence of σ on the incident and final ion energy and direction and the final velocity dependence of P^+ to keep the notation compact. The sensitivity of P^+ to the Na coverage is evident in Fig. 1, where we show calculated values of $P^+(\theta)$ for Na scattered at 45° from Cu(001) for a range of final energies. The calculations were performed with a one-electron model of resonant charge transfer [7], where the alkali-coverage-induced decrease in the copper work function Φ [8] facilitates the resonant transfer of electrons from the surface to the Na(3s) orbital. The calculation uses transition rates and energy levels calculated by Nordlander and Tully [9], and the Na/Cu(001) dipole moment measured by Ellis and Toennies [10]. This model has been shown to reproduce the neutralization behavior of alkali ions scattered from clean [11] and alkali-covered [12] metal surfaces. Note the rapid decrease of P^+ with θ, and the near-linear dependence at low coverages.

This linear dependence allows us to expand Eq. (1) to first order. Taking the time derivative, we find

$$\frac{\dot{I}(t)}{I(0)}=\frac{1}{P^+(0)}\frac{dP^+}{d\theta}\bigg|_{\theta=0}\frac{\int J_n(\vec{r})\dot{\theta}(\vec{r},t)\,dA}{\int J_n(\vec{r})\,dA}\,. \tag{2}$$

For low coverages, the coverage θ is proportional to the surface trapping probability $S(E_i,\hat{\Omega}_i)$:

$$\theta(\vec{r},t)=tS(E_i,\hat{\Omega}_i)J_n(\vec{r})\,, \tag{3}$$

where E_i and $\hat{\Omega}_i$ are the incident ion energy and direction, respectively. We thus have

$$\frac{\dot{I}(t)}{I(0)}=S(E_i,\hat{\Omega}_i)\frac{1}{P^+(0)}\frac{dP^+}{d\theta}\bigg|_{\theta=0}\frac{\int J_n(\vec{r})J_n(\vec{r})\,dA}{\int J_n(\vec{r})\,dA}\,. \tag{4}$$

$S(E_i)$ can therefore be determined directly from the time-dependent ion signal, the calculated ion survival probalities, and the measured current density $J_n(\vec{r})$.

These experiments were performed in an ultrahigh-vacuum scattering system [13] on a sputter-cleaned, annealed Cu(001) surface. For each trapping measurement a monoenergetic ($\Delta E < 0.5$ eV), mass-selected Na$^+$ beam of the desired energy was directed at the Cu(001) surface along the ⟨100⟩ azimuth. The incident current density $\vec{J}(\vec{r})$ was determined by profiling the beam with a 1 mm aperture Faraday cup. The true current density was obtained from the measured profiles using numerical deconvolution with Wiener optimized filtering. The beams were roughly Gaussian in profile, with typical widths of 1.0–2.0 mm. Two incidence angles α_i (measured from the surface normal) were used: 45° and 8°. The outgoing detection angle α_f was always 45°, with the scattering plane aligned along the ⟨100⟩ azimuth. The scattered ion energy spectra exhibit the usual well-resolved energy peaks (Fig. 2), arising from quasisingle, quasidouble, and zigzag scattering [14,15]. Setting $t=0$ when the surface is first exposed to the ion beam, in Fig. 3 we plot the fractional scattered ion intensity at the quasisingle (lowest energy) peak as a function of exposure time t. As expected, the ion intensity decreases linearly at early times. The nonlinear behavior at intermediate times is due entirely to the nonlinear θ dependence of P^+ at larger coverages. We have precisely reproduced this behavior by combining Eqs. (1) and (3) with a functional form for $P^+(\theta)$ accurate at larger θ as well. As this has no bearing on the early time behavior [16], we restrict ourselves here to the linear approximation to P^+.

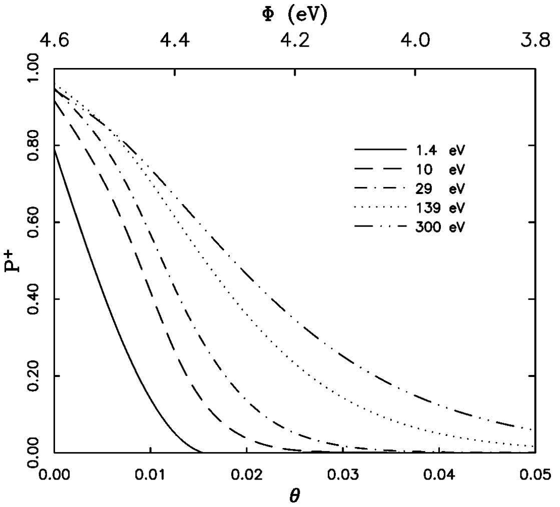

FIG. 1. Calculated ion survival probability P^+ for Na$^+$ scattered from Cu(001) at an outgoing angle of 45° with respect to normal, as a function of coverage and work function, for several final energies. Coverage is Na adsorbates per surface copper atom.

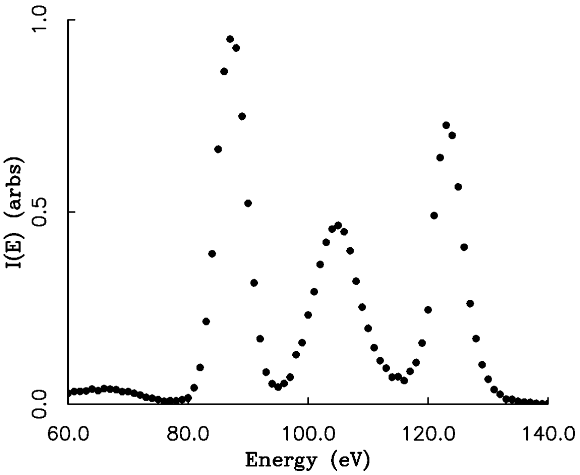

FIG. 2. Scattered ion final energy spectrum of Na$^+$ incident of Cu(001)⟨100⟩ for $E_i = 189$ eV, $\alpha_i = \alpha_f = 45°$.

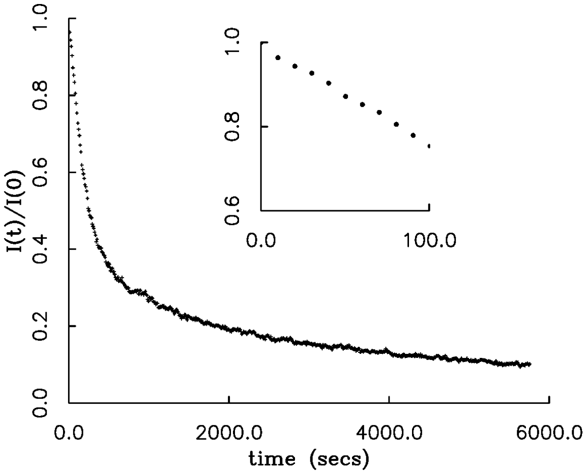

FIG. 3. Fractional ion intensity at quasi-single scattering peak energy as a function of elapsed time for scattering conditions of Fig. 2. The inset shows only the first 100 sec of the same data.

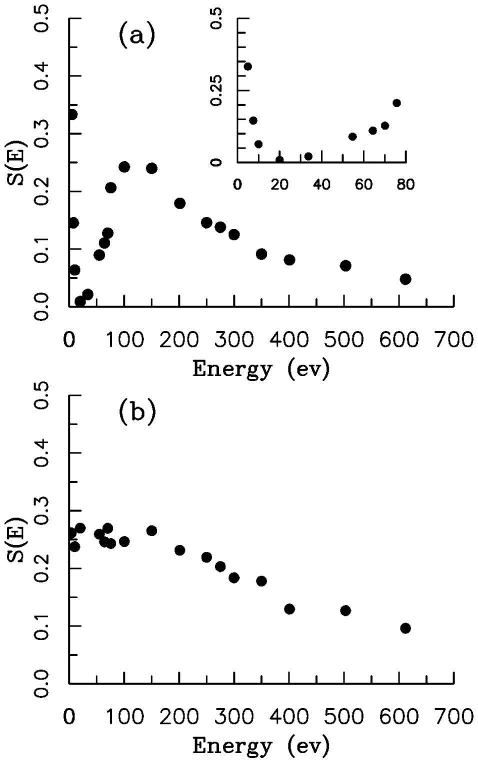

FIG. 4. Measured trapping probability $S(E)$ for Na^+ incident on Cu(001)⟨100⟩. (a) $\alpha_i = 45°$. The inset shows $S(E)$ at $\alpha_i = 45°$ from 5 to 80 eV. (b) $\alpha_i = 8°$. The lowest incident energy is 5 eV for (a), 10 eV for (b).

Curves similar to Fig. 3 were obtained at all energies between 5 and 600 eV, for both incident geometries. We found very little dependence on surface temperature until we approached the Na desorption temperature. In addition, if the beam was blocked for a finite period and then unblocked, the ion signal continued its decay from the value it had before blocking. These two observations indicate that diffusion of the trapped sodium does not occur over the time and length scales probed in these measurements.

Using our calculated values of P^+, measured current densities $J_n(\vec{r})$, and measured ion intensities, we determined the surface trapping probability $S(E_i)$, which we plot in Fig. 4 for both 8° and 45° incidence. As *absolute* surface trapping probabilities, these quantities are subject to several uncertainties, the largest being the use of calculated, rather than measured, values for P^+. For example, $S(E)$ may be exaggerated at higher energies, since the calculated values of P^+ ignore parallel velocity effects [17]. There may also be a small contribution to the work function shift from subsurface Na. As a measure of *relative* trapping probabilities, however, we expect the trends in Fig. 4 to be robust.

In both geometries, $S(E)$ is largest at the lowest incident energies. Because of constraints on scattering geometry and detector resolution, the 8° measurements could be performed no lower than 10 eV. We expect, and calculations indicate, that in both geometries $S(E)$ increases to nearly unity at lower incident energies. For $\alpha_i = 8°$ [Fig. 4(b), $S(E)$ decreases with increasing energy, as surface penetration and implantation become more likely. However, since $S(E_i, \alpha_i = 8°)$ does not drop quickly to zero above a few tens of eV, energy transfer from the incident Na^+ to the surface is apparently quite efficient in this geometry, even at higher energies. This is not surprising, since the large surface corrugation seen for near-normal incidence allows violent, large-angle collisions, and thus large energy transfers [18]. For 45° incidence [Fig. 4(a)], however, $S(E_i)$ drops nearly to zero as the energy increases to 25 eV. It appears the available collision types do not allow sufficient energy transfer for trapping to occur. However, above 25 eV, $S(E)$ begins to increase again. This nonmonotonic behavior suggests the onset of a new collision type that allows very large fractional energy transfer, and thus surface trapping.

To test this idea, we performed fully three-dimensional trajectory calculations using an ion-surface interaction potential which accurately models the scattering behavior of this system from 5 to 500 eV [19,15]. The imagelike part of this potential provides the binding which traps the sodium ions. Approximately 10 000 ion trajectories with random impact parameters were calculated for each energy and geometry probed in our experiments. Surface-atom–surface-atom forces were ignored, and the results were relatively insensitive to thermal vibrations up to 400 K. In Fig. 5 we plot the total trapping probability as well as the top-layer and subsurface trapping probabilities for $\alpha_i = 45°$. The qualitative trends observed in the experiment are reproduced in these calculations. There are quantitative discrepancies, especially in the overall magnitude of the trapping, due in part to the fact that the simulation assumes no neutralization of the sodium; some of the ions which trap in the simulation may in reality neutralize, and thus escape from the surface. Also, the simulations predict a faster dropoff of $S(E)$ above 100 eV.

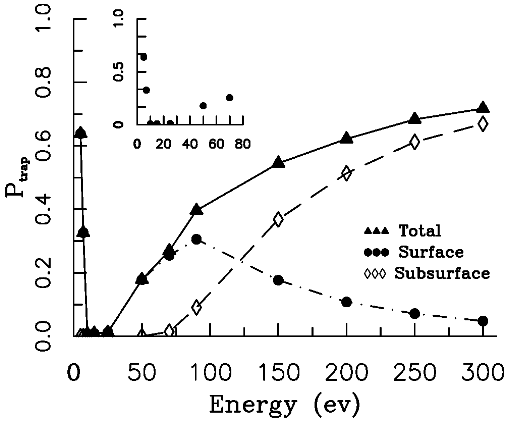

FIG. 5. Calculated trapping probability P_{trap} for Na^+ incident on Cu(001) ⟨100⟩ at $\alpha_i = 45°$. The inset shows just the surface component from 5 to 80 eV.

The trends, however, should be robust. Note that the simulation accurately predicts the minimum in $S(E_i)$, and shows an increase in surface trapping above 25 eV, while there is still *no* subsurface trapping until nearly 75 eV.

Looking at typical ion trajectories that lead to surface trapping at 45° incidence (Fig. 6), the effect of the changing energy-dependent surface corrugation is clear. The low energy trapping trajectories correspond to fairly gentle forward scattering from the surface; as the incident energy is increased toward 25 eV, these collisions do not permit enough energy transfer for trapping. However, as the incident energy increases further still, the increasing surface corrugation eventually allows very large-angle multiple collisions (the 40 eV trajectory in Fig. 6). Much larger energy transfer is possible in this type of collision, so once again surface trapping occurs.

We expect similar behavior in the initial stages of film growth in most systems with comparable ion-atom mass ratios and surface structure. The possibility of surface trapping without implantation above the first minimum in $S(E)$ means one may be able to study pure surface growth with incident beam energies above *and* below the threshold for surface damage. This should permit a more controlled investigation of the role of beam energy in film growth, isolating the effect of surface damage, island breakup, and enhanced surface mobility from the effect of surface vs subsurface deposition.

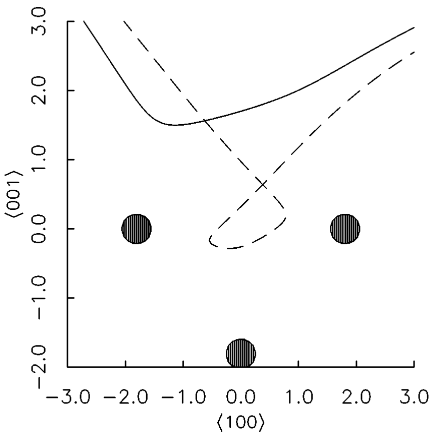

FIG. 6. Typical trajectories that lead to trapping at 5 (—) and 40 eV (- -). First and second layer copper atoms are indicated as shaded circles. All units are in angstroms.

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[1] Y. Lifshitz, G. D. Lempert, and E. Grossman, Phys. Rev. Lett. **72**, 2753 (1994).
[2] A. Hurkmans, E. G. Overbosch, and J. Los, Surf. Sci. **59**, 488 (1976); **62**, 621 (1977).
[3] D. Marton, K. J. Boyd, T. Lytle, and J. W. Rabalais, Phys. Rev. B **48**, 6757 (1993).
[4] W. Choi, C. Kim, and H. Kang, Surf. Sci. **281**, 323 (1993).
[5] T. C. M. Horn, Pan Haochang, and A. W. Kleyn, J. Vac. Sci. Technol. A **5**, 656 (1987).
[6] M. Scheffler (private communication).
[7] A. Dorsey, K. Jacobsen, Z. Levine, and J. W. Wilkins, Phys. Rev. B **40**, 3417 (1989).
[8] For small coverages, the decrease of the work function is linear in the coverage.
[9] P. Nordlander and J. C. Tully, Surf. Sci. **211**, 207 (1989).
[10] D. Ellis and J. P. Toennies (private communication).
[11] G. A. Kimmel and B. H. Cooper, Phys. Rev. B **48**, 12 164 (1993).
[12] G. A. Kimmel, D. M. Goodstein, Z. H. Levine, and B. H. Cooper, Phys. Rev. B **43**, 9403 (1991).
[13] R. L. McEachern, D. L. Adler, D. M. Goodstein, G. A. Kimmel, B. R. Litt, D. R. Peale, and B. H. Cooper, Rev. Sci. Instrum. **59**, 12 (1988).
[14] R. L. McEachern, D. M. Goodstein, and B. H. Cooper, Phys. Rev. B **39**, 10 503 (1989).
[15] C. A. DiRubio, R. L. McEachern, J. G. McLean, and B. H. Cooper, Phys. Rev. B **54**, 8862 (1996).
[16] Typical current densities were less than 10^{-3} incident ions per surface copper atom per second, implying monolayer formation times greater than 1000 sec, even for unity sticking.
[17] J. N. M. van Wunnik, R. Brako, K. Makoshi, and D. M Newns, Surf. Sci. **126**, 618 (1983).
[18] Large fractional energy transfer requires large angle collisions *and* a not-too-small ion–surface-atom mass ratio.
[19] D. M. Goodstein, R. L. McEachern, and B. H. Cooper, Phys. Rev. B **39**, 13 129 (1989).