Determination of the morphology of Ag deposits by photoreflectance

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The optical response of one Ag monolayer deposited on different Si surfaces has been studied by differential reflectance spectroscopy. The observation of the plasma resonance in the Ag deposits and its energy position, or the nonobservation of this plasma resonance, allows a qualitative determination of the morphology of the thin Ag film: either continuous or formed by quasispherical particles or by flattened three-dimensional particles.

The growth of a metal film on a substrate can follow two main modes, either a layer-by-layer mode of growth or an island mode of growth.[1] The first case, when perfect, is called the Frank–van der Merwe mode, while in the second case one can distinguish between the direct growth of three-dimensional particles on the substrate (Volmer-Weber) and the growth of three-dimensional particles upon an intermediate continuous layer (Stranski-Krastanov). The size and the shape of these metal islands depend strongly on the experimental conditions, such as the temperature and the deposition rate. In the case of Ag, we show in this report that one can take advantage of its peculiar optical response in order to determine the main characteristics of the morphology of a small amount of Ag [one (111)-compact-monolayer] deposited on different Si substrates. In order to distinguish the different ways of growth, we compare the differential reflectance (DR) spectra $\Delta R/R$ measured in each case, where the DR quantity is defined by $\Delta R/R = (R_{Ag} - R_0)/R_0$, with R_0 the reflectance of the bare substrate and R_{Ag} the reflectance of the Ag-covered substrate.[2]

Ag is well known to support intense plasmonlike collective electron oscillations.[3] For the present purpose, we are interested in two kinds of oscillations: the so-called plasma resonance in thin films and the dipolar Mie mode in Ag particles. Although the surface plasmon is a nonradiative mode and cannot be directly excited by photons, it has been shown that a radiative antisymmetric mode, the "plasma resonance," which couples the surface plasmon at both interfaces, can be excited in a thin Ag film by obliquely incident light with p polarization (electric field in the incidence plane).[3] Its energy position, for small wave vectors of the photon, is the same as the bulk plasmon position and is given by $\varepsilon^{Ag}(\hbar\omega_p)=0$, which yield the value $\hbar\omega_p \approx 3.8$ eV. However, this simple description is valid only for thick enough films. When the thickness is below about 20–30 Å, the resonance is broadened and shifted towards higher energies, then it disappears.[4-7] It has recently been shown that for 1- and 2-monolayers-thick Ag films (2.35 and 4.7 Å, respectively), no plasma resonance can be observed and that the minimal thickness for the appearance of the plasma resonance is 3 monolayers (ML), i.e., 7.05 Å.[8] The second kind of collective oscillations of electrons are supported in Ag particles We are interested here in the dipolar mode, which can be considered as the surface plasmon of the particle. This mode is radiating and can also be excited by light. Its position in energy is given by

$$\varepsilon^{Ag}(\hbar\omega_M)=-2$$

for spheres and by $\qquad$ (1)

$$\varepsilon^{Ag}(\hbar\omega_M)=-1/L_i+1$$

for ellipsoids with the electric field aligned along one of the principal direction i, where L_i is the depolarization factor in the i direction.[9] For oblate spheroids, the dipolar resonance along the small axis shifts from the sphere resonance ($\hbar\omega_M \approx 3.5$ eV) to the thin-film plasma resonance ($\hbar\omega_M = \hbar\omega_p \approx 3.8$ eV), as the polarization factor L_i increases from $\frac{1}{3}$ to 1 (i.e., as the sphereroid is flattened from the sphere to a flat film).

The same amount of Ag (mass thickness of 2.4 Å) has been deposited, under ultrahigh-vacuum condition, on three different Si surfaces, and the differential reflectance has been measured with p-polarized light. The amount of Ag was determined by a quartz-microbalance which has been previously calibrated. The accuracy of the measured thicknesses is estimated to be better than a few percent. The optical measurements are performed in the ultrahigh-vacuum chamber during Ag depositions, by use of an optical multichannel analyzer. More details on the experimental procedure can be found in Ref. 10. Figure 1 gives the experimental curves measured when depositing one ML Ag either on reconstructed clean Si surfaces: Si(111)-7×7 (a) and Si(100)-2×1 (b), or on an oxidized Si surface (c). The important point is that the three experimental spectra have very different shapes. The last spectrum (c) displays an intense minimum centered at 3.6 eV. This is due to an optical absorption in the Ag deposits, which is typical of the Mie resonance in Ag particles. The result of a calculation has been drawn in Fig. 2(c) for a regular distribution of Ag spheres on a Si substrate, taking into account the dipolar interaction between the particles following a model by Yamaguchi, Yoshida, and Kinbara.[11] The electromagnetic interaction between the particles and the substrate has been shown to have a small effect[12,13] and is not accounted for here. The best agreement with the experimental data has been obtained
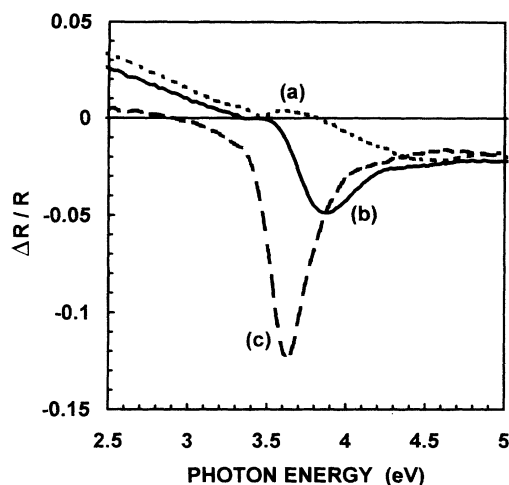
FIG. 1. Experimental DR spectra for 2.4-Å Ag deposited on (a) Si(111)-7×7; (b) Si(100)-2×1; (c) oxidized Si surface.

with sphere diameter equal to 25 Å. The mean free path of conduction electrons in the particles has been reduced with respect to the bulk, because of the small size of the particles and of the poor crystallographic structure which is expected. The modified dielectric function $\varepsilon_{Ag}^{mod}(\omega)$ used in the calculation has been obtained from the relationship

$$\varepsilon_{Ag}^{mod}=\varepsilon_{Ag}^{bulk}-\left[1-\frac{\omega_p^2}{\omega(\omega+i\tau_b^{-1})}\right]+\left[1-\frac{\omega_p^2}{\omega(\omega+i\tau_m^{-1})}\right],$$

(2)

where ω_p is the plasma frequency of the conduction electrons ($\hbar\omega_p=9.04$ eV), τ_b and τ_m are the relaxation times proportional to the inverse of the mean free path of the bulk Ag and of the particles, respectively. The mean free path in the particles has been taken here equal to 16 Å compared to about 450 Å in the bulk. The slight shift to higher energies of the Mie resonance, which has been shown when the diameter of the Ag particles decreases below about 100 Å,[14,15] has not been considered here. For this reason, only qualitative information on the morphology of the Ag deposits on the oxidized surface of Si can be drawn form the present DR results. Nevertheless, the agreement between the experimental data and the calculation is fairly good. This proves that Ag deposited on oxidized Si forms an island film, which is composed of small three-dimensional particles with mostly a spherical shape.

When Ag is deposited on Si(100) [curve (b) of Fig. 1], the resonance is still visible, but it is shifted to higher energies (3.86 eV) and is broadened. For larger amounts of Ag, the resonance becomes sharper and its position progressively tends to the position of the resonance in a Ag film: $\hbar\omega\approx3.8$ eV.[7,13] On the contrary, on Si(111)-7×7, no resonance at all is visible in curve (a). This is due to surface effects[15] and/or to nonlocal effects[4-7] in the thin Ag film: it has recently been shown, indeed, that the plasma resonance is not excited in continuous Ag films one or two monolayers thick but only for thicker films, where it is shifted to larger energies.[8] The comparison

between both spectra indicates, therefore, that on Si(111)-7×7 the 2.4-Å-thick Ag deposit forms a continuous (or quasicontinuous) film, where the plasma resonance cannot be excited. On the contrary, the plasma resonance visible for the DR spectrum obtained on the Si(100) surface indicates that in this case the film consists of flat (with depolarization factor close to 1) but three-dimensional islands, with a height larger than 3 monolayers.

Figure 2 shows the result of a calculation for a regular collection of flat spheroids of Ag (small axis equal to 20 Å and large axis equal to 180 Å). The mean free path of the conduction electrons has been taken equal to 50 Å. The agreement with the experimental data, Fig. 1(b), is not as good as in the previous case. Although a sharp resonance is displayed in the calculation, covering the 3.6–3.9 eV range, it is narrower than in the experimental curve and is centered at a smaller energy (3.8 eV against 3.86 eV). This shift in the experimental data is due to the surface effects[15] and to the nonlocal effects[4-7] in the small deposits as explained above. The width and the location in energy of the experimental minimum indicate that the 1-ML Ag film is formed by flat islands (whose optical response is very close of the one of continuous films), with heights larger than 3 ML for the resonance to be excited. The studies concerning the position of the plasma resonance in continuous Ag films as a function of their thickness have shown that the resonance is observed at 4.22 eV for 3-ML films, 4.14 eV for 4-ML films;[8] then it shifts slowly to the nominal value $\hbar\omega_M=3.8$ eV, which is reached for thicknesses larger than about 8 ML (≈20 Å).[7] The broad experimental minimum which covers the 3.6–4.2 eV range indicates a dispersion of the heights of the flat islands, from 3 ML to larger values, around a central value of about 5–6 ML (≈13 Å), corresponding to the center of the experimental minimum, 3.86 eV. It cannot be excluded also that some of the flat islands are thinner than 3 ML, yielding no resonance in the DR spectrum.
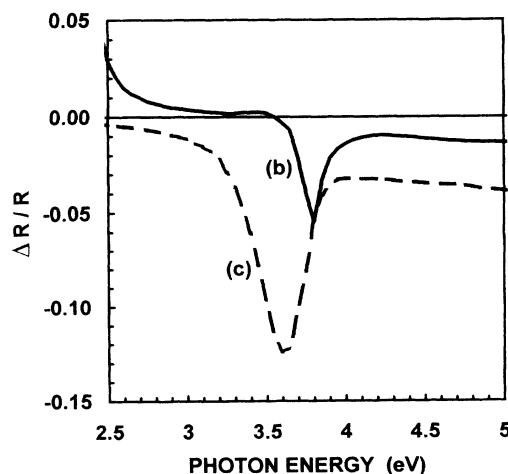
In summary, we have shown that the simple measure-

FIG. 2. Calculation of DR for a regular distribution of Ag spheroids on a Si substrate: (b) flat Ag spheroids with 20 Å/ 180 Å axis ratio; (c) Ag spheres with 25 Å diameter.

ment of the differential reflectance of a substrate covered by small Ag deposits (of the order of 1 ML) can lead to rich information on the morphology of the Ag film. In particular, one can easily distinguish between a continuous layer (no plasma resonance), an island film composed of flat three-dimensional particles (resonance around and above 3.8 eV) and an island film composed by spherical or quasispherical particles (resonance at 3.6 eV). These optical measurements can also be performed during the growth process, which permits a real-time monitoring of the Ag growth on a substrate. However, the limitations of the conclusions one can draw from these measurements are due to numerous factors which shift the position of the resonance, and which avoid a very precise description of the morphology of the film (as the precise dimensions and shapes of the particles), e.g., shapes of the particles, surface effects, nonlocal effects, dipolar interactions between particles, etc.

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