

Excitation of quasiparticles during grazing-angle ion reflection at Al surfaces

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(Received 26 October 1992; accepted 18 January 1993)

We have studied ion-induced electron emission during grazing-angle scattering of 150 keV protons at clean and oxygen-covered Al surfaces. The angle-resolved energy distribution of emitted electrons reveals, in the energy range of 0–30 eV, characteristic peaks, which are directly correlated to various electron excitation mechanisms. For clean Al surfaces, these processes include single electron excitation and excitation of electrons by decay of ion-excited surface and bulk plasmons. At submonolayer oxygen coverages of the Al surfaces, we already find a drastic decrease of the electron emission peak at 6 eV, which is due to the decay of surface plasmons, and an increase of the O(2s2p2p) Auger electron emission peak located at about 5 eV.

I. INTRODUCTION

Ion-induced electron emission is often described in terms of potential and kinetic emission. Potential emission of electrons is caused by neutralization and de-excitation of ions taking place at the topmost surface layer. Kinetic emission, on the other hand, involves a variety of complicated energy loss processes occurring during ion–solid interaction. Contrary to potential emission, the excitation of electrons is not confined to the surface, but extends deep into the bulk along the trajectory of the ions. During transport of these excited electrons towards the surface, electron cascading processes modify the intrinsic electron energy distribution (ED), thus leading to the well-known, 2 eV cascade electron peak^{1–3} in the final ED measured in the electron spectrometer. Due to the statistical nature of electron cascading processes, the ED of emitted electrons does not reflect, in the energy range of 0–30 eV, any details about the initial electron excitation processes occurring inside the solid.

Using angle-resolved secondary electron spectroscopy,^{1–3} several groups have reported weak fine structures in the electron ED which are superimposed on a smooth and broad cascade background. These weak fine structures, however, are correlated to the unfilled electronic states of the bulk and surface band structure of the solid above the vacuum level and do not allow us to extract any information about the initial electron excitation processes.^{3,4}

Using spin-polarized electron emission spectroscopy (SPEES), we have previously shown that electron cascade processes can be significantly suppressed by using grazing-angle ion-surface reflection for the electron excitation. In our first experiments, we employed 25 keV H⁺ and He⁺ ions and angles of incidence of 1° for the excitation of electrons at surfaces of Ni(110) picture-frame single crystals.^{5,6} The angle-resolved energy distribution (ARED) of the emitted electrons exhibits a series of distinct peaks which can be attributed to various electron excitation processes. In SPEES, we use energetic ions with beam energies varying from 5 to 150 keV. The suppression of the electron cascade background relies on the fact that,

at grazing angles of incidence, ions do not penetrate the surface, and they excite the electrons only at the topmost surface layer. The excited electrons have only a small probability to be scattered by other target electrons before escaping from the surface. Therefore, they retain information on the initial electronic excitation processes.

Despite extensive studies on ion-induced electron emission, both experimentally and theoretically, the status of understanding the phenomenon of kinetic emission from the surface of solids is still far from complete.^{7,8} The interpretation of experimental results and the development of microscopic theories on ion-induced electron emission are often complicated by the complexity of various electron excitation mechanisms and by the subsequently occurring electron transport and escape processes.

In this article, we present experimental results on ion-induced electron emission, using SPEES at clean and oxygen-covered Al surfaces. For the experiments, we used 150 keV H⁺ ions and angles of incidence ranging from 0.1° to 20°. The purpose of this work is to study a series of initial electron excitation processes occurring in kinetic electron emission, and their relative contribution to the total electron yield. From the experimental results obtained so far, there is evidence that the ARED of the emitted electrons contains important and direct information on the initially occurring electron excitation processes.

II. EXPERIMENTAL

The experiments are performed in our SPEES vacuum chamber,⁹ operating at a base pressure of 2×10^{-10} mbar. During ion-surface scattering, electrons are excited by a highly collimated (half-angle of beam divergence less than 0.025°) beam of 150 keV H⁺ ions. The angle of incidence α of the ions towards the target surface is varied between 0° and 45° with an accuracy of 0.01°. The emitted electrons are collected in a specifically designed electron detector oriented perpendicular to the direction of the incident ion beam (see Fig. 1). A detailed description of the electron spectrometer is given elsewhere. The electron detector system consists of an electron optical lens systems and a 90°—electrostatic energy analyzer possessing an energy resolu-

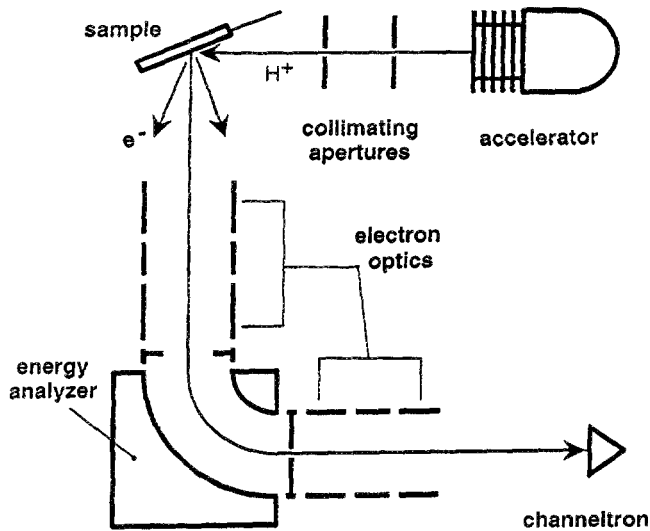


FIG. 1. Schematics of the experimental setup.

tion of 0.4 eV. The electron extracting lens in front of the analyzer is designed to provide a nearly parallel electron beam at the entrance of the energy analyzer.

The dimension of the polycrystalline Al samples, which are prepared *in situ*, is 8 mm \times 15 mm \times 1 mm, and they are flat within 30 Å (scan size: 2000 Å) as checked using scanning tunneling microscopy (STM) imaging. The oxidation of previously clean Al surfaces is performed at room temperature using oxygen partial pressures of 1×10^{-8} mbar. The oxygen coverage of the Al surfaces is monitored by using an Auger cylindrical mirror analyzer.

III. RESULTS

Figure 2 shows a typical ARED (solid line in Fig. 2) of electrons emitted from clean Al surfaces during 150 keV H^+ ion-surface interaction at $\alpha = 20^\circ$. The spectrum closely resembles those obtained in electron-induced secondary electron emission possessing a broad peak located at about 2.6 eV which is due to electron multiple scattering. In addition, we observe two weak shoulders in the

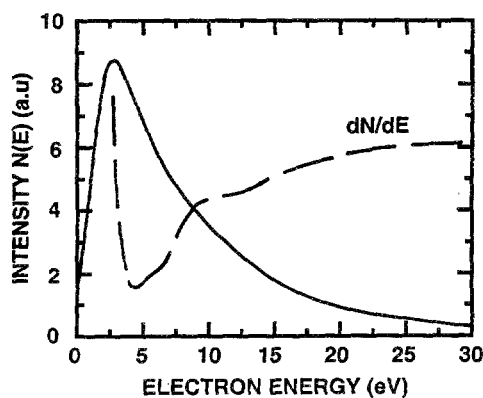


FIG. 2. (a) ARED of electrons emitted from clean Al surfaces for $\alpha = 20^\circ$ (solid curve) and (b) first derivative of the ARED, dN/dE (dashed curve).

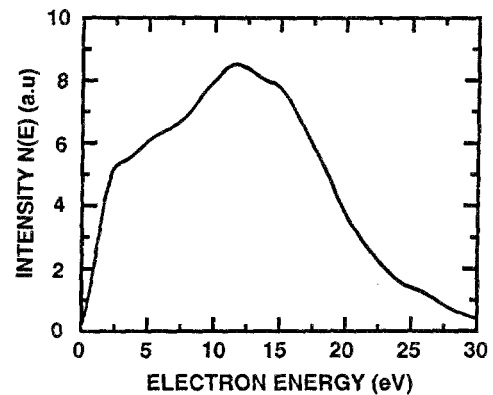


FIG. 3. ARED of electrons emitted from clean Al surfaces for $\alpha = 0.5^\circ$.

ARED, located at about 6 and 11 eV, which are easily observable in the first derivative of the intensity distribution dN/dE (dashed line in Fig. 2).

Decreasing α from 20° to small angles, the overall shape of the obtained AREDs remains unchanged, as compared to the ARED shown in Fig. 2, until $\alpha < 3^\circ$ is reached. For $\alpha < 2^\circ$, a drastic decrease of the peak located at 2.6 eV is observed and the previously smooth AREDs exhibit several new features. Figure 3 gives, for $\alpha = 0.5^\circ$, the ARED of electrons emitted from clean Al surfaces. Two peaks located at 6.0 and 11.0 eV, which, for $\alpha = 20^\circ$, are only observable in the first derivative dN/dE of the ARED, are now major features in the ARED. Besides these two peaks, we observe two additional peaks located at 15.0 and 25.6 eV, respectively. We note that the intensity of the electron peak located at 2.6 eV is much lower than the intensity of the peaks located at 6.0 and 11.0 eV, which directly shows that, for small α 's, electron cascades are significantly suppressed. This agrees with the results from our earlier SPEES experiments where, using $\alpha = 1^\circ$, 25 keV H^+ and He^+ ions were reflected at Ni(110) surfaces.^{5,6}

Figure 4(a) shows the integrated (between 0 and 30 eV) intensity I_0 as a function of the angle of incidence α which agrees well with a cosine law⁹ for $\alpha > 4^\circ$ [see solid line in Fig. 4(a)]. Filled circles and squares represent experimental data for clean Al and oxygen-covered Al surfaces (0.1 ML coverage), respectively. We note that changes in the detection angle which occur during changes of the angle of incidence are included in the calculation of the cosine-law distributions.

Further, we clearly observe an increase of I_0 with increasing oxygen coverage of the previously clean Al surfaces. Figure 4(b) shows, as a function of α , the ratio $I_0(O/Al)/I_0(Al)$ of the integrated intensity for O-covered Al surfaces to that for clean Al surfaces. This ratio is almost constant for $\alpha > 5^\circ$ and amount to approximately 1.3. This small enhancement of I_0 might be attributed to small, oxygen-induced changes in the work function.^{8,10} For $\alpha < 0.6^\circ$, we observe a strong increase in the ratio $I_0(O/Al)/I_0(Al)$ up to values of about 3 for $\alpha = 0.1^\circ$ which implies that, for $\alpha < 0.6^\circ$, electron excitation processes are confined to the topmost surface layer.

Figure 5 shows, for $\alpha = 0.5^\circ$, AREDs of electrons emit-

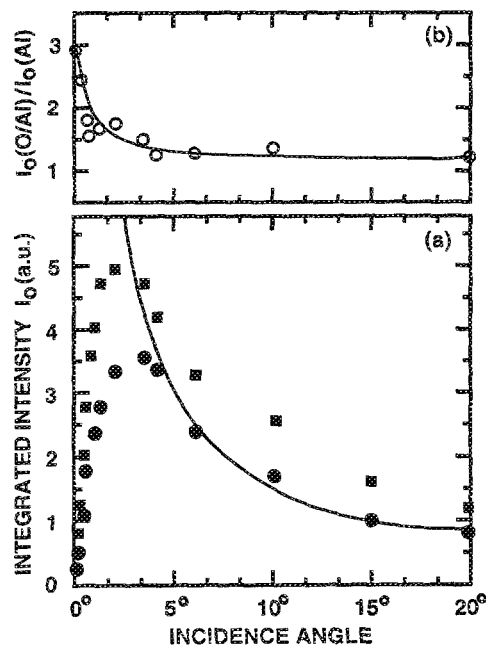


FIG. 4. (a) Integrated (from 0 to 30 eV) intensity I_0 as function of incidence angle α for clean (●) and oxygen-covered (■) Al surfaces; (b) Intensity ratio $I_0(\text{O/Al})/I_0(\text{Al})$ for oxygen-covered vs clean Al surfaces.

ted from clean and O-covered Al surfaces. For small oxygen coverages of previously clean Al surfaces, we already observe a strong decrease in the intensity of the peaks located at 6.0 and 15.0 eV. The electron peak located at 25.6 eV disappears already at a coverage of 0.1 ML of O. We further find, with increasing O coverage of the Al surfaces, a rapid increase in the intensity of a new peak located at 5 eV.

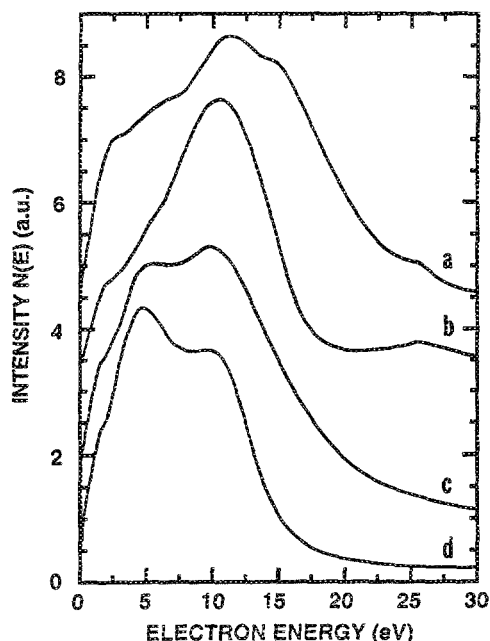


FIG. 5. AREDs of electrons emitted from (a) clean and (b)–(d) oxygen-covered Al surfaces for $\alpha = 0.5^\circ$. The oxygen coverage is (b) 0.05 ML, (c) 0.1 ML, and (d) 0.5 ML.

IV. DISCUSSION

Comparing the AREDs shown in Figs. 2 ($\alpha = 20^\circ$) and 3 ($\alpha = 0.5^\circ$), we qualitatively conclude that electron cascading processes contribute negligibly to the ARED of electrons emitted during grazing-angle ion-surface interaction.

We note that small features, located at 6.0 and 11.0 eV in the ED, were previously observed in both electron- and ion-induced electron emission spectra as weak shoulders superimposed on a broad electron cascade background.^{11,12} Tentatively, for these two shoulders in the ED, single electron excitation by decay of surface plasmons (SP) and bulk plasmons (BP) was suggested for the origin of these two features. With the vacuum level as reference to zero electron kinetic energy, the maximum (excitation from the fermi level) kinetic energies of electrons due to decay of SPs and bulk BPs amount to $E_{sp} - \phi$ and $E_{bp} - \phi$, where E_{sp} and E_{bp} are the energies for the excitation of surface and bulk plasmons, respectively, and ϕ is the work function. For Al, we use: $E_{sp} = 10.6$ eV, $E_{bp} = 15.0$ eV,¹³ and $\phi = 4.3$ eV.¹⁴ From this, we expect sharp rising edges located at 6.3 and 10.7 eV which is in good agreement with our experimental findings.

We remark that, due to the strong suppression of the electron cascade background in grazing-angle ion surface reflection experiments, a quantitative comparison of our experimental results with theoretical functions for the excitation and decay of plasmons should be feasible. Unfortunately, there is no theory presently available which incorporates such small angles of incidence as used in our experiments. We note that for large angles of incidence, proton-induced electron emission was studied theoretically by Rösler and Brauer.¹⁵

Further evidence for electron emission due to the decay of surface and bulk plasmons is given by the following discussion. We find two previously unobserved small features in the ARED located at 15.0 and 25.6 eV. It is tempting to correlate these shoulders to single electron excitation by decay of harmonics of SPs (2SP) and BPs (2BP), respectively. This is corroborated by electron energy-loss spectroscopy (EELS) experiments by Benndorf *et al.*¹⁶ These authors find in their initial oxidation studies of thin Al films two major electron loss peaks for the clean Al surface at 10.3 and 15.4 eV which they attribute to the excitation of SPs and BPs. In addition, they observed a small loss peak at 31.4 eV due to excitation of 2BP and a broad structure extending from 20 to 25 eV which they attributed to the excitation of 2SP and SP + BP. For our proton-induced AREDs, we expect these features to be located at 27.1 eV (2BP) and 16.3 eV (2SP). This agrees very well with our experimental findings of two shoulders located in the ARED located at 15 and 25.6 eV.

Further evidence to assign the two peaks located at 6.0 and 15.0 eV to electron excitation by decay of surface plasmons is given by the fact that these features disappear at small oxygen coverages of the Al surfaces.

The electron emission peak located at 5.0 eV can be attributed to O(2s2p2p) Auger electron transitions. The energy of the Auger electrons is given by

$\epsilon_k = \epsilon_{2s} - 2 \cdot \epsilon_{2p} - \phi$, where ϵ_{2s} and ϵ_{2p} are the binding energies of the O 2s and 2p levels, respectively. For oxygen chemisorbed on clean Al surfaces, ϵ_{2s} is located 23.6 eV and ϵ_{2p} is located 7 eV below the fermi energy.¹⁷ We note that changes of the work function due to oxygen chemisorption are small (<200 mV).¹¹ Using these values, we find $\epsilon_k = 5.4$ eV which coincides precisely with our experimental finding (see Fig. 5).

V. CONCLUSIONS

We have shown that grazing-angle ion-surface reflection experiments enable us to suppress electron cascade processes, and, therefore, AREDS obtained in SPEES exhibit electron emission peaks which can be directly related to various electron excitation mechanisms occurring during ion-surface interaction. For clean Al surfaces, the major electron excitation mechanism is single electron excitation by decay of ion-induced surface and bulk plasmons. The exposure of Al surfaces to even small amounts of oxygen immediately prevents the excitation of surface plasmons and induces electron emission due to O(2s2p2p) Auger processes. Finally, we note that grazing-angle ion surface reflection experiments offer great opportunities to explore the fundamental physical mechanisms inherently involved in ion-surface interaction.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, by the Welch Foundation and by the Texas Higher Education Coordinating Board.

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