

Multiply ionized atom production in keV-N⁺-Si-surface scattering

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A definite energy threshold is found for the appearance of doubly and triply charged ions when N⁺ ions are elastically scattered from surface atoms in a clean silicon surface. These threshold energies directly confirm the model in which multiply charged ions are created in binary encounters by molecular-orbital electron promotion, and then are partially neutralized as they leave the surface. Characteristic velocities for neutralization of scattered N²⁺, N⁺ and recoiled Si³⁺, Si²⁺, Si⁺ ions in silicon are in the same range as have been found for rare gas and metal ions. For each element they seem to scale roughly as the square root of ionization potential of each charge state, but there appears to be no other systematic dependence.

I. INTRODUCTION

A basic problem in low-energy ion-surface scattering, since the early work of Hagstrum,¹ is the mechanism of charge transfer (see the review by Boers²). Interpretation is complicated because several charge changes may occur in sequence. It is useful, at least conceptually, to separate the surface scattering into three regions: (a) the ingoing region from the initial encounter with the surface average potential through the increasing influence of separate atoms to a region (b) where a close encounter with an individual atom significantly changes the direction of the trajectory, and then (c) a final or outgoing region where there are more gentle interactions. Multiple collisions may be included by traversing region (b) more than once. The individual atoms play an increasingly important part when the scattering angles are not small or the energies are above a few keV.

There is some evidence in surface neutralization and ionization measurements that the final charge state is independent of the incoming ion-beam charge, and that the ingoing interactions do not significantly affect the outgoing charge-state fractions. Model calculations³ for low-energy atom-metal scattering support this. For example, the model predicts that what appears as neutral atom-surface scattering is often ionization of the incoming atom, followed by neutralization as it emerges from the surface. Experimental evidence for the energy loss in reionizing neutral helium is observed in He⁺-surface scattering up to 2 keV.⁴ To further support the "loss of memory" assumption, there is experimental evidence that positive and negative beams, under otherwise identical conditions, produce identical scattered charge-state ratios.⁵ Exceptions have been found: At energies below 10 keV, the ion fraction scattered from Cu, with an incident neutral Ne beam, was found to be quite different from the ion fraction with a Ne⁺ beam.⁶ The attractiveness of the "loss of memory" assumption is that it simplifies the interpretation of charge-state fractions. The

only surface-structure-dependent interactions which affect the charge fractions are then in the outgoing part of the trajectory.

Though the assumption is in doubt for neutral and singly-charged-ion fractions, the distinction between the three interaction regions is quite clear for processes which produce multicharged ions. These ions can only be created in the close-encounter region by inner-shell electron promotion under conditions which are sufficiently violent to erase the existing valence-electron structure, so that the initial beam charge and any changes in the charge during the ingoing trajectory are unimportant.

There have been relatively few investigations of multicharged-ion emission from ion-surface collisions. Multicharged ions have been reported in early secondary-ion-mass-spectroscopy (SIMS) measurements,⁷ but this technique measures only low-energy ions, which are the end result of a collision cascade. The multicharged ions which we report are from single collisions having well-defined trajectories, and we find no significant dependence on surface structure. The first examination of multiply-charged-ion production under well-defined scattering conditions was by Datz and Snoek⁸ of 40–80-keV Ar⁺ ions from copper single-crystal and polycrystalline surfaces. Van der Weg and Bierman,⁹ repeated these measurements in more detail, and they compared their ion-solid outgoing charge fractions with similar measurements using a Cu-vapor target. They were able to fit the smaller multiply-charged-ion fractions from the solid with calculations starting from the ion-vapor charge fractions and assuming that these decayed with a Hagstrum-type exponentially decreasing interaction on the way out of the solid. Barth, Mühling, and Eckstein¹⁰ observed both recoil and scattered multiply charged fractions in Ar⁺ and Ne⁺-Ti and Ni surface scattering at 9 keV. They measured the energy and exit-angle variation of the charge fractions, and found an exponential dependence on the perpendicular component of the exit velocity, again in agreement with a Hagstrum-type interaction.

Winter¹¹ identified N²⁺ and N³⁺ ion fractions when 350-keV N⁺ incident ions were scattered through 0.8° from a polycrystalline copper surface. His trajectories had a distance of closest approach to a copper atom of $r_c = 0.24$ Å, but he did not determine the threshold distance for the creation of multiply charged states.

We report evidence to support the model in which multiply charged ions are produced in solids at close binary encounters by electron promotion in the same way as in ion-gas collisions,¹² followed by their partial neutralization in the outgoing ion-solid interactions. We have observed definite energy thresholds for the appearance of N²⁺, Si²⁺, and Si³⁺, and we have selectively examined the effect of the solid surface on these ions by target tilting while keeping the binary-collision conditions constant.

There is much indirect evidence of multicharged-ion production in ion-solid interactions from electron- and x-ray-emission measurements. The energies associated with atomic energy levels of both the projectile and the solid can be identified.¹³ These generally agree with the inner-shell vacancy-filling model developed from ion-gas collision data, with some differences in the states populated. A limitation of electron or x-ray spectroscopy as a means of investigating this type of ion-solid interaction is that the ion trajectory is not well defined. Doppler effects establish that the ion is moving, but these effects are too small to accurately deduce the ion direction at the moment of emission. The observed spectra are thus the integrated results from all ion trajectories. The investigation of Auger electrons which are emitted when a multicharged incident ion beam interacts with a solid¹⁴ examines a quite different phenomenon. The Auger transitions which are then observed occur during the ingoing part of the ion-solid interaction, whereas multicharged ions created during the close encounter, which are reported here, only undergo Auger transitions on the way out.

II. EXPERIMENT

The system consists of a 2-keV–150-keV accelerator with an rf-type ion source. Adequate beams at low energies are produced by using about 30 kV across the first part of the accelerator column and then decelerating the ions near the column exit. The beam was mass analyzed and the neutrals removed by a 30° deflection magnet. At each end of a 1-m-long differential section at 1.0×10^{-8} Torr, small apertures (2-mm entry and 0.25-mm exit) both collimated the beam and isolated the vacuum of the accelerator from the 1.5×10^{-10} Torr of the scattering chamber. No difference was found in the chamber pressure due to gas flow from the differential section or to the beam passing through the apertures. The beam intensity on the target was typically 1 nA. Scattered ions were energy selected with an electrostatic analyzer ($\pi/\sqrt{2}$ deflection, 1.5% energy resolution, 5° angle of acceptance), and counted with a channel electron multiplier (CEM) detector. This electrostatic spectrometer was mounted on a racetrack inside the chamber such that it could be set

to any scattering angle between 0° and 45°. The target was rotatable about two axes, one perpendicular to the scattering plane and the other in the scattering plane.

In order to minimize crystal-structure effects an amorphous silicon surface was chosen for the present measurements. Van der Weg and Bierman⁹ found that shadowing and blocking effects in Cu(100) were different depending on the charge state of the emitted ion, as did Datz and Snoek,⁸ so that the charge-state ratios were dependent on the target orientation. However, the polycrystalline Cu surface gave similar charge ratios to a Cu(110) single crystal at exit angles away from a channeling direction.

It has been reported that temperatures above 550°C are required to anneal silicon.¹⁵ Target preparation before each measurement started by sputter cleaning a single-crystal Si(100) sample with 500-eV Ar⁺ ions, and then a brief heating period at a temperature slightly less than 500°C in order to outgas the surface argon without reforming the crystal surface structure. Heating was discontinued after about 1 min when the pressure returned to its value before heating. An amorphous silicon surface was confirmed by the absence of channeling or blocking in the scattered-ion angular distributions and the absence of diffraction spots in the reflection high-energy electron-diffraction (RHEED) pattern. Annealing the same target to about 900°C for 15 min produced a sharp Si(100) 2×1 RHEED pattern and the expected shadowing of surface atoms along the $\langle 110 \rangle$ direction. The scattered ion energy spectrum and peak intensities from the amorphous surface were compared under identical conditions with scattering from the single-crystal surface away from any main crystal symmetry direction. No statistically significant difference was found.

Ion spectroscopy has been shown to be a very sensitive test of a clean surface,¹⁶ being capable of 0.01 monolayer detection. The target was sputter cleaned at frequent intervals, and there was no significant change in the scattered-ion spectrum with time during the intervals between sputtering. Before sputtering at the start of measurements each day, the region of the energy spectrum between Si⁺ and N⁺ peaks, where N⁺-O or N⁺-C scattered ions would appear, was found to be slightly filled in, due to overnight exposure to the residual gas. Our measured charge ratios could not be very sensitive to surface impurities because this overnight contamination was not accompanied by any significant change in the multiply charged peak intensities.

In summary, the absence of carbon or oxygen peaks in the scattered-ion spectrum and the lack of either RHEED or scattered-ion target orientation dependence suggests that the target was a clean silicon surface having no significant crystal structure over the short-range order of ion scattering or the longer-range order of RHEED measurements.

III. RESULTS AND DISCUSSION

A. Energy spectra

Figure 1 shows the energy spectra of ions emitted from the target at 40° scattering angle, when bombarded with

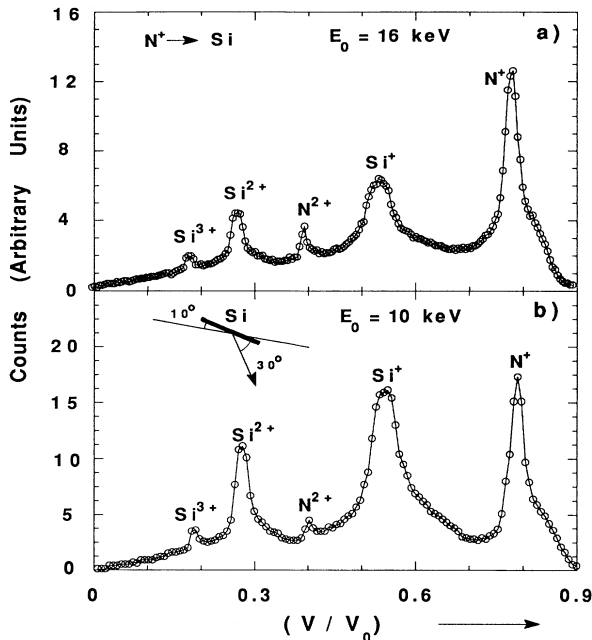


FIG. 1. Spectrum of ions which are scattered and recoil from a silicon surface, as a function of V , the electrostatic analyzer deflection voltage. V_0 is the voltage required to deflect the N^+ direct beam through the spectrometer: (a) 16-keV beam and (b) 10 keV beam.

16-keV and 10-keV N^+ ions. The peaks can all be identified as binary-collision events, with shoulders on the high-energy side from multiple collisions. The energies agree well with collision kinematics. To follow the same path through the analyzer, doubly charged ions require half the deflection voltage of singly charged ions, and the peaks which are labeled as doubly charged occurred at voltages exactly half (to one channel) of the singly charged peaks and one-third for the triply charged ions. The presence or absence of N^{3+} ions could not be determined because they would be buried in the Si^{2+} recoil peak.

B. Variation with beam energy

The energy variation of the ion intensities emitted from the surface at 30° when N^+ ions are incident at 10° (40° deflections) are shown in Fig. 2. The intensities were obtained by summing the counts in the peak after subtracting the background, which was estimated by linearly interpolating the intensities on either side. Measurements were made between 3.5 keV and 30 keV. The upper limit was set by the increase in subsurface scattering which generates a continuous energy background and at the lower energy by the disappearance of multiple ionization. We could not determine absolute ion yields because we were unable to measure directly, with any accuracy, the very small beam currents on target. As an accurate relative estimate of the beam intensity

the counts in each channel of the spectrometer were normalized to the count, over the same time interval, in a CEM which accepted all the scattered ions which passed through a fixed $15\text{-}\mu\text{m}$ aperture 12 cm from the target and at an angle of 110° to the beam direction. The backscattered-ion yield from the target is likely to vary with beam energy, so that no accurate normalization of the spectrometer count to beam charge on target was possible for the energy-variation measurements. However, this uncertainty cancels in the ratio of the intensities of the different charge states. Figure 2(a) shows the ratio of the areas under the N^{2+} peak to the area under the N^+ peak, and Fig. 2(b) shows the same ratio for the recoiling silicon ions. Figure 2(c) shows the ratio for triply charged recoils. At energies above a few keV the counting efficiency of a CEM is nearly the same for all charge states of the same element,¹⁷ and so we interpret these ratios as the ratios of the numbers of ions emitted from the surface.

The scattered ions of all charge states increase with beam energy. This cannot be produced in the close-encounter part of the interactions since the binary-

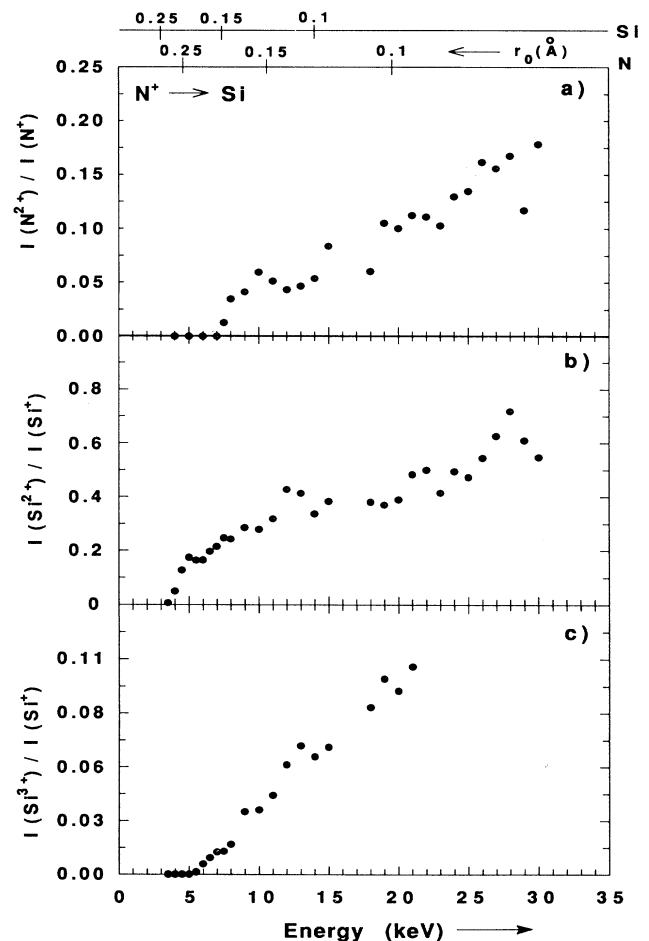


FIG. 2. Ratio of multicharged to singly charged ions emitted from silicon when N^+ ions strike the surface at 10° and exit at 30° : (a) N^{2+}/N^+ , (b) $\text{Si}^{2+}/\text{Si}^+$, and (c) $\text{Si}^{3+}/\text{Si}^+$.

scattering cross section at a fixed scattering angle decreases with increasing collision energy. Two effects contribute to the observed increase. The shadowing of neighboring atoms occurs even though these are located randomly in the amorphous surface. For 3-keV ions, the shadow-cone angle at a typical surface-atom spacing is about 16°, and so with 10° incident ions a high proportion of the surface atoms may be shadowed. Because of the random nature of the amorphous surface, the shadowing effect probably decreases gradually with increasing energy, contributing to the observed gradual increase in scattering. The second effect is the decrease in neutralization of the emerging ions with increasing ion energy.¹⁸

If the trajectories which determine the shadow-cone angles can be assumed to be the same for all charge states, then surface atomic spacing effects will cancel out when the ratios of different charge states are taken, and the ratios depend only on individual incoming ion-target atom interactions and subsequent surface neutralization effects. Van Der Weg and Bierman⁹ attributed the differences which they observed in the shadowing and blocking angular distributions to differences in the decay rates as the ions with different charges pass near neighboring atoms on the way out, not to differences in the shadow-cone angles. The trajectory dependence of the decay rates was directly confirmed⁶ for Ne⁺ ions emerging in directions which passed near other atoms in a Cu(100) surface and in a Ni(100) surface.¹⁹ With the assumption of charge-independent shadow cones our measured charge ratios can be interpreted as the relative probability that a particular ion which scatters or recoils out from the surface in the observed direction will be triply, doubly, or singly charged.

The ratio of multiply charged ions to singly charged ions is found in every case to have a definite energy threshold. This can be compared with ion-gas collisions where there is a sudden increase in ionization of one, or both, of the scattered particles when the distance of closest approach is small enough to reach a crossing of the molecular-orbital correlation diagram at which inner-shell vacancies can be produced.²⁰ On separation, these vacancies are filled mostly by Auger transitions which increase the ionization state of the system.

We have made exact calculations of two-body collision trajectories using the screened Coulomb potential in the “universal” form given by O’Connor and Biersack²¹ as best representing the average of a large body of scattering data. Our observed threshold for N²⁺ occurs at 7.3 keV, and the threshold for Si²⁺ recoil ions is 3.8 keV. At these energies the distance of closest approach is $r_c = 0.19$ Å for 40° nitrogen scattering, and for Si²⁺ it is $r_c = 0.22$ Å (at the nitrogen scattering angle of 72° which corresponds to the measured 40° silicon recoils). The Si³⁺ threshold is at 5.3 keV, for which the distance of closest approach is $r_c = 0.18$ Å.

According to the electron-promotion model,²⁰ one or more of the 2*p* electrons from the Si atomic state can be promoted from the 3*dσ* orbital at a level crossing in the correlation diagram to the 3*pπ* state which is only partially filled, having only two electrons from the 3*p* sub-shell of Si. Promotion may also occur to the 3*sσ* orbital

if this is also partially filled at the closest approach point, having lost electrons by transfer into the 4*fσ* orbital at a more distant interatomic spacing. Transfers between these outer-shell states have been found to be strong.²² Both these processes produce vacancies in molecular orbitals which become holes in the Si 2*p* shell on separation. There are no reported quantitative calculations of the correlation energies of (N-Si), but Larkins²³ has made detailed calculations for (Ne-Ar) which has a similar atomic number ratio. He predicted a radius of 0.112 Å for the 3*dσ* to 3*pπ* and 3*sσ* crossings. Ignoring the difference in the atomic number ratio between ¹⁰Ne-¹⁸Ar and ⁷N-¹⁴Si, the separations on the correlation diagram should scale by a factor $(Z_1 Z_2)^{-1}$. This crossing radius then gives good agreement with our observed distance of closest approach for doubly-charged-ion production. If promotion of one of the two 2*p* electrons in N⁺, by way of the 4*fσ* orbital, was the main process which creates N²⁺, then this would occur at a larger crossing radius than for Si²⁺. However, we find that the threshold for N²⁺ is the same or slightly smaller than that for Si²⁺. Vacancies in the 3*dσ* molecular orbital do not lead directly to inner-shell vacancies in nitrogen. However, if Auger transitions occur before the molecular orbitals become separated atom states, then N²⁺ production is possible, and it should have the same distance-of-closest-approach threshold as for Si²⁺ production. It may be that this is an example of “Rydberg sharing” which Doweck *et al.*²² found to be strong in ion-gas C⁺-Ne and N⁺-Ne measurements.

The energy threshold for Si³⁺ is slightly higher than for Si²⁺ ions. It may be that we were unable to detect the much lower intensity Si³⁺ peak near its energy threshold. However, semilogarithmic plots of the Si³⁺ and Si²⁺ intensities had very similar shapes, which could only be superimposed by an energy displacement of 1.5 keV, with an appropriate intensity scale factor. This smaller distance of closest approach may relate to Si³⁺ production requiring two Auger transitions to fill two inner-shell vacancies, whereas doubly charged ions can be produced by one inner-shell vacancy.

Preliminary measurements have been made with other ions. O⁺, Ne⁺, Cl⁺, and Ar⁺ beams have been scattered from the same amorphous silicon target. We find that Si²⁺ is present in every case, but that only O²⁺ and Ne²⁺ ions are produced in our energy range, suggesting that the number of vacancies in the 2*p* shell of the light partner determines the 3*dσ*-3*pπ*-3*sσ* mixing and Auger deexcitation path.

C. Target-tilting measurements

The ion intensity of each of the emitted charge states are shown in Fig. 3 as a function of target orientation. The monitor CEM, which counted the total ion yield from the target, was calibrated in a separate experiment so that the monitor count for a fixed beam charge was known for each target orientation. It was thus possible to normalize the spectrometer counts and to determine the absolute dependence of each charge-state yield on target orientation.

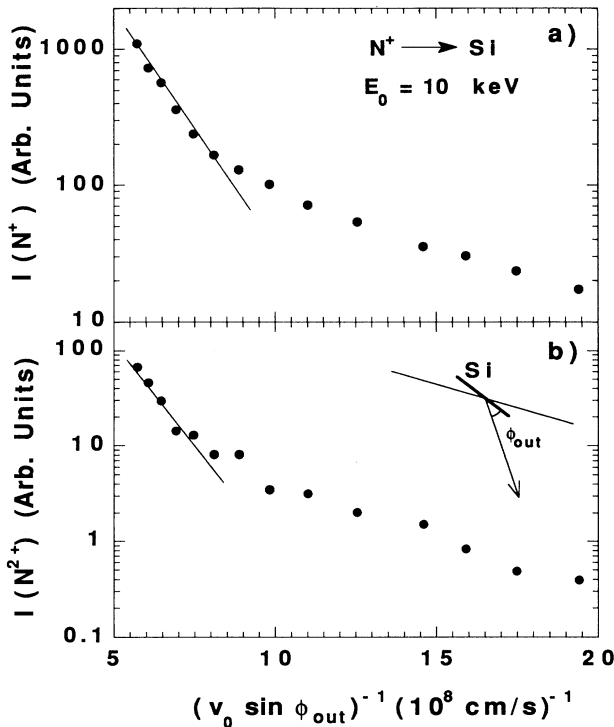


FIG. 3. Intensity of ions scattered from a silicon surface for different surface orientations. Ions are detected at a fixed angle of 40° to the 10-keV N^+ incident beam. $v_0 \sin \phi$ is the velocity component perpendicular to the surface: (a) N^+ and (b) N^{2+} .

Close encounters occur at separations much smaller than the atomic spacing. The amount of electron promotion occurring should depend only on details of the trajectory in the neighborhood of the close encounter, and so depend only on the scattering angle θ and the ion energy. Any ϕ_{out} dependence in the ion yields must therefore be caused by the outgoing interactions as the ions leave the surface (region c).

Figure 3 shows the yields of N^+ and N^{2+} ions plotted on a logarithmic scale as a function of v^{-1} , where $v = v_0 \sin \phi_{\text{out}}$ is the ion-velocity component perpendicular to the surface. These graphs thus show the charge yields as a function of the time that the ion spends in the outgoing region. v^{-1} was varied by changing the exit angle ϕ_{out} while keeping all other conditions constant (40° scattering angle, 10-keV beam). Figure 4 shows similar target-tilting measurements for the three charge states of the recoil silicon under the same experimental conditions (72° scattering angle, 10-keV beam).

Hagstrum assumed a transition rate for surface neutralization of the form $A \exp(-as)$, where s is the distance from the surface and A and a are constants. This leads to a survival probability for an ion to leave the surface unneutralized, which is proportional to $\exp(-A/av)$. The ratio of the two parameters A/a is thus a characteristic velocity for the neutralization of the charge as it traverses the surface region.

The nearness of individual atoms to the ion trajectory has been shown by Hsu and Rabalais¹⁹ to have a considerable influence on the backscattered- Ne^+ -ion fraction from a Ni(100) surface. The Hagstrum model ignores the influence of the atomic nature of the surface on the transition rate, and they could only make this type of fit to the ion fractions when scattering was mainly from the top surface layer. A quite different dependence was found along directions where subsurface-ion scattering was important and the trajectories passed close to surface atoms. The electron-detachment rates of O^- ions recoiling from the surface have been found²⁴ to be so influenced by the atomic periodicity of the surface electrostatic potential that blocking minima at large exit angles became maxima at grazing exit angles. These structure effects suggest that there may be significant departures from the simple Hagstrum model even when averaged out by the random atomic spacing on the amorphous surface.

In all the plots of Fig. 3 and Fig. 4 there appears to be an angular region which agrees with the exponential decay model, but at large $(v_0 \sin \phi_{\text{out}})^{-1}$, corresponding to small ϕ_{out} values and long interaction times, we find much less decay than this theory predicts. It seems probable that this nonexponential dependence is at least

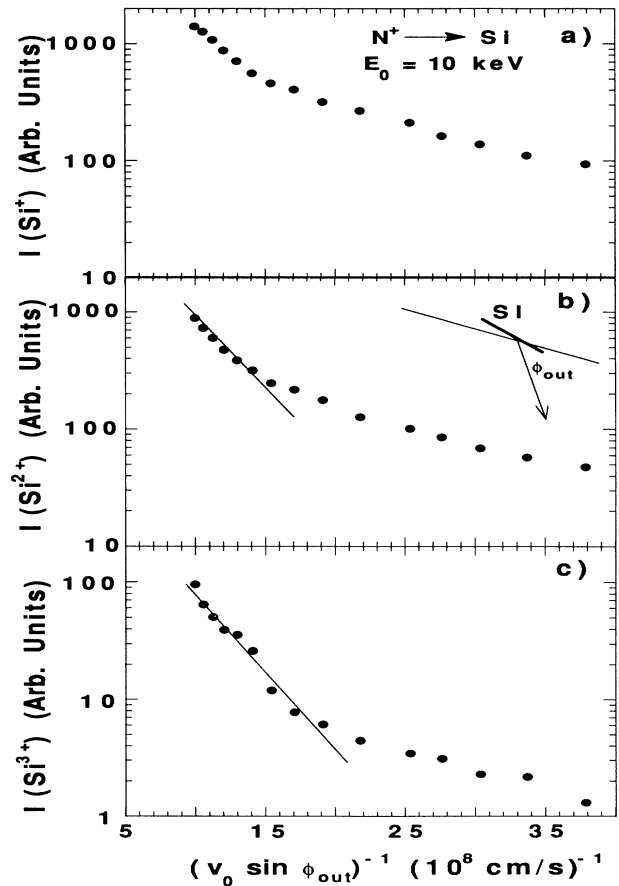


FIG. 4. Intensity of recoil ions emitted from a silicon surface for different surface orientations. Ions are detected at a fixed angle of 40° : (a) Si^+ , (b) Si^{2+} , and (c) Si^{3+} .

partly an artifact due to departures from an ideally flat surface, and not to time dependence of the ion decay. Roughness of the surface can be expected to cause deviations from the calculated exit-path length in two ways. On a macroscopic scale, changes in the plane of the surface effectively change the local value of ϕ_{out} . On a microscopic scale, if atoms are missing from, or added to the ideal surface, then there may be fewer or more atoms to interact with along the outgoing trajectory. At the other extreme, when the entrance angles are small, shadow-cone effects decrease the number of close encounters and hence the ion yield, and so the data at these angles must also be ignored to obtain the characteristic velocity.

At values of ϕ_{out} between 22° and 32°, where the data fit well to an exponential dependence and both shadowing and surface roughness should be insignificant, we obtain the characteristic velocities shown in Table I.

The theoretic exponential dependence on v^{-1} is derived assuming the decay of one charge state only. In our data the Si²⁺ ions are almost as intense as the Si⁺ ions, so that some account should be taken of that component in the Si⁺-ion yield which is the result of Si²⁺ decay after the close encounter on the way out. Only for Si⁺ is cascading important. For all the other ions the higher charge state has a yield which is an order of magnitude smaller, so that cascading was ignored in determining these characteristic velocities.

Van der Weg and Bierman⁹ have given the general relation for the sequential decay of many charge states. For the cascade decay of two states the rates of change of each population is defined by

$$\frac{dP_2}{dt} = -P_2R_2(s)$$

and

$$\frac{dP_1}{dt} = +P_2R_2(s) - P_1R_1(s).$$

When the Hagstrum forms $R_1 = A_1e^{-as}$ and $R_2(s) = A_2e^{-as}$ are assumed for the decay-rate dependence on the distance from the surface, these equations can be solved and integrated from the close encounter to $t = \infty$, with the result

$$P_2 = \exp\left(-\frac{A_2}{av}\right),$$

TABLE I. Characteristic velocities for scattered and recoil ions.

Experiment	Ionization potential	Scaled to square root of ionization potential
(10 ⁷ cm/s)	(eV)	(10 ⁷ cm/s)
N ²⁺	10	29.6
N ⁺	8.6	14.5
Si ³⁺	3.2	33.5
Si ²⁺	2.5	16.3
Si ⁺	1.7	8.1

and

$$P_1 = \frac{A_2}{A_2 - A_1} \left[\exp\left(-\frac{A_1}{av}\right) - \exp\left(-\frac{A_2}{av}\right) \right].$$

If only a fraction F of the Si⁺ ions is produced at the close encounter, so that the remaining fraction $(1 - F)$ is the result of Si²⁺ decay, then the Si⁺ yield becomes

$$P_1 = \frac{(1 - F)A_2}{A_2 - A_1} \left[\left(1 + \frac{F(A_2 - A_1)}{(1 - F)A_2}\right) \exp\left(-\frac{A_1}{av}\right) - \exp\left(-\frac{A_2}{av}\right) \right].$$

A reasonable fit to the data is obtained when the coefficient $(1 - F)A_2/(A_2 - A_1)$ is about unity, so that, with the characteristic velocities shown in Table I, about a third of the Si⁺ ions which emerge from the surface are from Si²⁺ decay, and the remaining two-thirds have survived from the close encounter.

Several characteristic velocities for ion-surface decay of ion charges passing through surfaces have been previously reported. Nearly all are for rare-gas ions on metal surfaces. Barth, Mühlhling, and Eckstein¹⁰ used 9-keV ion beams and found values between 1.9 and 3.4×10^7 cm/s for Ti²⁺ recoils and $0.5\text{--}1.5 \times 10^7$ cm/s for Ti⁺ recoils, with Ar⁺ ions producing higher values than Ne⁺ ions. Hsu and Rabalais¹⁹ obtained 1.5×10^7 cm/s for Ne⁺ scattering in the (100) plane from the surface-layer atoms of Ni(001) and 0.6×10^7 cm/s for scattering in the (210) plane. The values found by Van der Weg and Bierman⁹ at 60 keV and 90 keV for ion Ar⁺-Cu recoils are considerably smaller, 0.94 and 1.16×10^6 cm/s. He⁺ characteristic velocities have been measured by Luitjens *et al.*⁶ in 10-keV scattering from polycrystalline Cu. They found values in our range, 2.2×10^7 cm/s for Ar⁺ ions and $1.1\text{--}1.5 \times 10^7$ cm/s for Ne⁺ ions.

The multicharged-ion best fit of Van der Weg and Bierman⁹ assumed that the characteristic velocity would vary inversely as the ionization potential energy which is required to produce the ion. However, we find a smaller variation, and a square-root dependence is more appropriate. There is some theoretical justification for such a dependence.²⁵ In Auger capture the transition rate involves the square of the integral of the surface and the atomic electron wave functions. The integral decreases with separation distance because of the decrease in overlap of the wave functions. Asymptotically, the decrease is exponential with exponents which are proportional to the square root of the electron binding energies. For the atomic part of wave function this binding energy is the ionization potential. The exponentially decreasing transition rate of the Hagstrum model is therefore predicted, with a coefficient A which is proportional to the square root of the ionization potential. In Table I the ionization potentials are listed and the characteristic velocities scaled in this way to the singly-charged-ion characteristic velocity. Though they fit reasonably for each element, there is no common fit between N and Si, or for the rare-gas or metal ion of the previous data.

IV. CONCLUSIONS

Multiply charged ions which are produced in N^+-Si surface scattering are found to be relatively abundant, with up to 15% of the scattered ions being emitted as N^{2+} , up to 40% of the recoil ions as Si^{2+} , and up to 6% as Si^{3+} ions. There is a definite beam energy threshold at which each of these multicharged ions appears, which supports the theory that they are produced at definite atomic separations during close $N-Si$ binary collisions. The interaction process is electron promotion from an inner shell, and the resulting vacancies are then filled by Auger deexcitation. Molecular-orbital calculations can be used to estimate the atomic separations at which the diabatic crossings of these orbitals transfer an inner-shell electron to an unfilled shell. All the thresholds seem to be associated with the $3d\sigma-3p\pi-3s\sigma$ orbital crossings for which we estimate an atomic separation near to 0.2 Å. This value agrees well with trajectory calculations of the distance of closest approach of N^+ ions to Si atoms at each of the threshold energies (0.19 Å for Si^{2+} , 0.18 Å for Si^{3+} , and 0.22 Å for N^{2+}). Vacancies in the $3d\sigma$ molecular orbital become $2p$ vacancies in Si, which can be filled by Auger capture to produce Si^{2+} and Si^{3+} ions. The capture process must be rapid because, to produce a

significant proportion of N^{2+} ions, the molecular-orbital vacancy must be filled before the molecule separates into two atoms.

There is no ambiguity in which of the three interaction regions the multicharged ions decay by partial neutralization as may occur for singly charged ions, since they are created at the close encounter. The neutralization along the outgoing path seems to be described by the Hagstrum exponential model, at least over a limited range of trajectories, but it is difficult to distinguish the failure of the model from surface roughness effects. The characteristic velocities which parametrize this model do not seem to fit the ionization dependence which was assumed by Van der Weg and Bierman, and a square-root dependence may be more appropriate. More data with other beams and targets are needed to determine the systematic dependence of the characteristic velocities. The increase in the transition rate when an ion passes near to an atom during the outgoing trajectory, which has been observed for singly charged ions scattered from single-crystal surfaces, may contribute to the observed departure from exponential decay. It is possible that the angular variation of the multicharged-ion yields may provide a useful supplement to channeling and blocking data when using ion scattering as a technique to determine surface structure.

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