Angular Studies of Potential Electron Emission in the Interaction of Slow Ions with Al Surfaces

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We report energy distributions of electrons emitted from Al surfaces under impact by 1 keV Ar^+ and 1–5 keV Ne^+ ions. The variation of the energy distributions with the angle of incidence is different for both ions and provides information on the mechanism responsible for electron emission. For Ar^+ electron emission results mainly from Auger neutralization, while for Ne^+ an important emission mechanism is the decay of plasmon excitations. We find a transition between surface and bulk plasmon excitations as the energy of the ion is increased.

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Ion neutralization and electron emission are fundamental phenomena in slow ion-surface interactions and important in applications like electrical discharges, surface analysis, and the space environment. Ion-induced electron emission from solids is generally attributed to two main processes [1]. In kinetic electron emission, electron excitation results from the transfer of kinetic energy from the incoming ion. In potential electron emission, excitation results when the potential energy stored in the ion is released upon neutralization with a surface electron. Potential emission can occur by three mechanisms. In Auger neutralization (AN) the energy released in neutralization, E_n, excites electrons via an Auger process involving two electrons of the solid [2–4]. AN can occur if $E_n = I' - \phi$ is larger than ϕ, the surface work function, where I' is the ionization potential of the parent atom shifted by Δ, the image interaction [2]. For low work function surfaces, the incoming ion may be neutralized to an excited state, which can then decay by an interatomic Auger process (Auger deexcitation) leading to electron emission. A third mechanism involving plasmon excitation and decay has recently been identified in experiments of singly charged [5] and multiply charged [6] ions interacting with surfaces of free-electron metals. Plasmons of energy E_{pl} can be excited if $E_n > E_{\mathrm{pl}}$. Their subsequent decay by the excitation of valence electrons (interband transitions) may result in the emission of electrons that produce a characteristic structure in the electron energy distribution [7]. This broad structure has a maximum energy, $E_m = E_{\mathrm{pl}} - \phi$, corresponding to the absorption of the plasmon energy by an electron at the Fermi level, and a width similar to that of the valence band.

Theoretical studies [8–10] have predicted only the excitation of *surface* plasmons during neutralization, when the velocity of the ion perpendicular to the surface is small so that the ions do not penetrate. However, Baragiola and Dukes [5] found that the structure in the energy spectra of electrons emitted from Al and Mg surfaces by slow He^+ and Ne^+ corresponds closely in energy to that expected from the decay of *bulk* plasmons. In the theory by Monreal [10] neutralization may produce surface plasmons of high momentum q that, for this reason, have relatively large energies approaching those of bulk plasmons. However, experimental studies of surface plasmon dispersion in Al [11] have not shown energies as high as those observed in the slow ion impact experiments.

To answer the question of whether surface or bulk plasmons are excited we measured energy spectra of electrons emitted from clean Al surfaces impacted by keV Ne and Ar ions, as a function of incidence angle. The variation in the electron energy distributions with angle allows us to conclude that electron emission results mainly from Auger neutralization for 1 keV Ar^+ and mainly from surface plasmons for 1 keV Ne^+. The relatively high plasmon energy implies that the surface plasmon oscillations are either high-q monopole or multipole modes. More energetic Ne^+ can excite bulk plasmons, most likely indirectly via fast electrons, including Auger electrons from the decay of Al L-shell vacancies produced in violent atom-atom collisions.

Experiments were performed in a UHV chamber with a base pressure of 3×10^{-10} Torr. Ions were produced in a differentially pumped Atomika ion source. The discharge voltage in the ion source was set at 35 V for Ne^+ and 30 V for Ar^+ to eliminate contamination of the ion beam by double charged ions. A polycrystalline Al sample (purity 99.999%) was mounted on a manipulator that allowed variation of the ion incidence angle θ_i relative to the surface normal. The sample was sputter cleaned by 5 keV Ar^+ and Ne^+ ions that removed C and O contamination below the sensitivity of electron-induced Auger spectroscopy, $\approx 1\%$. The emitted electrons were collected by a rotatable hemispherical electrostatic energy spectrometer that lies in the incidence plane, and has a semiacceptance angle of 1.5°. It was operated at a constant pass energy (50 eV), and therefore with an approximately

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constant transmission over the measured energy range. To measure accurately low energy electrons the chamber was shielded with μ-metal to reduce the effect of stray magnetic fields on the electron trajectories. The energy scale was calibrated from the high-energy cutoff of the Al-LVV Auger spectrum. Electron energies are referenced to the vacuum level of the sample with an accuracy of 0.1 eV by comparing the energy of electrons from the autoionization lines of Ne^{**} $2p^4 3s^2$, with published values [12].

Figure 1 shows $N(E)$, the spectrum of the electrons emitted by the Al surface bombarded by 1 keV Ne^+ ions at an incidence angle $\theta_i = 60°$ and an observation angle $\theta_e = 0°$. The spectrum is compared with those induced by 5 keV Ne^+ and 2 keV electrons in the same geometry. $N(E)$ excited by electron impact shows the two structures attributed to decay of low-q surface and bulk plasmons when exciting with fast electrons [7]. These structures are more clearly visualized in the derivative of the spectra, $dN(E)/dE$, with minima at energies $E_m = E_{\rm pl} - \phi$, 6.5 eV and 11 eV corresponding, respectively, to surface and bulk plasmons with $q = 0$ ($\phi = 4.3$ eV for polycrystalline Al). The ion-induced spectra compare well with previous results [5,6]. They show features due to kinetic emission: a low energy peak due to electrons excited in the electronic collision cascade inside the solid, and two autoionization lines at $E \approx 20$–25 eV from Ne^{**} excited by electron promotion in violent collisions with surface atoms [12]. In addition, $N(E)$ for 5 keV Ne^+ impact on Al shows a broad feature which results in the minimum at 11.2 eV in $dN(E)/dE$. This structure has been attributed to the decay of bulk plasmons [5,6]. The spectrum for 1 keV Ne^+ impact shows the shoulder also attributed by Baragiola and Dukes [5] to decay of bulk plasmons excited upon neutralization of the incoming ion. However, $dN(E)/dE$ for 1 keV Ne^+ impact has a minimum at 10.5 eV, i.e., downshifted by 0.7 eV from that observed in the spectra induced by electrons and 5 keV Ne^+, and attributed to zero momentum bulk plasmons.

Figure 2 shows energy spectra of electrons for 1 keV Ne^+ ions vs incidence angle, for a fixed observation angle of 30°. If plasmon excitation occurred inside the solid, the plasmon intensity would decrease with

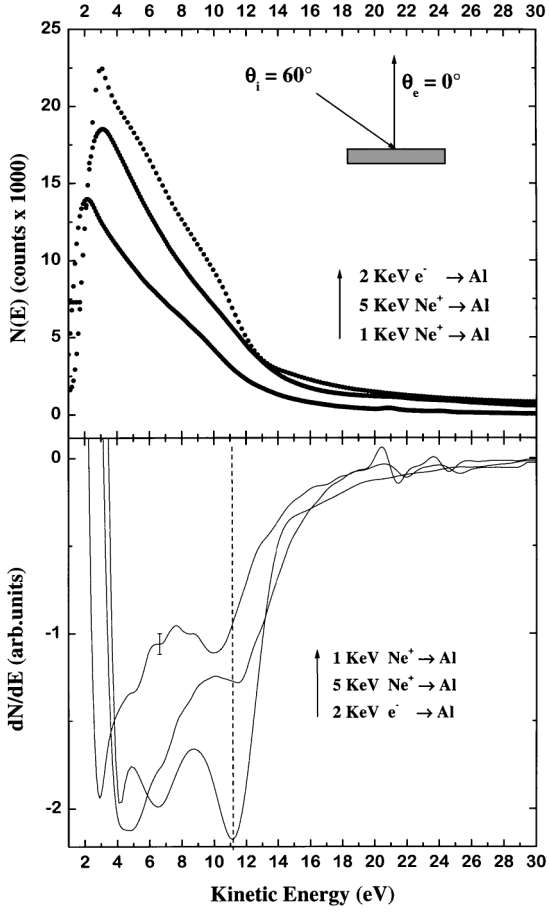

FIG. 1. Top: Energy spectra $N(E)$ of electrons emitted by the Al surface by impact of 1 keV Ne^+, 5 keV Ne^+ ions, and 2 keV electrons, using the geometry shown in the inset. Bottom: Derivative $dN(E)/dE$ that enhances the structure due to plasmon decay. A representative error bar is shown.

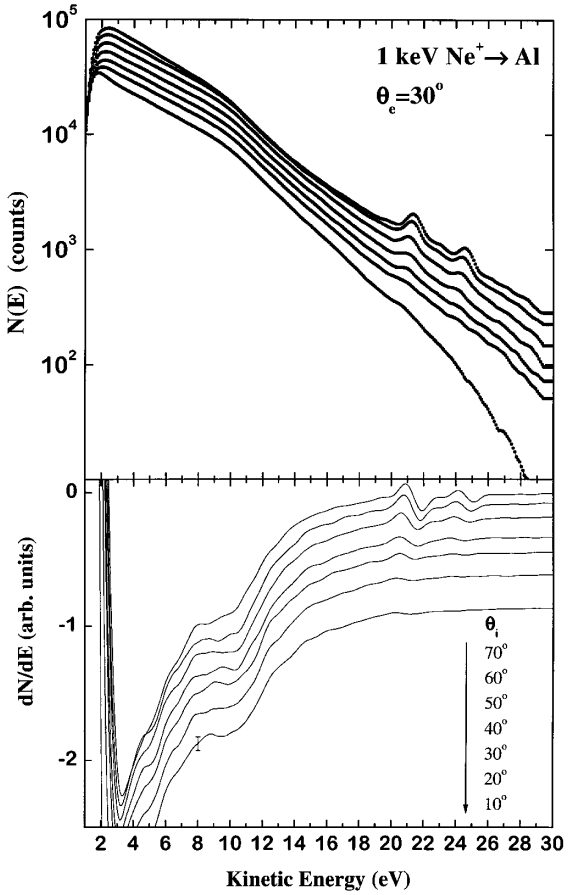

FIG. 2. Top: Electron energy spectra from Al induced by 1 keV Ne^+ ions vs ion incidence angle, for a fixed observation angle of 30°. Spectra are successively displaced by multiplying by 1.2 for clarity. Bottom: Derivative $dN(E)/dE$. The structure at 20–26 eV is due to the decay of autoionizing Ne^{**} $2p^4 3s^2$ formed in violent Ne-Al atomic collisions.

incidence angle, as the probability of penetration decreases. In contrast, as shown in Fig. 3, the intensity of the plasmon structure and its energy is largely independent on the incidence angle. This significant finding strongly suggests that the plasmons are excited *at or above the surface,* consistent with the idea of excitation by a shake-up caused by the sudden disappearance of the dipole formed by the ion and its image charge [5]. We note that violent collisions with surface atoms leading to electron promotion, such as those producing Ne^{**}, don't play a significant role in plasmon excitation since the plasmon intensity does not decrease with incidence angle as does the intensity of the two Ne^{**} autoionization lines [Fig. 2 and Ref. [13]].

When the Ne^+ energy is increased to 5 keV, we find that the energy of the plasmon increases to approximately the $q = 0$ bulk value and also, unlike the 1 keV case, there is a strong increase of plasmon intensity with incidence angle (Fig. 3). This can be explained by assuming that, for 5 keV Ne^+, plasmon excitation occurs mainly in the bulk of the solid. This means that the intensity of the emission from plasmon decay depends on the depth where the excitation occurred. At small incidence angles, ions can excite more deeply and the electrons from plasmon decay will be more attenuated by collisions on their way to the surface than those excited at the shallower depths that are accessible at smaller glancing angles. The closeness of the plasmon energy to the bulk values also supports the interpretation. Plasmon excitation may occur by neutralization inside the solid (below the image plane), but also by fast Auger electrons resulting from the decay of Al-2p vacancies that are efficiently excited at these energies in atom-atom collisions [14].

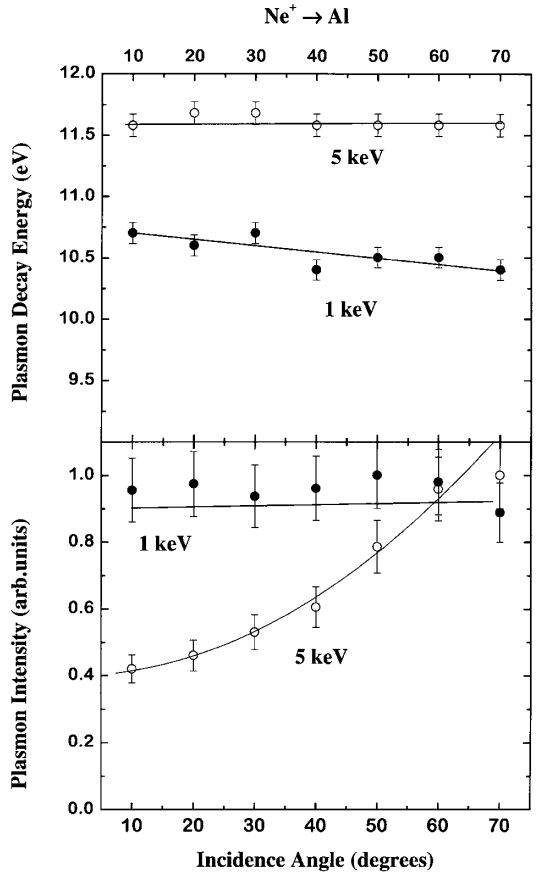

FIG. 3. Plasmon intensity (bottom) and energies (top) for 1 and 5 keV Ne^+ on Al vs incidence angle. To obtain plasmon intensity we integrated the structure remaining after subtraction of an exponential background from the derivative. The maximum values have been set to unity to ease comparison.

Thus, two observations support the interpretation of *surface* plasmon excitation. First, the energy of the plasmons excited by 1 keV Ne^+ is lower than that of even $q = 0$ bulk plasmons but is possible for a monopole surface plasmon of high momentum [11], as postulated by Monreal [10] or for a multipole surface plasmon [15]. The second observation supporting the surface plasmon interpretation is that the excitation occurs at or above the surface, where *bulk* plasmon excitation is thought to be suppressed (*begrenzung*) [16]. In addition, recent studies of the effect of Cs adsorption on this potential plasmon excitation on Al surfaces [17] showed that the plasmon structure is very sensitive to surface electronic structure, since it disappears after a very small Cs coverage.

In the case of slow Ar^+ on Al, Baragiola and Dukes [5] observed a structure in dN/dE at ~5 eV which could correspond either to a low-q surface plasmon or the high-energy edge of Auger neutralization. To resolve this ambiguity we measured the electron spectra for 1 keV Ar^+ at different incidence angles. Figure 4 shows the spectra, taken at a fixed observation angle of 30° and normalized to the same area, corresponding to an electron yield independent of perpendicular velocity [2], which applies to this case. The spectra exhibit a small peak below 3 eV that increases with incidence angle; thus it is assigned to kinetic emission. The main broad distributions and their derivatives, with a minimum at about 5 eV, are consistent with previous measurements [5]. We observe a dramatic broadening of the high-energy edge of $N(E)$ as the incidence direction of the ion beam approaches the surface normal, that is, as the velocity of the ion normal to the surface increases. Broadening of the high-energy edge is typical of Auger neutralization. It results from the atomic energy level shift near the surface (which depends on the distance at which AN occurs), and incomplete adiabaticity caused by the finite ion velocity normal to the surface (Heisenberg uncertainty) [4]. Furthermore, one can see in Fig. 4 that all curves cross at a point, another characteristic of velocity-broadened AN spectra [18]. For these reasons we conclude that Ar^+ neutralization on Al proceeds via the usual Auger process and not mediated by plasmon excitation, a possibility mentioned earlier [5]. The lack of plasmon excitation for incident Ar^+ can be understood if the smaller energy released by neutralization of Ar^+, 11.5 eV $- \Delta$ is insufficient to excite even a $q = 0$ surface plasmon. This

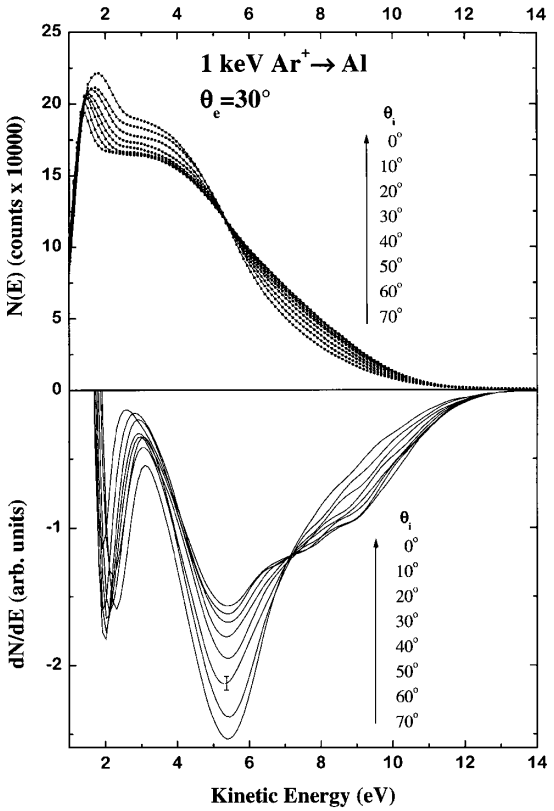

FIG. 4. Top: Electron energy spectra from Al induced by 1 keV Ar^+ vs ion incidence angle, for a fixed observation angle of 30°. Bottom: $dN(E)/dE$.

means an image shift $\Delta > 1$ eV at the neutralization distance, supporting previous estimates [2]. The behavior of Al contrasts with that of Mg, where the smaller work function and plasmon energy allow surface plasmon excitation by slow Ar^+ [5].

Comparison between Figs. 2 and 4 clearly demonstrates fundamental differences between Auger and plasmon-assisted neutralization: unlike the Auger spectra of Fig. 4, the plasmon decay feature in Fig. 2 does not broaden with projectile velocity normal to the surface. This is because in plasmon-assisted neutralization, electron emission results from the decay of an elementary excitation of the solid, decoupled in time from the neutralization event by the plasmon lifetime [19]. Thus the plasmon edge is broadened by a constant value, as shown in Fig. 2, determined only by the finite plasmon lifetime, and not by the normal velocity of the ion. Our finding thus means that the separation of Auger from plasmon-assisted neutralization can be done not only in cases where they produce spectral structures in $N(E)$ clearly separated in energy (by I'-ϕ-E_{pl}), as for Mg [17], but also by observing the behavior of $N(E)$ with changes in the projectile velocity.

In conclusion, angular studies can provide important information about potential electron emission mechanisms at surfaces and can be used to separate Auger neutralization and plasmon-assisted neutralization processes. Excitation by Ne^+ ions shows a transition between surface and bulk plasmons when the kinetic energy is increased.

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