Plasmon-Assisted Electron Emission from Al and Mg Surfaces by Slow Ions

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We report energy distributions of electrons emitted from Al and Mg surfaces bombarded by 30–4500 eV He^+, Ne^+, and Ar^+ ions, which contain structure consistent with the decay of surface and bulk plasmons. We propose that plasmon excitation is due to the sudden change of the surface dipole (incident ion plus image charge) resulting from the disappearance of the image charge and appearance of a hole in the metal.

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Electron emission during collisions of slow, singly charged, positive ions with solids has proved to be a very sensitive probe of the electronic structure of surfaces. For impact energies below a few hundred eV, potential electron emission can occur at the expense of the potential energy brought by the ion. This can occur either through Auger neutralization, if the incoming hole state is bound by more than twice the work function of the surface, or through resonance neutralization and Auger deexcitation [1,2]. In an Auger process, the Coulomb repulsion between two electrons in the solid leads to one of the electrons tunneling through the surface barrier to fill the incoming hole, and the other one being transferred to vacuum. Since Auger rates are very high near the surface, neutralization occurs outside the solid, before the ion can penetrate. Therefore, the process samples electronic wave functions outside the surface [3], making the spectroscopy of emitted electrons (ion or Auger neutralization spectroscopy [4,5]) one of the most surface-sensitive tools for studying solids. The information obtained using the technique is the self-convolution of the density of states in the valence band of the solid, weighted by an energy dependent tunneling rate. Surprisingly, ion neutralization spectroscopy has never been fully tested with free electron metals. In this Letter we report measurements on potential electron emission from Al and Mg surfaces bombarded by He^+, Ne^+, and Ar^+ ions with energies in the range 30 eV–4.5 keV. We find structure in the energy spectra of electrons not explainable by an Auger neutralization mechanism. This structure, which can be a dominant feature in the spectra, can be caused by a neutralization mechanism involving the excitation of both surface and bulk plasmons, provided the energy released in neutralizing the incoming ion exceeds the plasmon energy. We find that bulk plasmons are excited even under conditions where the majority of the ions do not penetrate the surface.

The experiments were done in ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr) in a Perkin-Elmer 560 x-ray photoemission spectroscopy (XPS) and Auger microprobe system equipped with a double-pass cylindrical mirror electron energy spectrometer. For these experiments, the spectrometer was operated at a constant pass energy of 40 eV, a resolution of 0.16 eV, and an approximately constant transmission over the measured electron energy range. The energy scale of the spectrometer was calibrated with XPS photoelectron spectra of Au and high energy cutoff of the Al *LVV* Auger spectrum. To ease discussion of the results, the energy scale was shifted to refer to the vacuum level of the sample. A shift of -0.6 eV for Mg and no shift for Al, with an uncertainty of 0.2 eV, was obtained by comparing the energy of electrons from the autoionization of $Ne(2p^4 3s^2)$ formed in collisions with surfaces with published values [6]. The surfaces of the samples were normal to the axis of the spectrometer and at 12° with respect to the ion beam direction. In this geometry, the spectrometer collects electrons emitted in a cone around 43° to the surface normal. The high-purity polycrystalline surfaces were sputter cleaned by 3 keV Ar ions at 12° glancing incidence. The sputtering was continued beyond that required to remove any detectable level of contamination by Auger spectroscopy and until the structure in the electron energy spectra became constant.

Ions were produced in an electron bombardment source which was operated at low electron energies (~58 eV) to prevent significant amounts of doubly charged ions from reaching the surface with twice the energy. For comparison, and to detect possible shifts in the work function of the spectrometer during the experiments, we obtained electron spectra excited by 1 keV electrons at normal incidence, immediately before and after measuring each ion-excited spectrum. These spectra are very similar to well known electron-excited spectra reported previously [7–9].

Figure 1 shows representative electron energy spectra $N(E)$ obtained from an Al surface, together with the derivative dN/dE. The $N(E)$ values are normalized so the total area under the curves equals known total electron yields [10]; this procedure has an uncertainty of about 20%. The $N(E)$ curves for ions show a high energy edge, indicative of Auger neutralization [1], at $I - 2(\phi - \delta)$. Here I is the ionization potential of the projectile, ϕ the work function of the sample, and $\delta = mvv_F + mv^2/2$ a kinematic shift due to the increase of the Fermi energy

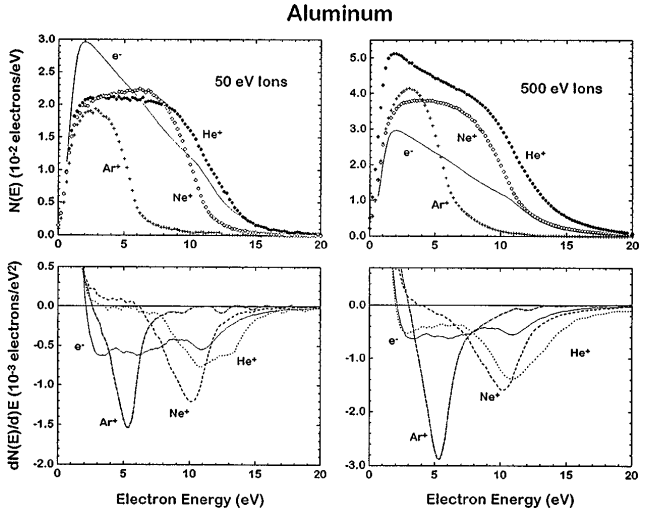

FIG. 1. Top: electron energy spectra $N(E)$ from Al bombarded by 50 and 500 eV He^+, Ne^+, and Ar^+ at 12° grazing incidence, and by 1 keV electrons at normal incidence. Bottom: derivative spectra $dN(E)/dE$. The scale for the electron excited spectrum is arbitrary.

$mv_F^2/2$ in the frame of a projectile moving with velocity v [11]. This high energy edge is broadened by the incomplete adiabaticity caused by the finite ion velocity normal to the surface [12]. In addition to the Auger neutralization edge, a prominent shoulder is observed for impact with He^+ and Ne^+ ions, but not for Ar^+ ions. This shoulder is not due to Auger neutralization involving structure in the density of valence states, as proposed by Hitzke *et al.* [13], since its position is not correlated with the ionization potential of the projectile. The shoulder is similar to that observed for electron impact, which has been attributed to the decay of a bulk plasmon excited by the fast electrons. Plasmon decay by excitation of a valence electron (interband transition) with simultaneous momentum exchange with the lattice [7] produces an electron energy spectrum with a maximum electron energy of $E_m = \hbar\omega - \phi$. This energy corresponds to the case where the plasmon is absorbed by an electron at the Fermi level, and is broadened by a finite lifetime of the plasmon. This broadenings is ~1 eV for surface plasmons and ~2 eV for bulk plasmons decaying near the surface [9].

The visualization of the plasmon structure, which is superimposed on a background of electrons originating from other processes, is usually enhanced by differentiating the energy spectra [8,9]. This produces minima at energies $\hbar\omega_s - \phi$ and $\hbar\omega_b - \phi$. The derivatives were obtained digitally, using a Sawitsky-Golay algorithm, which introduces a broadening of ~1 eV. The derivative spectrum of Fig. 1, dN/dE, shows a minimum at an energy close to $\hbar\omega_b^0 - \phi = 11.0$ eV, where $\hbar\omega_b^0 = 15.3$ eV is the energy of a zero momentum bulk plasmon in Al. The width of this dip is also similar to that seen under electron impact. A dip in dN/dE close to, but somewhat lower than, $\hbar\omega_s^0 - \phi = 6.3$ eV due to a $k = 0$ surface plasmon decay is apparent in the three ion spectra but cannot be distinguished as clearly. We notice that the bulk plasmon for Ne^+ impact is displaced 0.7 eV to lower energies, compared to that excited by electrons. This shift is independent of impact energy between 50 and 4500 eV. A similar shift is seen for the minimum obtained for Ar^+ impact, which is attributed to a surface plasmon.

Although plasmon structures have been seen in the past for *fast* ion impact on metals at energies of tens and hundreds of keV [14–16], they were not expected in collisions with slow ions. This is because for ions moving inside solids with low plasmon damping, like Al, the conservation of energy and momentum constraints direct excitations to particle velocities larger than $\sim 1.3v_F$ [17]. The appearance of bulk plasmon structure is particularly intriguing not only because we are in the adiabatic regime, where the projectile velocity is much smaller than the Fermi velocity of the solid, but also because at the lowest energies, most of the ions do not penetrate the solid [18]. To gain insight on where the excitations occur, we measured energy spectra from Al bombarded with Ne^+ as a function of ion energy E_i. We notice in Fig. 2 that the electron spectra does not change significantly

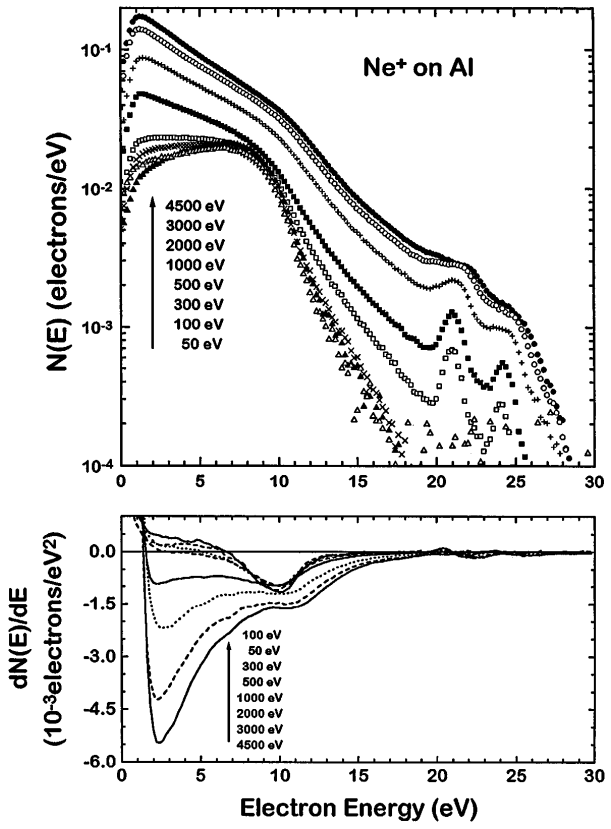

FIG. 2. Top: electron energy spectra for 50–4500 eV Ne^+ on aluminum at 12° grazing incidence. Bottom: derivative spectra $dN(E)/dE$.

with projectile energies for $E_i < 300$ eV. The constancy at low E_i is similar to that characteristic of Auger processes near surfaces, and results from fast transition rates which ensure complete neutralization before the ion reaches the surface [1]. The features that appear in the electron spectra at high projectile energies are indicative of kinetic electron emission: a low energy peak of "cascade" electrons, a high energy tail, and discrete peaks around 21–24 eV due to the autoionization of backscattered Ne $2p^4 3s^2$ atoms [6,19]. It is apparent from Fig. 2 that the intensity of the plasmon shoulder is unrelated to that of the tail of energetic electrons, which leads us to discard plasmon excitations produced by fast secondary electrons as an important mechanism in these experiments.

We propose that plasmons are excited during electron capture by the incident ion. The energy required to excite plasmons is provided by the potential energy released when the ion neutralizes near the surface $E_n = I' - \phi + \delta - \varepsilon$, where I' is the ionization potential of the ion I shifted by the image interaction ($\sim$2 eV), and ε the energy of the final hole in the solid, measured from the Fermi level. With a work function of 4.3 eV for Al, slow He^+ ($I = 24.6$ eV) and Ne^+ ($I = 21.6$ eV) can excite the bulk plasmon of Al but Ar^+ ($I = 15.8$ eV) cannot, in agreement with observations ($\hbar\omega_b^0 = 15.3$ eV for $k = 0$ and increases with momentum transfer k [20]). On the other hand, excitation of surface plasmons is allowed for the three ions ($\hbar\omega_s^0 = 10.6$ eV). This plasmon-assisted neutralization mechanism is similar to the *surface-plasmon* excitation mechanism proposed theoretically by Almulhem and Girardeau [15] and recently improved by Monreal and Lorente [21].

To test the idea of plasmon-assisted neutralization, we performed experiments on Mg, which has bulk and surface plasmon with lower energies ($\hbar\omega_b^0 = 10.6$ eV and $\hbar\omega_s^0 = 7.15$ eV), allowing plasmon excitation even by neutralizing Ar^+ ions. Indeed, Fig. 3 shows that the bulk plasmon peaks ($\hbar\omega_b - \phi \sim 6.9$ eV) appear for the three types of incident ions. The structure due to the decay of the surface plasmon ($\hbar\omega_s - \phi \sim 3.5$ eV) cannot be separated with certainty from the surface barrier peak in the energy distribution. The minimum in the derivative at 11.9 eV (14.9 eV) for Ne^+ (He^+) on Mg is attributed to an Auger neutralization or deexcitation mechanism, since its position is correlated with the ionization potential of the ion. This peak is analogous to what is observed in the Auger decay of a $2p$ vacancy in Mg, and is due to a peak in the transition density for *LVV* Auger transitions involving two valence band electrons [22]. For low energy He^+ and Ne^+ projectiles, the spectra suggest that plasmon-assisted neutralization is more important than the Auger neutralization mechanism of electron emission.

While the observed surface plasmons confirm the prediction of Almulhem and Girardeau [15], the excitation

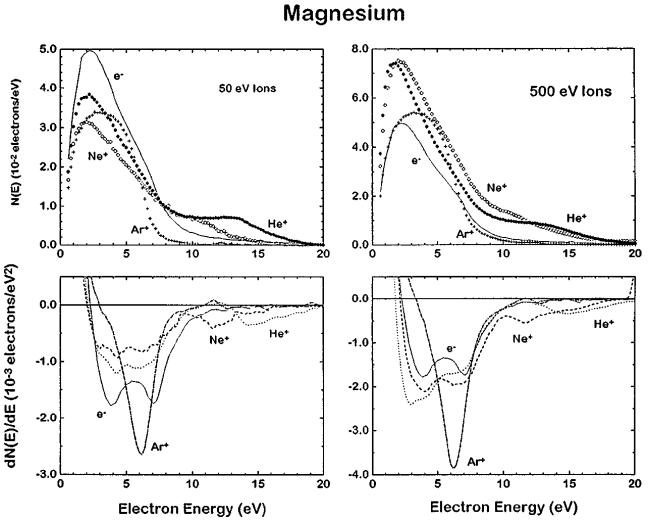

FIG. 3. Top: electron energy spectra $N(E)$ from Mg bombarded by 50 and 500 eV He^+, Ne^+, and Ar^+ at 12° grazing incidence, and by 1 keV electrons at normal incidence. Bottom: derivative spectra $dN(E)/dE$. The scale for the electron excited spectrum is arbitrary.

of *bulk* plasmons is unexpected, at first glance, since neutralization occurs most likely when the ion is outside the surface. The remarkable excitation of bulk plasmons is not due to the projectile penetrating the solid, since bulk plasmon structures are dominant even at energies as low as 30 eV. There is also no indication of an ion energy threshold in the data. Current theories of plasmon excitations by external charges do not predict bulk plasmon excitation outside the solid. In core level XPS of adsorbates, where both the hole and the emitted electron remain outside the surface, only a surface plasmon shake-up is seen. This situation is different from the case of ion neutralization, where the resulting hole is in the metal. We envision that plasmon excitation in our case is due to the rapid switch of the surface dipole formed by the incoming ion and the image charge. During neutralization, the image charge disappears (transfers into the ion) and a hole is transferred to the solid.

At first sight it appears surprising that plasmon-assisted neutralization, which appears so prominent for Al and Mg, has not been observed before. Inspection of the literature reveals that the vast majority of potential electron emission studies [2] have been limited to metals like W, Mo, Ta, and Cu which exhibit plasmons with energies higher than the energy released in the neutralization of the projectile ions or have a very broad plasmon structure that cannot be resolved above the background of electrons from Auger neutralization. Plasmon structure in Al has been observed before for impact of 0.4–5 keV Ne^+ and by thermal metastable He, but not analyzed as such [6,13]. The experiments by Zampieri, Maier, and Baragiola [6] have also shown that the structure is absent for 1 keV

neutral Ne projectiles, further supporting the idea that the plasmon features result from the neutralization process.

In conclusion, we have shown that plasmon-assisted electron emission can occur for slow ions on Al and Mg surfaces when the energy released by electron capture exceeds the energy of the surface or bulk plasmon. Plasmon excitations can occur at impact velocities which are orders of magnitude below those expected previously [17] and, in fact, there is no apparent velocity threshold for the process. In the case of Mg, the process is more likely than direct Auger neutralization and dominates electron emission. Plasmon-assisted neutralization needs to be accounted for in the description and practice of ion neutralization spectroscopy and may be an important source of electrons in the interaction of slow multiply charged ions near surfaces. It may also play a role in determining the charge state, energy loss, and energy loss straggling for slow ions moving through solids.

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