Splitting of the surface-plasmon dispersion on a slightly rough surface studied by attenuated total reflection

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In situ measurements of surface-plasmon dispersion made on smooth and slightly electrochemically roughened electrodes by attenuated total reflection are reported. The anomalous shape of the dispersion curve for rough surfaces is studied over the entire visible range and analyzed. Experimental results may be consistent with theoretical studies of randomly rough surfaces.

Since phenomena like surface-enhanced Raman spectroscopy are strongly dependent on the surface properties of materials, attempts are being made to more exactly characterize actual surfaces. Surface-plasmon (SP) excitation at the interface between a nearly-free-electron metal and a dielectric has been proven to be a selective probe very sensitive to the interfacial properties and to their modifications. In the high-wave-vector region, recent theoretical studies[1-3] have shown that in the the presence of surface roughness the dispersion curve for surface plasmons consists of two branches, while it consists of a single branch on a flat surface. Koetz, Lewerentz, and Kretschmann[4] have observed such splitting for Ag(111) by electroreflectance spectroscopy. In the low-wave-vector region, the dispersion relation for a rough surface has been discussed mainly in connection with the broadening of the surface-plasma resonance and the increase of the wave vector.[5-7] In a small-roughness limit, Toigo, Marvin, Celli, and Hill[8] have deduced the dispersion relation for periodic and randomly rough surfaces. The occurrence of a splitting in the $\omega(k)$ curve has been clearly shown, the frequencies on the two sides of the gap being dependent on the surface roughness profile and the wave vector. We report here observation of this splitting on slightly rough surfaces measured by attenuated total reflection (ATR) over a wide (ω, k) range.

The samples consisted of a composite electrode made of a thin silver layer (5 to 20 nm) deposited onto a thick aluminium film (100 nm) in contact with an oxygen-free $0.1M \mathrm{K_2SO_4}$ solution. As we have pointed out in a previous publication,[9] such a composite electrode allows extension of the SP method to the uv range using Al as the optical probe and Ag as an electrode. It is then possible to study in a wide range of energy (including the bulk plasmon of silver) the optical properties of the interfaces via the modifications induced on the SP of Al and to study, for instance, the randomly rough surfaces in the small wave-vector range, as we are dealing with, for the first time, in this work.

Measurements were performed in the ATR arrangement using focused light[10] in the so-called Otto configuration.[11] The SP resonance appears for each wavelength (λ) as a minimum in a p reflected light (R_p) versus the incidence angle (ϕ_0); its position and its width being dependent on the interfacial properties. The originally flat electrode was immersed at a controlled potential[9] [-0.25 V relative to a standard hydrogen electrode (SHE)] in the double-layer region and a SP dispersion curve was measured [Fig. 1(a)]. The surface was then roughened by anodic dissolution and subse-

quent partial redeposition of the silver using cyclic voltammetry. Three positive limits which correspond to three roughening processes were applied and SP dispersion curves of the system were measured at -0.25 V relative to a SHE after each process (Fig. 1).

Figure 1(b) shows the SP dispersion measured after one cycle up to 0.65 V corresponding to the dissolution and subsequent redeposition of the same small amount of silver. Figure 1(c) shows the same electrode after polarization at 0.70 V; during this process part of the dissolved silver is redeposited. Figure 1(d) is obtained after polarization at 0.85 V, where the largest amount of silver is dissolved.

Figure 2 shows dispersion curves calculated for smooth surfaces of bare [Fig. 2(a)] and silver-covered Al: $d_{\mathrm{Ag}} = 18$ nm [Fig. 2(b)] and $d_{\mathrm{Ag}} = 5$ nm [Fig. 2(c)], which correspond, respectively, to thicknesses of our experimental samples before and after the largest electrochemical dissolution of Ag.

Two experimental features can be pointed out. For flat surfaces, the SP dispersion curve is smooth and does not exhibit any structure. (It is the case of the electrode just after immersion.) In contrast, structures appear in the dispersion curves after the electrochemical treatment has been applied. Two kinds of experimental features can be ob-
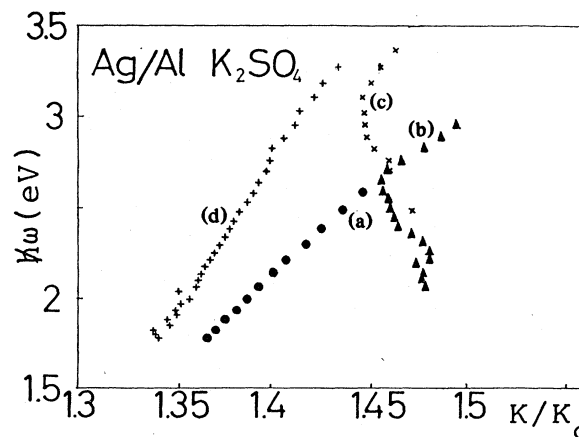

FIG. 1. Surface-plasmon dispersion curves of Ag/Al—$0.1M \mathrm{K_2SO_4}$ electrolyte measured at -0.25 V after (a) immersion, (b) electrochemical cycle up to 0.65 V, (c) electrochemical cycle up to 0.70 V, (d) electrochemical cycle up to 0.89 V.
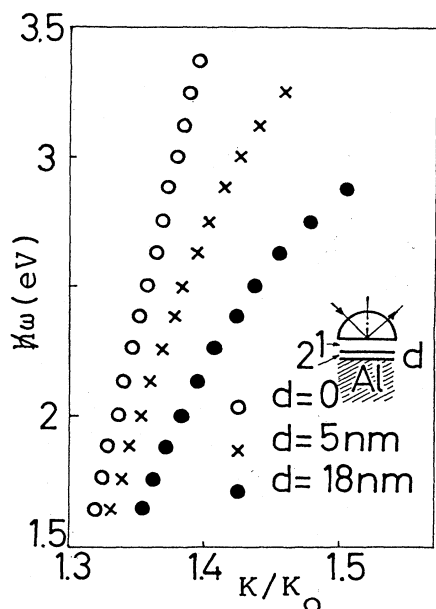
FIG. 2. Surface-plasmon dispersion curves computed for Ag/Al-electrolyte system in our experimental conditions (1 electrolyte, 2 Ag layer).

FIG. 3. Frequencies of surface plasmons measured after processes (b) and (c) in Fig. 1.

served. Anomalous dispersion is seen as small oscillations in the curve [Figs. 1(b) and 1(d)]. Such oscillations may appear on the SP dispersion curve of a metal covered by a thin dielectric film in its absorption band, as discussed by Pockrand and Swalen[12] and Tadjeddine.[10] We have assigned the appearance of these structures both in the red and blue edges of the visible spectrum to surface shape resonances at the silver clusters built up in the electrochemical cycle. Clusters have been seen and observed actually by transmission electron microscopy. A model of hemispheroidal protrusions of a flat surface proposed by Das and Gersten[13] enables us to explain this phenomena in a paper submitted for publication elsewhere.[14]

The second effect is seen for very slight electrochemical treatments where only a small amount of Ag is dissolved and redeposited totally [Fig. 1(b)] or partially [Fig. 1(c)]. It appears as a negative dispersion of the SP in the energy range accessible on the flat surface, while the SP's display a normal dispersion at higher energy. We shall focus our discussion on this tremendous effect which could be a splitting of the dispersion curve due to the electrochemical oxidation-reduction cycle. Since this effect does not appear after the strongest electrochemical process, it does not originate from the clusters of silver and has to be explained by surface structures of size smaller than 5 nm.

As discussed before, the random-roughness-induced SP splitting occurs both in the low- (Ref. 8) and the high-k (Refs. 1–3) regimes. The boundary between these regimes is soft[1] and depends on the system under study. Nevertheless, our data can be explained in the approach proposed by Farias and Maradudin[3] for a randomly rough surface. In the small-roughness limit they found a splitting of the dispersion curve which depends on the mean square departure of the surface from the flatness and the transverse correlation-length ratio. This splitting starts at the surface-plasmon energy of the smooth surface ($\omega/\omega_s = 1$) and in-
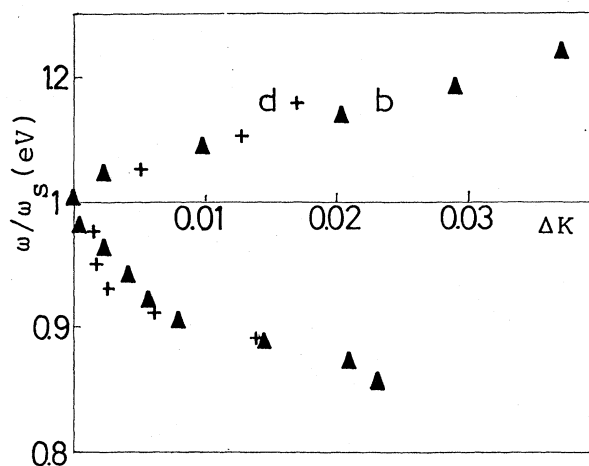
creases with the wave vector. As we are using samples made of Al covered with silver, the surface-plasmon energy is dependent on the thickness of the transition layer[15] and consequently on the amount of silver lost during the electrochemical cycle.

Let us discuss the results of Fig 1(a) (smooth electrode) and Fig. 1(b) (rough electrode covered with the same effec-
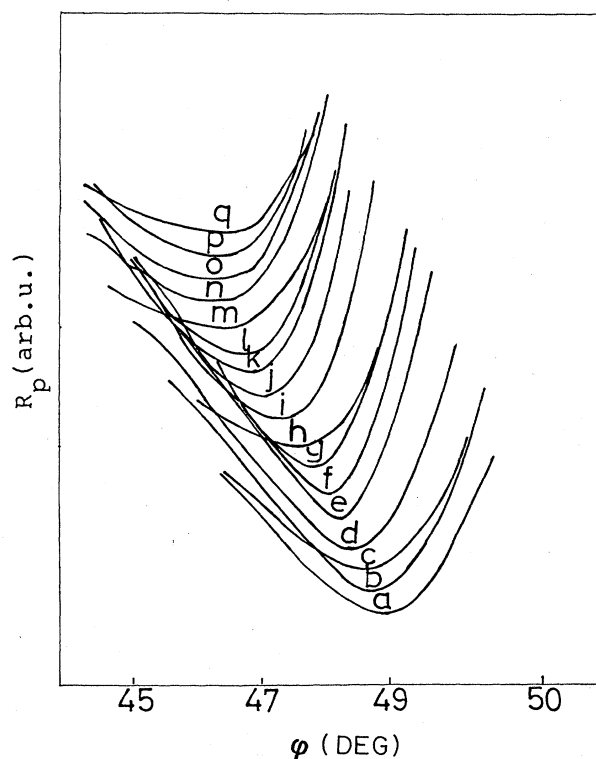

FIG. 4. p-polarized reflectance factor (R_p) vs the angle of incidence (ϕ_0) at constant wavelength (curves are shifted in the y scale). ATR experiments were performed with a quartz hemicylinder: (a) $\lambda = 620$ nm; (q) $\lambda = 460$; $\Delta\lambda = 10$ nm.

tive thickness of Ag). The splitting starts at the point $[\omega_{s0}=2.64$ eV, $(K/K_0)_{s0}=1.457]$; ω_{s0} can be seen as the surface-plasma energy of the composite electrode in contact with water and used to normalize the frequencies of the two SP resonances as shown in Fig. 3(a), where we have plotted the energies of the SP versus the wave vector referred to $(K/K_0)_{s0}$. The experimental splitting increases in the same way as the theoretical one while its magnitude is larger, due to the contribution of Al (for the same energy $-\epsilon_{1Al} > -\epsilon_{1Ag}$).

The same effect is observed after the thickness of the Ag layer has been reduced by anodic dissolution. While the effective surface-plasmon frequency is increased up to 3.1 eV as expected,[15] the normalized splitting is practically the same [Fig. 3(b)] indicative of the same surface structure in both cases. Lastly, measurements performed *ex situ* after electro-chemical roughening have shown the same splitting (Fig. 4) indicative of the high stability of the samples after the electrochemical roughening.

In summary, we may have observed a splitting of the SP dispersion curves on slightly randomly rough surfaces in a small-wave-vector range, where the SP resonance can be excited and detected by ATR. So, our approach introduces a new powerful tool to study the surface properties.

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