Observation of Skipping Motion in Small-Angle Ion-Surface Scattering

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We report the observation of skipping motion of 200–2000-eV Si^+ beams on a smooth Cu(111) surface under grazing (1°–14°) angles of incidence. The kinetic-energy distributions of specularly scattered Si^+ and Si^- ions exhibit discrete energy-loss features corresponding to an integral number of reflections. Energy losses up to 20% of the incident beam energy, associated with five reflections in a binding potential, are identified. Classical trajectory calculations imply that the beam is trapped following an energy loss, by substrate electron-hole pair or collective excitation, which exceeds the incident-beam-energy component normal to the surface.

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The concept of "resonant scattering" or "selective adsorption" of low-energy beams of light atoms scattered from crystalline surfaces was invoked in 1936 by Lennard-Jones and Devonshire[1,2] to explain experimental results by Frisch and Stern.[3] The concept is usually associated with bound-state resonances which permit adsorbed atoms to move freely parallel to the surface. The possibility that ion beams, incident at grazing angles to a metal surface, may also experience such "skipping motion" was proposed in 1979 by Ohtsuki, Koyama, and Yamamura.[4] At velocities greater than the Fermi velocity v_F of electrons in the metal, the dynamical polarization of the valence-electron cloud induced by the moving ion provides the binding potential. At lower velocities ($v \ll v_F$), the image and chemisorption potentials could provide the binding potential.[5] In this Letter we report the first experimental observation of skipping motion, namely, of 200–2000-eV Si^+ beams on a Cu(111) surface.

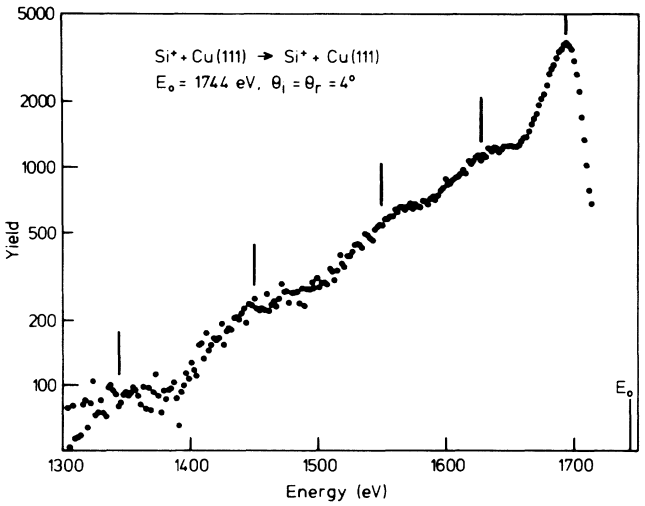

FIG. 1. Kinetic-energy distribution of Si^+ ions scattered from a Cu(111) surface [incident beam energy $E_0 = 1744$ eV, incidence angle to surface θ_i = observation angle to surface θ_r = 4°, azimuth −5° to $\langle\bar{1}10\rangle$ direction (Fig. 2)].

The Si^+ ions were generated in an ion source, accelerated, and focused onto the (111) face of a Cu single crystal, which was mounted on a two-axis goniometer in an UHV chamber. The scattered positive and negative ions were energy analyzed by a 180° hemispherical energy analyzer operating in the $\Delta E/E$ = const mode. This spectrometer was also mounted on a two-axis goniometer. Both goniometers were under computer control via stepper motors. The crystal was oriented to within 0.5° by back Laue diffraction and polished with diamond paste down to 1 μm. The crystal was cleaned and further polished by a combination of glancing incidence sputtering[6] and annealing. The surface cleanliness was monitored with use of negative recoil spectroscopy (sensitive to 10^{-5} of a monolayer of oxygen[7]). The surface flatness was monitored by a combination of surface channeling and angular distribution measurements.[6] Mass analysis of scattered or recoil ions was performed by modulating the primary beam and measuring the phase delay in detection. This method was shown to have a mass resolution of better than 0.2 u, based on the mass spectrum of O^+, OH^+, and OH_2^+ from H_2O. Energy calibration was performed by passing the primary beam directly through the energy analyzer.

The energy spectrum of specularly scattered Si^+ ions obtained from a 1744-eV Si^+ beam incident at 4° to the target surface is reproduced in Fig. 1. The spectrum of negative ions is similar. The spectra exhibit several structures, identified by their centroids (which we use to define their positions) in Fig. 1. In the following discussion we call these structures "peaks." The azimuthal dependence of the integrated intensity of each of regions 1–4 in the Si^- energy spectrum (Fig. 2) is shown in the upper portion of Fig. 2. The scattered-ion yield, as a function of scattering angle, for each of regions 1–4 in Fig. 2, is characteristic of specular scattering.[6] The width of these angular distributions increase only marginally with increasing energy loss of the incident ions. The energy loss of each peak in the Si^- energy spectra as a function of incident beam energy is shown in Fig. 3. Similar curves are obtained for the positive ions.

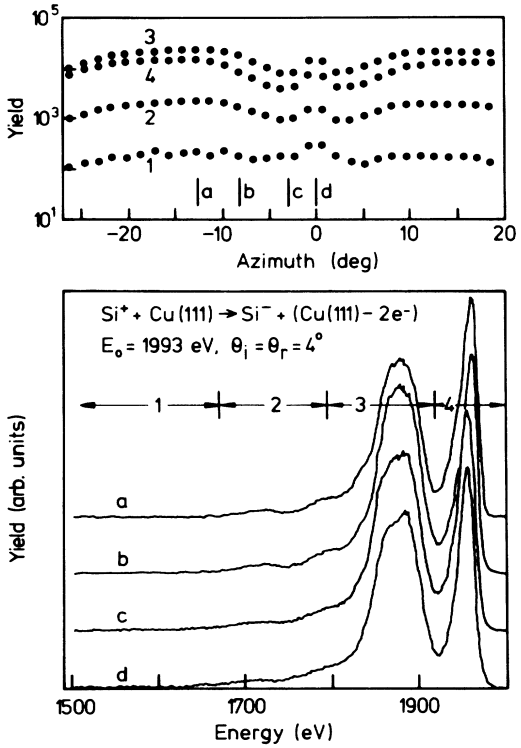

FIG. 2. Azimuthal scans (top) of the integrated yield in the energy regions 1–4 of the kinetic-energy distribution (bottom) of Si^- ions produced in the glancing incidence scattering of 1993-eV Si^+ from Cu(111). The energy spectra *a–d* were measured at the azimuthal angles indicated in the top, and are displaced and normalized for clarity. The origin of the azimuth scale is defined to be the $\langle\bar{1}10\rangle$ direction.

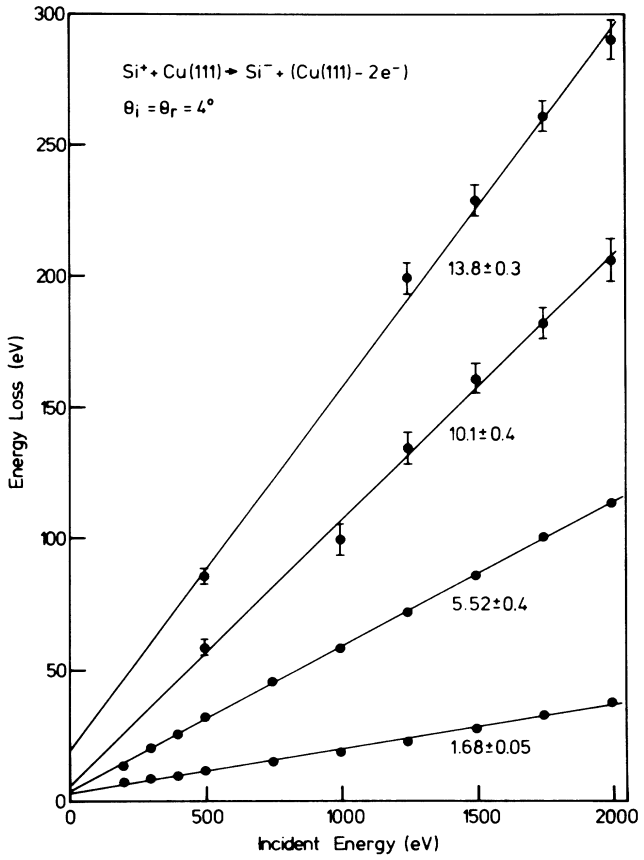

FIG. 3. Dependence on incident energy E_0 of the energy loss of each peak in the energy spectrum of Si^- ions produced in the glancing incidence scattering of Si^+ from Cu(111). The slopes ($\times 10^2$) of the least-squares-fitted lines are indicated (crystal azimuth $-5°$ to $\langle\bar{1}10\rangle$ direction).

Energy spectra containing discrete energy-loss peaks, which exhibit a loss dependent on incident beam energy, have been observed in bulk channeling experiments.[8] Such peaks are ascribed to particles that have made an integral number of reflections in a crystal channel. However, in our experiment, the effective beam energy perpendicular to the surface ($E_\perp = E_0 \sin^2\theta_i$, where E_0 is the incident beam energy, and θ_i the incidence angle to the surface plane, ranging from 1 to 10 eV) is insufficient for penetration of the surface layer.[9] Thus subsurface channeling and subsequent dechanneling cannot explain our results, unless the ions penetrate inside the crystal via surface steps, and subsequently exit at the rear of small island structures after a small number of subsurface channeling oscillations.[10] To investigate this possibility, we have studied the incidence-angle dependence of the scattered positive- and negative-ion energy spectra. The relative intensity of the second-highest to the highest-energy peak in the negative-ion energy spectra, at the specular scattering angle, for incident beam energies of 1 and 2 keV is shown in Fig. 4. The ratio of step area to terrace area of a stepped surface, as seen by the beam, is proportional to $\cot\theta_i$. The island subsurface channeling model,[10] in which the highest-energy peak represents simple scattering from terraces, and the second peak represents subsurface channeling, thus predicts to first order a peak intensity ratio varying with $\cot\theta_i$, and independent of beam energy. Experimentally (Fig. 4), this peak intensity ratio exhibits a minimum, rather than monotonic decrease with θ_i, and scales exactly with $E_\perp = E_0 \sin^2\theta_i$, in contradiction with both model expectations. Classical trajectory calculations using a purely repulsive Si-Cu interaction potential,[11] and including thermal vibrations and inelastic energy loss, show 100% reflection and reproduce the experimentally observed azimuthal dependence of the scattered particle yield. These calculations suggest that the small cusp at 0° in the azimuthal scans arises from a focusing effect in the wedge structure formed by the $\langle\bar{1}10\rangle$ atomic rows. This focusing or surface channeling effect, however, does not lead to multiple peaks in the calculated energy spectra. Surface hyperchanneling trajectories[12,13] are therefore not responsible for the observed multiple-peak structure in the energy distributions. Furthermore, the in-

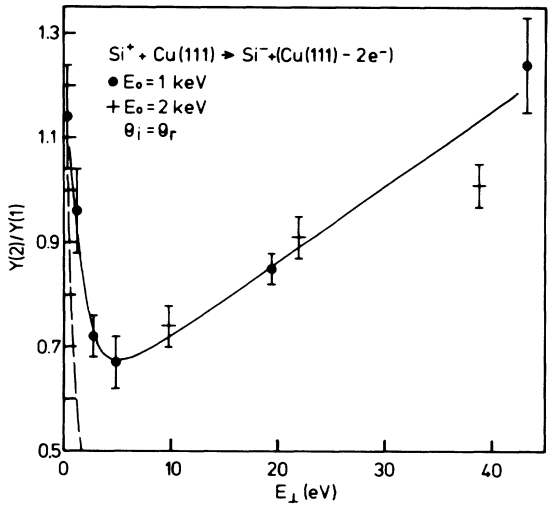

FIG. 4. Dependence of the relative intensity of the second-highest to highest-energy peak in the Si^- spectra on incident beam energy perpendicular to the surface ($E_\perp = E_0 \sin^2\theta_i$) for beam energies of 1 and 2 keV. The broken curve is the function $\cot\theta_i$, normalized to the first data point. The full curve is drawn to guide the eye.

dependence of the *shape* of the energy distribution on azimuth implies that the multipeaked structure of the energy distribution is not caused by the surface corrugation.

Local-density-functional calculations suggest that Si would be adsorbed on a metal with the electron density of Cu.[14] The use of a purely repulsive potential in the above mentioned trajectory calculations is therefore unrealistic. We have repeated the above classical trajectory calculations using a model Morse potential and the inelastic energy-loss function of Núñez, Echenique, and Ritchie.[15] The creation on the incident trajectory of substrate electronic excitation (through inelastic energy loss) with total energy exceeding $E_\perp$ results in the trapping of the projectile on the corresponding excited-state potential surface (Fig. 5). The particle remains trapped provided that energy loss of sufficient magnitude continues. Escape occurs because of the stochastic nature of

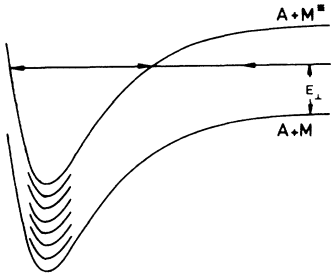

FIG. 5. One-dimensional schematic representation of the family of potential surfaces arising from a ground-state-projectile–surface binding potential with substrate electron-hole or collective excitation.

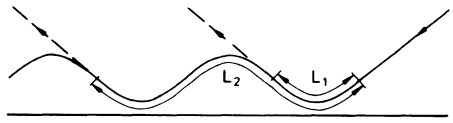

FIG. 6. Schematic trajectory for skipping motion of an ion beam on a planar surface. The effective trajectory lengths for one (L_1) and two (L_2) reflections are indicated.

the inelastic loss.[16] The calculation reproduces the observed incidence-angle and incidence-energy dependences, and produces multiple-peaked energy spectra. A trajectory analysis correlates the highest-energy peak with single scattering from the surface, and each subsequent peak with an additional inelastic reflection in the binding potential. The observed near exponential decrease in peak intensity (Fig. 1) with number of reflections is also reproduced in the calculations. We thus interpret our experimental results as representing the first observation of skipping motion of an energetic beam on a crystal surface.

The data of Fig. 3, and the corresponding data for the positive ions, suggest that the energy loss for the Si^+-Cu(111) interaction, in this energy range, can be described well by the equation $dE/dx = -(\alpha_n/L_n)E$, where L_n is an effective path length for the trajectory corresponding to the nth peak, and α_n is a constant for each peak, equal to the slope of the least-squares-fitted curves (Fig. 3). For the simple model trajectory of Fig. 6 we see that if n represents the number of reflections, $L_n \approx (2n-1)L_1$. The function $\alpha_n/\alpha_1(2n-1)$ would have a constant value (≈ 1) in this model. This is observed to a good approximation (Table I), for both positive and negative final charge states. However, the slight by statistically significant difference between the data for positive and negative ions implies that scattered Si^+ and Si^- arise from different trajectories along the surface. Our trajectory calculations imply $L_1 \approx 25$ Å for $\theta_i = 4°$ and a beam energy of 2000 eV.

Extrapolating the energy-loss curves to zero incident beam energy (Fig. 3) shows that nonzero energy losses of 13.6 ± 2.5 and 3.4 ± 0.5 eV are associated with the interactions $Si^+ + Cu(111) \rightarrow$ collision complex $\rightarrow Si^+ + Cu(111)$ and $Si^+ + Cu(111) \rightarrow$ collision complex $\rightarrow Si^- + (Cu(111) - 2e^-)$, respectively. The observation of a significant yield of Si^-, combined with the long interaction time, suggests that a negative-ion *intermedi-*

TABLE I. Dependence of the function $\alpha_n/\alpha_1(2n-1)$ on n for Si^+ and Si^-.

	$\alpha_n/\alpha_1(2n-1)$			
q	$n=1$	$n=2$	$n=3$	$n=4$
+	1 ± 0.1	0.88 ± 0.05	0.86 ± 0.05	1.08 ± 0.06
−	1 ± 0.1	1.1 ± 0.03	1.2 ± 0.08	1.17 ± 0.06

ate is generally formed during the interaction. The energy required to remove Si^- from a Cu(111) surface is simply the energy difference between the Fermi level of Cu(111) and the affinity level of Si (Ref. 17) or $4.6-1.24=3.4$ eV. To remove Si^+ from the same surface would require the loss of two electrons from such an intermediate state. The loss of the first electron can proceed adiabatically as the affinity level crosses the Fermi level on the exit trajectory.[18] The loss of the second electron would then be energetically equivalent to the excitation of a single electron from the bottom of the valence (*sp*) band to the Fermi level, i.e., 8.5 ± 0.3 eV.[19] The value for Si^- is precisely the energy loss that we observe, while that for Si^+ is a little smaller, and suggests that ionization occurs to the vacuum. The observation of an extrapolated nonzero energy loss at zero beam energy is clear evidence that over the full collision energy range studied here, the Si^+ ions that we observe are formed in a reionization process on the exit trajectory, and do not represent ions which remain unscreened throughout the collision.

The observation, reported in this Letter, of skipping motion of a glancing incidence energetic ion beam on a crystal surface is clear evidence of the potential of ion-surface scattering techniques to probe the dynamics of chemisorption and reaction at surfaces. We expect the skipping motion to appear for other projectile-surface combinations, provided an attractive potential and sufficient inelastic energy loss characterize the interaction. Species which at thermal energies are unbound or only weakly bound to a given surface (e.g., inert gases on metals) would not be expected to exhibit skipping motion in the velocity regime $v \ll v_F$.

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