Low-energy electronic excitations of a clean Al(111) surface

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(Received 8 February 1984)

The low-energy electronic excitations of a clean Al(111) surface have been studied by means of angle-integrated high-resolution electron-energy-loss spectroscopy (EELS). The improvement in the energy resolution of the present experiment compared with the preceding ones allows detection in the low-incident-electron-energy range ($E_p < 50$ eV) of two peaks A (1.5–2 eV) and B (4–5 eV). From the relationship of the intensity of these peaks with the incident-electron penetration, it is argued that peak A corresponds to bulk interband transitions at the W point of the bulk Brillouin zone, while peak B corresponds to transitions between surface states at the $\bar{M}$ point of the surface Brillouin zone.

I. INTRODUCTION

The strong inelastic interaction of low-energy electrons (10 eV $< E_p <$ 100 eV) with a solid surface is still not well known. In this energy range, the Born approximation is no more valid and the momentum transferred to the electrons of the solid is not negligible. Furthermore, diffraction effects are of primary importance and lead to strong intensity variation of the electron-energy-loss peaks (EELS), due to the necessary coupling between inelastic and elastic events in order to detect the inelastically scattered electrons. However, this incident-electron-energy range is of capital importance for at least two reasons: (i) The strong inelastic interaction in this energy range makes EELS extremely surface sensitive. The total inelastic mean free path λ_{in} in aluminum is lower than 3.5 Å in the energy range 30 eV $< E <$ 50 eV.[1,2] (ii) For very-low–incident-electron energies $E_p < 50$ eV, the strong decrease in the intensities of the collective excitations allows the detection of weaker EELS peaks which are generally due to single-electron excitations.

This second point (ii) was demonstrated[3] on a polycrystalline Al surface presenting large grains oriented (111) within a few degrees.[4] An EELS peak located 4 eV below the energy of the elastic peak appeared when the primary energy was decreased to 30 eV. From its sensitivity to oxygen adsorption, it was concluded that this peak was due to transition between surface states. Nall, Jette, and Bargeron[5] confirmed the existence of such a peak and studied its energy position versus primary energy. They showed a 3-eV shift of this peak in the primary energy range 23 eV $< E_p <$ 36 eV. They concluded that this peak was due to nonvertical direct inter- and intraband transitions of the bulk material.

It is the purpose of this Brief Report to present experiments with higher-energy resolution (0.2 eV) in order to get a deeper insight in the single-electron excitations of the Al(111) surface.

II. EXPERIMENTAL

The sample is an aluminum single crystal (metal research 99.99%) cut along the (111) face, mechanically and electrochemically polished. The experiments were performed on a VG Escalab MK II fitted with an x-ray source, an uv source, a scanning electron gun, and an electron monochromator EMU 50. The sample was cleaned in the preparation chamber by means of cycles of Ar sputtering (1 keV, 10 μA) and annealed at 550 °C. The sample cleanliness was monitored by means of Auger electron spectroscopy (AES) and electron-energy-loss spectroscopy (EELS). The sample was considered clean when the two following conditions were realized: (i) On an AES spectrum ($E_p = 3$ keV), only the LVV Auger line of pure aluminum was observed (no KLL Auger line of oxygen). (ii) On an EELS spectrum obtained with the scanning electron gun ($E_p = 250$ eV), the bulk plasmon (BP) and surface plasmon (SP) loss peaks were well defined, and the ratio of the intensities of surface plasmon to bulk plasmon was the most intense (greater than 1.1).

The high-resolution EELS spectra were obtained with the EMU electron monochromator, the energy of which ranges from 0 to 100 eV. The voltage across hemispheres for both the EMU and analyzer was adjusted to get a full width at half maximum of the elastic peak of 0.2 eV, which is sufficient for the study of electronic losses on aluminum. The angle between the incident beam of electrons and the axis of the input lens of the analyzer was 90°. The sample rotation was set for specular reflecion ($\theta_i = \theta_s = 45°$). The angular aperture of the input lens, seen from the sample, was 24°.

III. RESULTS

Figure 1 shows the plot of the intensity I_{00} of the elastic peak in the specular reflection, normalized to the primary current I_p, as a function of incident-electron energy E_p (20 eV $< E_p <$ 100 eV). Arrows pointing downwards correspond to the position of the kinematical Bragg peaks assuming an inner potential of 16.7 eV.[6] Figures 2 and 3 show EELS spectra recorded in the same incident-electron-energy range.

For $E_p > 50$ eV, the EELS spectrum is dominated by bulk plasmon (BP) and surface plasmon (SP) loss peaks. A peak labeled B, located 5 eV below the elastic peak, appears for

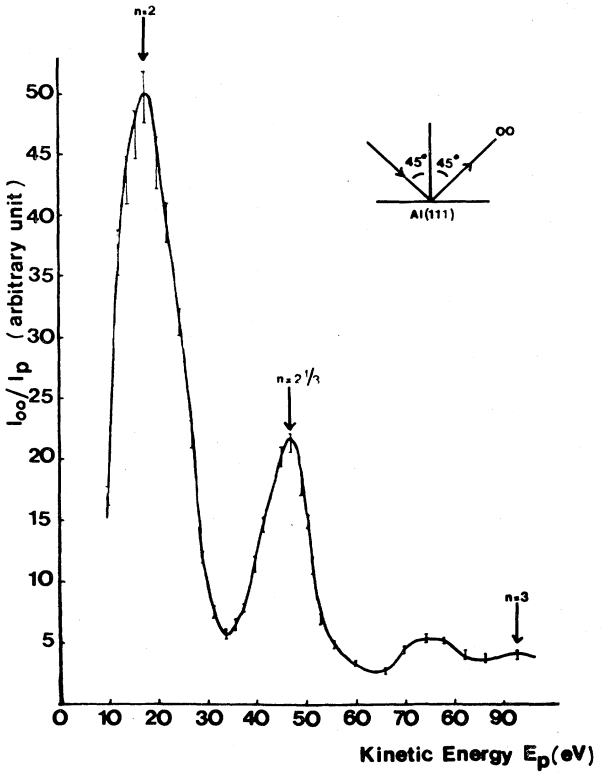

FIG. 1. Intensity I_{00} of the elastic peak normalized to the primary current I_p, vs primary energy, for an Al(111) surface with a polar angle of $\theta_i = 45$ °C, and in the specular reflection ($\theta_s = 45°$). Arrows pointing downwards correspond to the calculated kinematical position of the Bragg peak assuming an inner potential of 17.6 eV.

$E_p = 50$ eV, disappears for $E_p = 40$ eV, and appears again for $E_p = 30$ eV. Below $E_p = 30$ eV (Fig. 3), the intensity of SP is decreasing rapidly. A new peak labeled A appears for $E_p = 27$ eV, while peak B disappears. Figure 4 shows the low-energy-loss part of the spectrum in this incident-energy range, expanded for clarity. Peaks A and B are dispersing towards lower energy when the incident energy is reduced.

The two important aspects of these experimental results

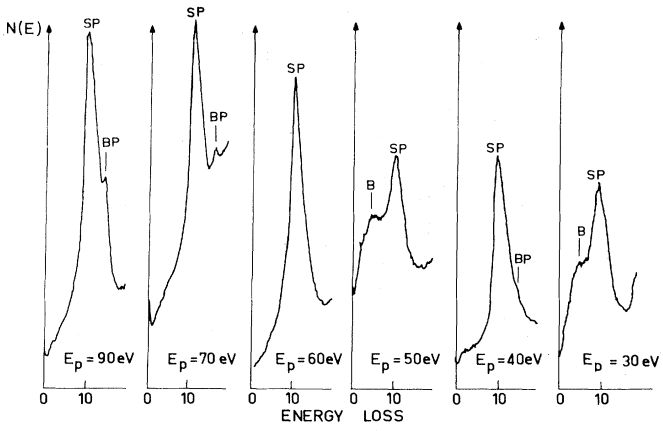

FIG. 2. Electron-energy-loss spectra (EELS) of an Al(111) surface recorded in the incident-electron-energy range 30 eV $< E_p <$ 90 eV. $\theta_i = \theta_s = 45°$. SP: surface plasmon. BP: bulk plasmon.

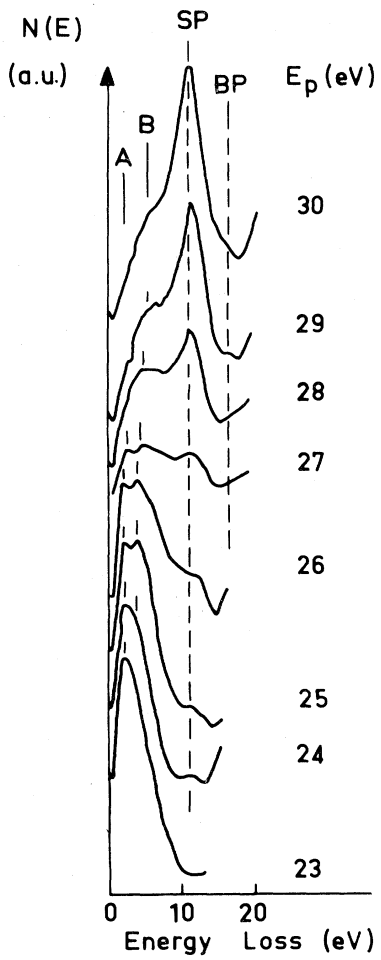

FIG. 3. Electron-energy-loss spectra (EELS) of an Al(111) surface in the incident-electron-energy range 23 eV $< E_p <$ 30 eV. $\theta_i = \theta_s = 45°$. SP: surface plasmon. BP: bulk plasmon.

are (i) the observation for the first time of two resolved peaks A and B in the low-energy-loss region and (ii) the respective influence of diffraction effects and inelastic mean-free-path variation on the intensity of the EELS peaks when the incident-electron energy is varied in the range of 20–100 eV. This point will be discussed in Sec. IV.

IV. DISCUSSION

Two different kinds of low-energy-electronic excitations can account for peaks A and B:

(a) Interband transitions in the bulk band structure of aluminum. These interband transitions occur between degenerate free-electron bands which are split by the weak periodic crystal potential. The first two Fourier coefficients of the pseudopotential (V_{200} and V_{111}) give rise to a 1.6-eV band gap at X and a 0.5-eV gap at L, respectively.[7,8] These split bands cross the Fermi energy close to W, and, in this region of the bulk Brillouin zone, interband transitions between filled and empty states of these bands can occur. At room temperature, only the 1.6-eV transition has been observed experimentally by optical methods[9] and by transmission-electron-energy loss spectroscopy (TEELS),[10] the 0.5-eV

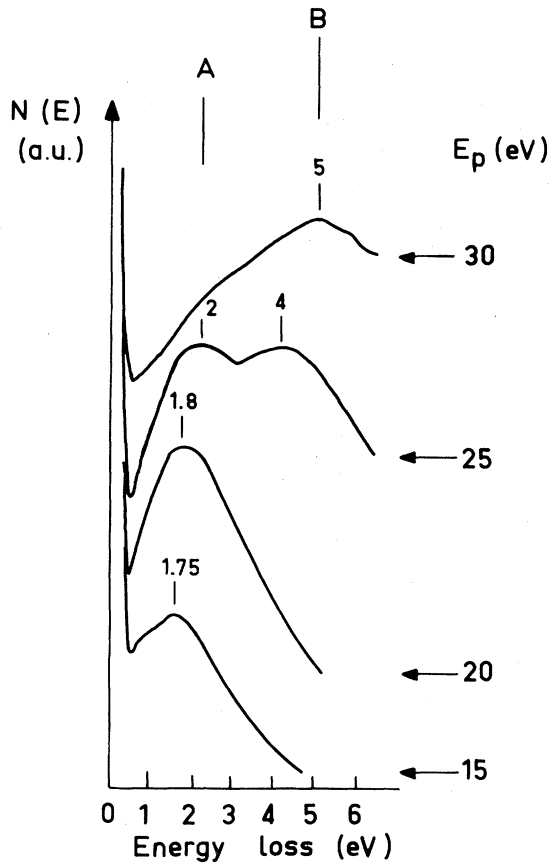

FIG. 4. Expanded low-energy part of EELS spectra recorded for $E_p = 30$, 25, 20, and 15 eV.

transition being concealed by the Drude absorption. Dispersion of the 1.6-eV transition has been studied by means of wave-vector-resolved TEELS.[11,12]

(b) Transitions between surface states. Surface states on the Al(111) surface have been predicted theoretically[13–15] and observed experimentally by angle-integrated[16] and angle-resolved photoemission[17] for the filled states, and by surface-soft x-ray-absorption spectroscopy[18] for the empty states. Strongly localized filled surface states close to the Fermi level have been found theoretically at the $\bar{K}$ point of the surface Brillouin zone (SBZ).[13,15] A band of surface states is predicted in the $\bar{\Gamma}\bar{M}$ direction, extending from halfway of $\bar{\Gamma}\bar{M}$ to the $\bar{M}$ point.[15] This band of surface states has been observed experimentally by angle-resolved photoemission.[17] These states lie within the projection on the (111) surface of the bulk energy bands at point X in the (100) plane. Experimental evidence for these states is limited to the $\vec{k}$ range $\frac{1}{2}k_{\bar{\Gamma}\bar{M}}$ to $\frac{3}{4}k_{\bar{\Gamma}\bar{M}}$ probably due to grazing emergence conditions for the latter value.[17] Empty surface states are predicted at the $\bar{M}$ point[13,15] lying between 1–1.5 eV above the Fermi level.

In order to interpret peaks A and B in terms of bulk interband transitions (a) or transitions between surface states (b), a discussion of the relative importance of Bragg reflection and of inelastic mean-free-path variation in the incident-energy range considered here is now necessary.

In the high-energy part of the incident-energy range ($E_p > 30$ eV, Fig. 2), there is only a small variation of the inelastic mean free path λ_{in} [$E_p = 100$ eV, $\lambda_{in} = 4$ Å; $E_p = 30$ eV, $\lambda_{in} = 3$ Å (Ref. 1)]. In this energy range, the changes in the relative intensity of the EELS peaks are mainly due to the variation of the penetration of the incident-electron beam related to Bragg reflection: a maximum in the elastic reflection intensity means a minimum in the elastic mean free path and vice versa. This effect explains the disappearance of the bulk plasmon (BP) loss peak for $E_p = 50$ eV (Fig. 2), which corresponds to a maximum in the $I_{00} = f(E_p)$ curve (Fig. 1) and the reappearance of the BP for $E_p = 40$ eV, when penetration increases (Fig. 1).

For lower-incident energies ($E_p < 30$ eV), there is a strong variation of the inelastic mean free path: it increases from $\lambda_{in} = 3$ Å for $E_p = 30$ eV to $\lambda_{in} = 10$ Å for $E_p = 20$ eV.[1,2] This variation is due to the plasmon excitation thresholds: The experimental values we have found for these thresholds are $E_p = 28$ eV for the bulk plasmon and $E_p = 22$ eV for the surface plasmon (Fig. 3).

These remarks lead us to the conclusion that B is surface related while A is bulk related for the following reasons: (i) In the incident-electron-energy range 30 eV < 100 eV: when the penetration of the incident beam is minimum ($E_p = 50$ eV), peak B is maximum and the bulk plasmon disappears (Fig. 2); when the penetration of the incident beam increases (for example, $E_p = 90$ eV, $E_p = 40$ eV) the bulk plasmon intensity increases and peak B disappears (Figs. 2 and 3). (ii) When the incident-electron energy is decreased from $E_p = 30$ eV to $E_p = 23$ eV, the great increase in λ_{in} leads to a decrease of the intensity of peak B and to the rise of the intensity of peak A. The great sensitivity of peak B to oxygen adsorption[3] is a further argument for it to be surface related.

In an EELS experiment, the transitions are equally likely from any area of the Brillouin zone (in the constant matrix element approximation).[19] In the case of the two-dimensional SBZ, the area of $\vec{k}$ space near the zone boundary is much greater than the area close to the center of the zone, so that the EELS spectrum is dominated by transitions near $\bar{M}$ and $\bar{K}$ in the hexagonal Brillouin zone.[19] These remarks lead toward attributing B to transitions between surface states, probably at the $\bar{M}$ point, starting in the filled surface states lying 3 eV below the Fermi level and ending in the empty state 1–1.5 eV above E_F [see Sec. IV, part (b)]. Peak A is probably due to bulk interband transitions occurring at the W point of the bulk Brillouin zone [see Sec.IV, part (a)]. Angle-resolved experiments are in progress in order to determine the dispersion of these features.[20]

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