Formation of multiply charged Al ions by direct recoil

X. Chen,[1] Z. Sroubek,[1,2] and J. A. Yarmoff[1,*]

[1]*Department of Physics, University of California, Riverside, California 92521, USA*
[2]*Institute of Radio Engineering and Electronics, Czech Academy of Sciences, Chaberská 57, 182 51, Prague 8, Czech Republic*
(Received 24 January 2006; published 19 April 2006)

Significant yields of fast, monoenergetic Al^+, Al^{2+}, and Al^{3+} are directly recoiled from Al(100) during bombardment by low energy Si^+ ions. The large fraction of multiply charged particles is in contrast to the secondaries formed during bombardment by noble gas ions. The production of multiply charged Al is attributed to electron promotion during hard collisions between the electronically nearly symmetric Si and Al atoms, and subsequent shake-off processes. The experiments enable a quantitative determination of the absolute yields of various charge formation mechanisms.

Low energy ions that impact a solid surface can remove material by sputtering, which produces slow secondary particles through a collision cascade, or by direct recoil (DR),[1] which involves the emission of a fast particle following a hard collision between the incident ion and a surface atom. Inner-shell promotion during hard ion-atom collisions is a well-established process that has been investigated since the mid-1960s.[2–7] The excitations are enhanced in symmetric or nearly symmetric collisions due to an overlap in the electronic states.[8–11] Multiply charged ions can result from these excitations during the sputtering of solids, but few of them survive the collision cascade to be emitted from the surface. Hence, it is difficult to ascertain and quantify particular charge formation mechanisms from sputtering experiments. In contrast, DR ions have well-defined trajectories and energies.

In the work reported here, large yields of multiply charged Al ions are generated through DR by the impact of low energy Si^+ projectiles. This observation is in sharp contrast to the relatively small yields of multiply charged ions found in the sputtering of Al. Si^+ ions from 1000 to 5000 eV were incident onto an atomically clean Al(100) surface in a configuration that favors DR. The nearly symmetric projectile-target (*P-T*) combination leads to an inner-shell excitation during the hard Si–Al collision, instead of during a subsequent target-target (*T-T*) collision in the sputtering cascade. The particles are emitted quickly from the outermost atomic layer so that the excitation can survive a possible decay via interaction with the substrate. Instead, multiply charged ions are created when the excited states decay above the surface. The mechanism is verified by the observation of an energy threshold for the process, and by spectra of the emitted Auger electrons. This arrangement enables the production of fast, monoenergetic multiply charged ions, and can be used to clearly separate the processes involved so that the thresholds can be precisely determined and the contributions of various ionization mechanisms can be quantified.

Si ions were produced from a Colutron ion source. $SiCl_4$ vapor was leaked into a quartz cylinder, and a plasma was formed by electron emission from a 0.5 mm diameter thoriated tungsten filament. A 0.05 mm thick Pt foil with a 0.25 mm^2 aperture was spot welded to the Ta anode to minimize erosion of the anode from Cl species in the plasma. This arrangement produces Si^+, Cl^+, and $SiCl^+$. The Si^+ ions were mass separated with a velocity filter, focused by two Einzel lenses and guided by deflection plates into the main UHV chamber. Typically, 15 nA of Si^+ were produced in a 3.0 mm^2 spot at the sample. There were three stages of differential pumping between the ion source and the main chamber, which had a base pressure of 6×10^{-11} Torr that rose to 1.1×10^{-10} Torr during the measurements.

The Al(100) sample was cleaned by repeated cycles of 800 eV Ar^+ sputtering and annealing at 470 °C for 10 min. The surface purity was checked with Auger electron spectroscopy and the surface order and alignment were monitored with low energy electron diffraction.

Ions and electrons emitted from the sample were measured with a Comstock electrostatic analyzer (ESA) mounted on an adjustable turntable and operated in the constant pass energy mode. The pass energies were set to 200 and 40 eV for ions and electrons, respectively, which give resolutions of 8.0 and 1.6 eV. The incoming beam was aligned along the [001] azimuth, and the ions were incident at 22.5 deg with respect to the surface plane and collected after scattering at 45 deg into the specular angle.

The absolute ionization probabilities of scattered Si and recoiled Al were measured independently with time-of-flight (TOF) spectroscopy.[12] It was found that 100% of the scattered Si was neutralized, which is expected because of its large ionization potential. Fast Al ions were observed in the TOF spectra, however, which result from the process described here.

Figure 1 shows the positive ion spectrum collected during bombardment by 2000 eV Si^+. There are three main features, each of which has two components. The spectrum was numerically fit to a combination of six Gaussians under particular constraints (detailed below). Note that the actual line shapes are not necessarily Gaussian, but the fits do match the experimental data reasonably well. The following analysis confirms that the three features represent Al^{1+}, Al^{2+}, and Al^{3+} ions, while the two components in each feature represent different trajectories.

A binary collision of 2000 eV Si^+ with an Al atom would produce a DR with approximately 1000 eV of kinetic energy, although the actual trajectories involved are more complex and involve more than a single surface atom. The general position of the two components at the highest energy (in the range of 800–1200 eV) is thus consistent with the expecta-
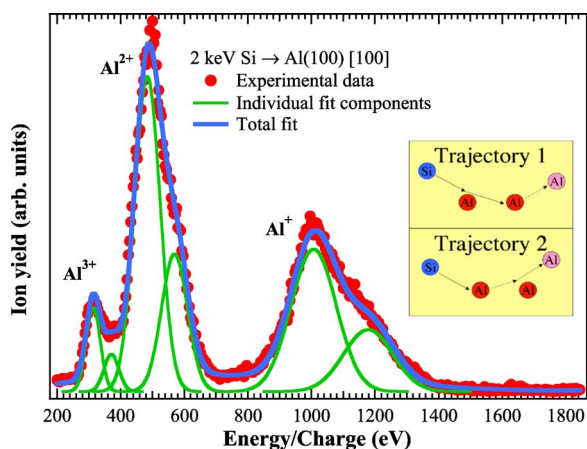
FIG. 1. (Color online) Spectrum of the ions emitted when 2.0 keV Si^+ is incident onto Al(100) along the [100] azimuth, shown along with a fit to the data (see text). Inset: Two possible trajectories that lead to DR.

FIG. 2. (Color online) Yield of each of the charge states shown as a function of the incident ion energy.

tions for DR. The need for two components can be explained by considering the two types of trajectories displayed in the inset to Fig. 1. A simple estimate by molecular dynamics gives values for the separation of the components that are roughly consistent with the measured difference of 170 eV.

Multiply charged ions would appear at an apparently reduced kinetic energy, since the ESA actually provides a measure of the kinetic energy per charge. To verify this interpretation, six Gaussian components were used to fit the spectrum in Fig. 1 in the following manner. First, the two highest energy components were fit independently and assumed to represent the energy distribution for DR Al^+ that can be explained purely by kinematics. Next, the middle doublet was fit by dividing the positions and widths of the first two components by two, and then optimizing the total area of the components while keeping their relative areas fixed. This basically assumes that the middle two peaks are due to Al^{2+}, and that the kinematics are identical to those which produce Al^+. Similarly, the lowest energy peaks were fit by dividing the positions and widths by three to represent Al^{3+}. The good correspondence between the fits and the experimental data supports the interpretation of multiply charged Al.

This procedure was then applied to spectra collected with incident energies from 1000 to 5000 eV, and the data was consistent over the entire range with the notion of singly, doubly, and triply charged species. A summary of the data is presented in Fig. 2, which shows the absolute intensity of each of the charge states as a function of the incident ion energy. The yield of all of the ions initially increases with energy, and reach maxima between 2000 and 3000 eV. Note that the drop-off of all the ion yields at the highest energies is most likely a consequence of the kinematics of the DR process, but this region far above the threshold requires further study. An important distinction between the charge states is that while there is some Al^+ formed down to the lowest incident energy used (1000 eV), the production of Al^{2+} and Al^{3+} have thresholds at around 1300 eV.

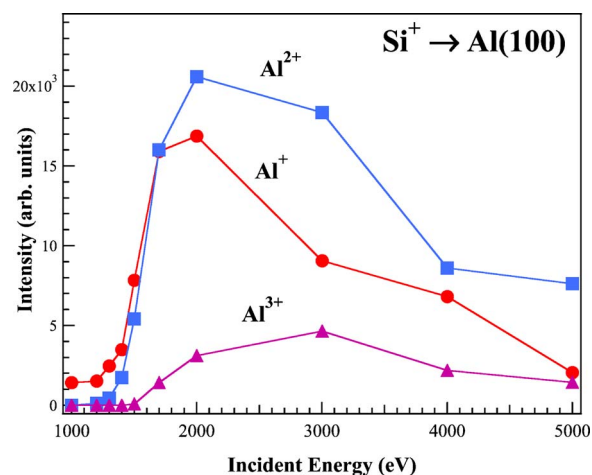The Al^+ ions produced below 1300 eV must be ionized by

a different process, which is presumably resonant charge transfer (RCT) as discussed previously.[13] The data of Ref. 13 show that the RCT ionization probability of Al emitted in this configuration is on the order of 1%–2%, which would be detectable by the ESA. The formation of Al^+ by RCT does not show an abrupt increase with energy,[13] however, which indicates that the excess Al^+ yield above 1300 eV is also a result of the inner shell excitation. An estimate based on comparison with RCT indicates that the Al^+ production by inner shell excitation is very efficient, accounting for about 20% of the total DR yield for 2000 eV Si impact. An analysis such as this, in which the RCT is separated from inner-shell processes, can be used for the quantitative determination of the contributions of each ionization mechanism.

The formation of multiply charged Al can be understood by considering that each of the trajectories shown in the inset to Fig. 1 includes a hard collision of the incident Si atom with the Al atom that is emitted. In trajectory 1, the incident Si makes a grazing collision with a surface atom, followed by a hard collision to induce DR. In trajectory 2, a hard collision is made by the initial impact, followed by a grazing collision along the exit trajectory. Such hard collisions can have a small enough distance of closest approach between the Si and Al that charge promotion forms an excited state, which subsequently leads to multiply charged Al ions.

Figure 3 shows a correlation diagram for the Si–Al system calculated with GAUSSIAN 98. The Al $2p$ interacts with the Si $2p$ just below, so that the Al $2p$ is promoted above the Fermi level when the distance between the atoms is less than ~0.42 Å. A threshold for the production of excited Al is thus expected for an impact energy that correlates to this distance of closest approach. A careful analysis of the 1200–1500 eV data (not shown) indicates that no Al^{2+} is produced below a value of energy/charge=340 eV, so that the threshold of $2p$ hole formation is approximately 680 eV. An Al atom emitted with 680 eV corresponds to a 1360 eV Si–Al collision that has a distance of closest approach of 0.41 Å, which is consistent with the correlation diagram.

The promotion of an Al $2p$ electron would leave the Si and/or Al atoms in an excited state that involves one or two
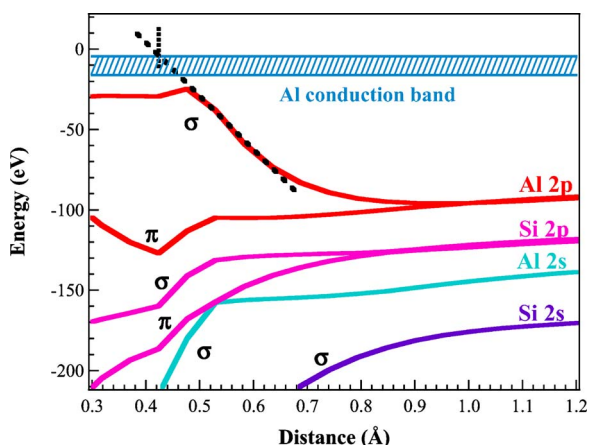
FIG. 3. (Color online) Correlation diagram for a Si–Al collision.

$2p$ holes. The holes would subsequently decay by an auto-ionization or Auger process and emit electrons. This is illustrated by the data shown in Fig. 4, in which spectra of the emitted electrons are shown for incident Si and Ar ions. When using Ar projectiles, there are three main features, labeled Al-I, Al-II, and Al-III, at 63.7, 56.9, and 49.9 eV, respectively. These represent Al Auger electrons emitted due to de-excitation of Al with a single $2p$ hole[14]. When using Si ions, however, there are two additional features at 76.0 and 85.7 eV. The feature labeled Al-IV at 76.0 eV is consistent with the de-excitation of Al that initially had two $2p$ holes.[3] The peak labeled Si-I at 85.7 eV represents the decay of excited Si that had one $2p$ hole. Note that additional peaks are expected during the Auger decay of Si, including one at ~76 eV, but they would all be much smaller than the Si–I peak and are thus not observed. Analysis of the energy dependences of multiply charged Al ions close to the $2p$ hole excitation threshold and the associated Auger electron spectra leads to the following tentative conclusions regarding the Al charge formation processes.
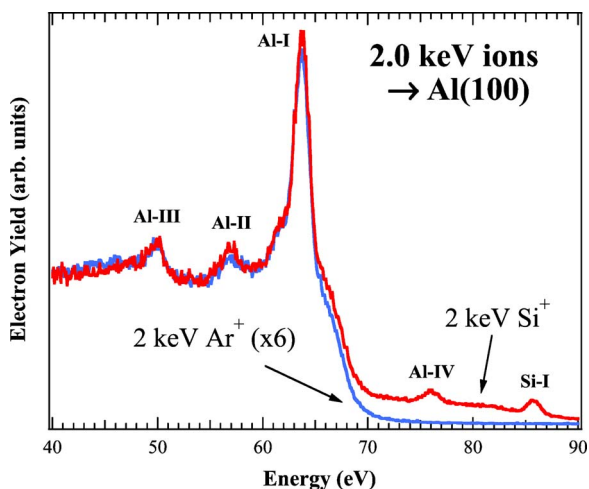

FIG. 4. (Color online) Electrons emitted from Al(100) during bombardment by 2 keV Si$^+$ and Ar$^+$ ions. The incident angle was 67.5 deg with respect to the surface normal, and emitted electrons were measured along the normal.

The most likely mechanism leading to the formation of Al^{2+} is one in which Al is emitted as an excited neutral with one $2p$ hole ($2p^53s^23p^2$). If a single $2p$ hole is formed, the Al would exit the surface as a neutral because the $3p$ levels would be rapidly filled from the Al valence band. The lifetime of a single $2p$ hole in Al is about 190 fs,[15] which is sufficiently long that the excited DR atom can escape the sample but short compared to the transit time to the ESA. After escape, the hole decays, leading to the production of Al ions. Al$^+$ can be created by a single Auger decay, and Al^{2+} by an Auger decay with a shake-off process, i.e., two electrons are emitted during the deexcitation. The latter process can be quite effective, leading to comparable intensities for Al$^+$ and Al^{2+}. The probability for a multiple deexcitation via shake-off for Al with one $2p$ hole has been estimated at 0.35.[16] It is also quite likely, although not directly proved in this experiment, that two shake-off electrons are emitted during the decay to produce Al^{3+}. Such a process is energetically possible and is not contradicted by the electron spectra, as the emitted shake-off electrons would be hidden in the low energy background. The slight shift of the maximum in the Al^{3+} signal to higher Si incident energies in Fig. 2 is likely due to the higher energy needed to form Al^{3+}.

Another possibility is that multiply charged Al ions originate from the decay of double $2p$ holes, which are created simultaneously during the hard Si–Al collision. As indicated by the Al-IV peak $[2p^43s^23p^2 \rightarrow 2p^53s3p(^3P)]$ in Fig. 4, some of the recoiled Al exits the surface as Al$^+$ with two $2p$ holes, but then decays along the exit trajectory to Al^{2+} through $L_{2,3}MM$ Auger emission. The ejected electrons form the Al-IV peak.[3] It is unlikely that Al^{2+} would survive, however, as the Auger decay time of excited Al^{2+} $[2p^53s3p(^3P)]$ should be on the order of the 190 fs lifetime of a single Al $2p$ hole.[15] The excited Al^{2+} would thus further disintegrate to Al^{3+} ($2p^53s3p \rightarrow 2p^6$). Electrons would be emitted from this decay at about 50 eV,[17] but would not be detected as they would be buried under the Al-III peak. This could be an effective mechanism of Al^{3+} formation, but the low intensities of the relevant transitions in the Auger spectra suggest that this is probably a less important contribution to the Al^{3+} intensity.

Note that a similar transition but with an initially neutral two $2p$-hole state ($2p^43s^23p^3 \rightarrow 2p^53s3p^2$) would lead to Al^{2+} in the ground state ($2p^53s3p^2 \rightarrow 2p^63s$) and possibly to Al^{3+} by shake-off processes. Such a transition is in principle possible, but the corresponding Auger electron peak expected at about 82 eV (Ref. 18) is clearly not observed.

It is thus concluded that in the DR of Al with Si projectiles, singly charged Al ions are formed with probabilities on the order of 20% by the decay in vacuum of excited neutral Al with a single $2p$ hole. A majority of the multiply charged Al^{2+} is formed with similar high efficiencies from the same excited Al by shake-off processes.

The origin of multiply charged metallic ions formed during sputtering is a long-standing issue in secondary ion mass spectrometry (SIMS).[15,19–25] In related SIMS studies, the incident particles were generally noble gas ions with energies from 1 keV to 1 MeV. Multiply charged secondary particles were attributed to electron promotion during symmetric

T-T collisions.[26,27] The ratio of the yields of singly, doubly and triply charged ions is typically 100:10:1.[20,28–30] The large number of doubly and triply charged ions observed in our experiment is thus quite unusual.

This disparity results from the different ways that multiple charged particles are generated and in the ways they survive. When a noble gas ion initially collides with the surface, the efficiency of electron promotion in the *P-T* collision is small because of the dissimilar electronic structures of the colliding atoms. Inner-shell holes in the target atoms can be made, however, following *T-T* collisions in the sputtering cascade, and multiply charged particles would then be created through Auger decay, but most of these sputtered particles have low velocities and are likely to be reneutralized before escaping. Higher incident energies are thus needed in order to enhance the yields of multiply charged ions in SIMS.

In our experiment, Si^+ is employed as the incident particle. Si has an electronic configuration very close to that of Al, so that the Si and Al $2p$ levels repel each other because of the Pauli exclusion principle, with the Al level moving up and the Si level moving down. This enables one or two $2p$ holes to be created effectively during the *P-T* collision, even at a few kilo-electron-volt incident energies, without significant formation of holes in the Si.

Note that several previous investigations reported multiply charged ions in DR.[31–35] They involved mismatched projectile-surface systems, however, so that the only mechanism to produce an inner shell hole is a level crossing during a very close *P-T* encounter (<0.2 Å), which requires higher energy (typically 10 keV or above). Thus, in these studies singly charged ions were the primary product and the yield of doubly and triply charged ions was small.

We have shown that direct recoils in the nearly symmetric Si–Al system are very efficient at producing fast, monoenergetic multiply charged ions even at relatively low impact energies. The simplicity of the DR trajectories facilitates the identification and quantification of the ion formation mechanisms. In particular, this arrangement enables a separate quantitative determination of the absolute yields of Al^+ by resonant charge transfer and Auger processes, and the absolute yield of Al^{2+} by shake-off. The shake-off mechanism was found to be very efficient, yielding Al^{2+} with a probability on the order of 20% of the total recoil yield.

---

*Corresponding author. Email address: yarmoff@ucr.edu

[1] W. J. Rabalais, *Principles and Applications of Ion Scattering Spectrometry: Surface Chemical and Structural Analysis* (Wiley, New York, 2003).

[2] U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965).

[3] S. Valeri, Surf. Sci. Rep. **17**, 85 (1993).

[4] F. Xu, R. A. Baragiola, A. Bonanno, P. Zoccali, M. Camarca, and A. Oliva, Phys. Rev. Lett. **72**, 4041 (1994).

[5] K. A. H. German, C. B. Weare, and J. A. Yarmoff, Phys. Rev. Lett. **72**, 3899 (1994).

[6] Y. Matulevich, S. Lederer, and H. Winter, Phys. Rev. B **71**, 033405 (2005).

[7] N. Mandarino, P. Zoccali, A. Oliva, M. Camarca, A. Bonanno, and F. Xu, Phys. Rev. A **48**, 2828 (1993).

[8] R. A. Baragiola, L. Nair, and T. E. Madey, Nucl. Instrum. Methods Phys. Res. B **58**, 322 (1991).

[9] S. Kyoh, K. Takakuwa, M. Sakura, M. Umezawa, A. Itoh, and N. Imanishi, Phys. Rev. A **51**, 554 (1995).

[10] M. H. Shapiro, T. A. Tombrello, and J. Fine, Nucl. Instrum. Methods Phys. Res. B **74**, 385 (1993).

[11] H. Brenten, H. Moller, and V. Kempter, Surf. Sci. **271**, 103 (1992).

[12] X. Chen, Z. Sroubek, and J. A. Yarmoff (unpublished).

[13] X. Chen, Z. Sroubek, and J. A. Yarmoff, Phys. Rev. B **71**, 245412 (2005).

[14] R. A. Baragiola, E. V. Alonso, and H. J. L. Raiti, Phys. Rev. A **25**, 1969 (1982).

[15] S. N. Schauer and P. Williams, Phys. Rev. B **46**, 15452 (1992).

[16] P. Joyes, J. Phys. (Paris) **30**, 243 (1969); **30**, 365 (1969).

[17] P. Dahl, G. H. M. Rodbro, B. Fastrup, and M. E. Rudd, J. Phys. B **9**, 1581 (1976).

[18] F. Xu, M. Camarca, N. M. A. Oliva, P. Zoccali, and A. Bonanno, Surf. Sci. **247**, 13 (1991).

[19] W. F. Van der Weg and D. J. Bierman, Physica (Amsterdam) **44**, 177 (1969).

[20] G. Blaise and A. Nourtier, Surf. Sci. **90**, 495 (1979).

[21] K. Wittmaack, Surf. Sci. **53**, 626 (1975).

[22] P. G. Blauner and R. A. Weller, Phys. Rev. B **35**, 1492 (1987).

[23] J.-F. Hennequin and J.-L. Bernard, Surf. Sci. **235**, 287 (1990).

[24] J. Lorincik and Z. Sroubek, Nucl. Instrum. Methods Phys. Res. B **187**, 447 (2002).

[25] N. Imanishi and S. Ninomiya, J. Nucl. Radiochem. Sci. **5**, R9 (2004).

[26] J.-F. Hennequin, R.-L. Inglebert, and P. Viaris de Lesegno, Surf. Sci. **140**, 197 (1984).

[27] P. Joyes, Radiat. Eff. **19**, 235 (1973).

[28] P. A. W. van der Heide, J. B. Metson, D. L. Tui, and W. M. Lau, Surf. Sci. **280**, 208 (1993).

[29] A. Tolstogouzov, S. Daolio, C. Pagura, and C. L. Greenwood, Int. J. Mass. Spectrom. **214**, 327 (2002).

[30] S. Ninomiya, N. Imanishi, J. Xue, S. Gomi, and M. Imai, Nucl. Instrum. Methods Phys. Res. B **193**, 745 (2002).

[31] S. Datz and C. Snoek, Phys. Rev. **134**, A347 (1964).

[32] W. Eckstein, Nucl. Instrum. Methods Phys. Res. B **27**, 78 (1987).

[33] B. Hird, R. A. Armstrong, and P. Gauthier, Surf. Sci. **292**, 305 (1993).

[34] B. Hird, R. A. Armstrong, and P. Gauthier, Phys. Rev. A **49**, 1107 (1994).

[35] S. Ahmad, M. N. Akhtar, A. Qayyum, B. Ahmad, K. Babar, and W. Arshed, Nucl. Instrum. Methods Phys. Res. B **122**, 19 (1997).