Blue shift of the dipolar plasma resonance in small silver particles on an alumina surface

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Surface reflectance spectroscopy performed on an alumina surface covered by silver particles shows a blue shift of the dipolar plasma resonance in very small silver spheres. Theoretical calculations which take into account the surface-diffuseness effect or quantum-size effect reproduce the experimental shift.

I. INTRODUCTION

The optical absorption of small metal particles has been investigated for a long time, either using discontinuous thin metal films or isolated metal clusters. As concerns the dipolar plasma resonance, the spectral position $\hbar\omega_0$ of the absorption peak for a metallic sphere in vacuum was calculated by Mie at the beginning of this century,[1] and is given by

$$\epsilon(\omega_0)+2=0 \ , \tag{1}$$

where $\epsilon(\omega)$ is the frequency-dependent dielectric function of the metal. This relationship is valid if the particle size is small enough for the quasistatic approximation to be applied. However, the situation is not so clear for very small particles (radii smaller than 5 nm). A few experiments have been performed with silver particles imbedded in glass or in solid argon. One of them gave a shift of the resonance peak towards lower energies (red shift) for radii smaller than 4 nm, with respect to the frequency ω_0 given by Eq. (1) ($\hbar\omega_0=3.5$ eV).[2,3] The other experiments showed a blue shift, in one case the shift being of the order of the experimental dispersion,[4] while in the other case the shift was larger (up to 0.20 eV) for radii below 4 nm.[5] Several theoretical explanations have been proposed to interpret this contradictory behavior. Different phenomena have to be accounted for, e.g., quantum size effects due to a breakup of the conduction band into discrete levels with decreasing sphere size,[6–8] and the effect of the diffuseness of the metal-particle surface.[9–12]

We present in this paper some results obtained in a rather different experimental configuration. Here the silver particles are supported on an amorphous alumina substrate. A blue shift is observed for radii below 4 nm and is qualitatively reproduced by nonlocal calculations which include or do not take into account quantum size effects.

II. EXPERIMENT

The aluminum substrates were prepared by *in situ* evaporation onto fused silicate plates maintained at room temperature, the pressure being in the 10^{-9}-torr range during evaporation. Afterwards they were exposed to several thousand langmuirs (1 langmuir = 1 L = 10^{-6} torr sec) of oxygen, leading to the formation of a continuous film of amorphous alumina (Al_2O_3), one or two nanometers thick. Auger-electron spectroscopy showed a large 54-eV peak, characteristic of oxidized aluminum, while the 68-eV metallic aluminum $L_{23}VV$ transition had almost disappeared. Then silver was deposited onto this alumina surface, the pressure being maintained below 4×10^{-10} torr. The amount of silver deposits was accurately controlled with a calibrated 5-MHz quartz microbalance. On the oxidized aluminum surface silver atoms collected to form clusters. Electron transmission micrographs were obtained from various mean thicknesses of the deposits. Figure 1 shows the micrograph obtained for a silver film of 0.025-nm mean thickness. The mean thickness is the thickness of the film which would be formed by the silver atoms if the growth were continuous rather than by clustering. The silver coverage is therefore measured in values of the mean thickness. The large spots are disoriented aluminum crystallites. The silver particles are the small spots and are indicated by arrows. For low coverages, the silver clusters are spherical and isolated. With increasing coverage the number and the size of the particles increase. The deformation of the clus-

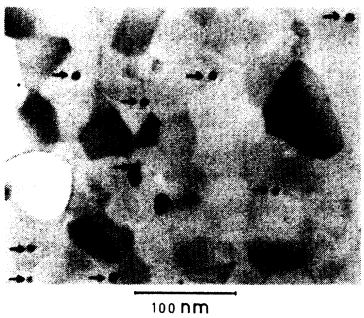

FIG. 1. Electron micrograph for a silver deposit of mean thickness 0.025 nm. The silver particles are indicated by arrows.

ters and the electromagnetic interaction between particles occur for relatively large coverages (> 0.3 nm), but we are interested here only in very low coverages (< 0.05 nm). Each sample displays a silver-cluster size dispersion with a distribution of the radii of the silver spheres that is approximatively Gaussian; as an example, the mean diameter corresponding to Fig. 1 is $2\langle r\rangle = 7.2$ nm and the mean width deviation is 0.8 nm. The mean sphere radius $\langle R\rangle$ is a function of the coverage, varying from 2.5 to 4 nm when the mean thickness varies from 8×10^{-3} up to 5×10^{-2} nm.

The optical measurements were performed *in situ* with a differential reflectometer.[13] One measures the differential reflectance $\Delta R/R = 2(R - R_0)/(R + R_0)$, where R_0 and R are the reflectances at normal incidence of the oxidized aluminum surface and the same surface covered by silver clusters, respectively. This quantity is almost proportional to the negative of the optical absorption in the silver particles.

III. RESULTS AND DISCUSSION

Figure 2 shows the experimental differential reflectance measured for different coverages of silver on oxidized aluminum. The minima in the spectra are due to the dipolar plasma resonance absorption in the silver spheres. The different mean radii $\langle r\rangle$ of the silver spheres are given in the figure. A shift of the plasma resonance towards high energies (blue shift) as a function of the silver coverage (or the sphere radius) is clearly visible. Figure 3 collects these results: It gives the position of the plasma resonance as a function of the mean sphere radius $\langle r\rangle$ for two experiments. One can notice that for increasing mean radius the position is fixed at 3.50 eV, while for small radii ($\langle r\rangle < 4$ nm) the blue shift appears. The interaction between the particles is negligible because of the large distance between them (Fig. 1), and the interaction between the particles and the substrate is not the explanation of the blue shift, because it should yield a red shift.[14] This observed blue shift is therefore an intrinsic property of the spheres due to their small size.

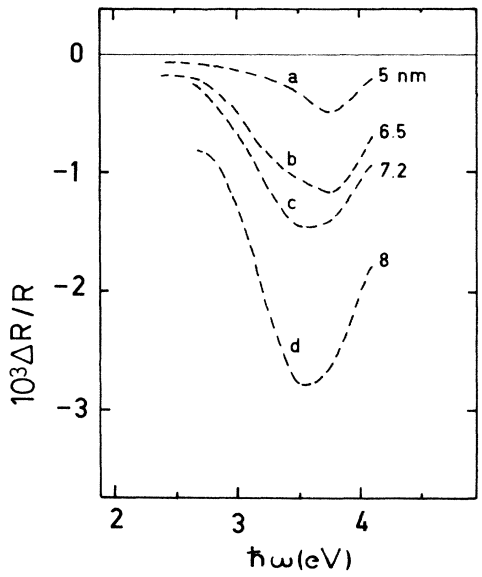

FIG. 2. Differential reflectivity at normal incidence for different mean thicknesses of the Ag deposits: a, 0.008 nm; b, 0.0017 nm; c, 0.025 nm; d, 0.025 nm. The mean dimensions $2\langle r\rangle$ of the Ag particles in nm are indicated on the right side of the figure for each curve.

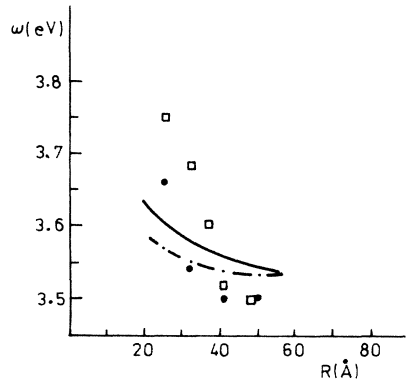

FIG. 3. Spectral position of the dipolar plasma resonance for two experiments (squares and dots) vs the radii of the Ag particles. Calculations with a smoothly varying surface profile (solid line) and with a semiclassical infinite barrier model (dot-dashed line) are also shown.

The optical absorption in the spheres has been calculated using two different approaches. In the first model, corrections to the classical situation are included by considering a nonlocal response with a smoothly varying surface profile.[9] These corrections enter as two lengths $d_r(\omega)$ and $d_\theta(\omega)$, which are measures of the nonlocality range. One obtains, to describe the optical properties of the small silver spheres, an effective dielectric function $\tilde{\epsilon}(\omega)$ defined by

$$\tilde{\epsilon}(\omega) = \epsilon(\omega)\left[\frac{1+2[d_\theta(r,\omega)/r]}{1+(\epsilon-1)[d_r(r,\omega)/r]}\right] , \tag{2}$$

where $\epsilon(\omega)$ is the local dielectric function for silver given by

$$\epsilon(\omega) = \epsilon_d(\omega) - \frac{\omega_p^2}{\omega(\omega + i\gamma)} , \tag{3}$$

where $\epsilon_d(\omega)$ is the contribution of the d electrons to the dielectric function, and ω_p and γ are the plasma frequency and the damping coefficient of the s electrons, respectively. Therefore the plasma resonance frequency is given by Eq. (1) applied to $\tilde{\epsilon}(\omega)$:

$$\tilde{\epsilon}(\omega) + 2 = 0 . \tag{4}$$

For the purposes for this paper, d_θ turns out to be negligible[12] and $d_r(r,\omega)$ may be approximated by $d_\perp(\omega)$, which is the center of gravity of the induced charge density at a planar surface.[15] Equations (2) and (4) therefore yield the following frequency shift for the dipolar plasma resonance in the silver spheres:[10]

$$\frac{\Delta\omega}{\omega_0} = \frac{3}{2+\epsilon_d(\omega_0)}\frac{\mathrm{Re}[d_\perp(\omega_0)]}{r} , \tag{5}$$

where $\omega_0 = 3.5$ eV is the classical dipolar plasma resonance given by Eq. (1). In our calculations, $\epsilon_d(\omega_0)$ is obtained from the values of Johnson and Christy,[16] with $\hbar\omega_p = 9.1$ eV and $\hbar\gamma = 1.6\times10^{-2}$ eV, which gives $\epsilon_d(\omega_0) = -2.004$.

$\mathrm{Re}[d_\perp(\omega_0)]$ is obtained from Feibelman's calculations for a free-electron gas,[17] using $r_s=3$ (silver density) and $\omega_0/\omega_p^*=0.90$, where ω_p^* is the renormalized plasma frequency defined by $\epsilon(\omega_p^*)=0$. This yields the value $\mathrm{Re}[d_\perp(\omega_0/\omega_p^*)]=1.65$ Å. Finally, one obtains the following result for the resonance shift:

$$\Delta\hbar\omega=\frac{0.258}{r}\ , \tag{6}$$

where r is given in nm and $\Delta\hbar\omega$ in eV. The result of this calculation is given in Fig. 3, in comparison with the experimental data.

An alternative calculation has been done by using a semiclassical infinite barrier (SCIB) to describe the sphere and to include quantum size effects. We have used a local transverse dielectric function and the following longitudinal dielectric function:

$$\epsilon_L(q,\omega)=\epsilon_d(\omega)+\epsilon_0(q,\omega)-1\ , \tag{7}$$

where the d-electron contribution $\epsilon_d(\omega)$ is local. $\epsilon_0(q,\omega)$ is the nonlocal s-electron contribution and includes the quantum-size effects.[7] In fact, for the radii of interest here, the quantum size effects turn out to be small and the calculation gives results showing the same behavior as the ones given by Eq. (6) and presented in Fig. 3. The reason is that for $\omega_0\lesssim\omega_p^*$ the values of $d_\perp$ in the SCIB model are close to the results of a more elaborate calculation.[17]

The main result of these two calculations is the blue shift found for the plasma resonance, in qualitative agreement with the experimental result. This can be easily understood by considering Eq. (5): The direction of the shift is associated with the sign of $\mathrm{Re}[d_\perp(\omega_0)]$. For a free-electron gas, $\omega_0/\omega_p=1/\sqrt{3}$ and this value is negative, leading to a red shift. However, when considering the screening due to the d electrons, ω_0 becomes close to the bulk plasma frequency ω_p^* and $\mathrm{Re}[d_\perp(\omega_0)]$ changes its sign. This shows that the d electrons are mainly responsible for the blue shift of the dipolar plasma resonance in small silver spheres. However, some discrepancy between the experiment and the calculations is visible in Fig. 3: The experimental shift is about twice the theoretical one. Several reasons can be given to explain this difference, especially a low accuracy in determining the size of the particles and the dispersion in the sphere sizes for a given sample. The particles also may not be perfectly spherical. In any case, we think that our experimental results unambiguously show a blue shift of the dipolar plasma resonance in small silver spheres; our theoretical calculations give evidence of the role of the d electrons of silver in this shift.

ACKNOWLEDGMENTS

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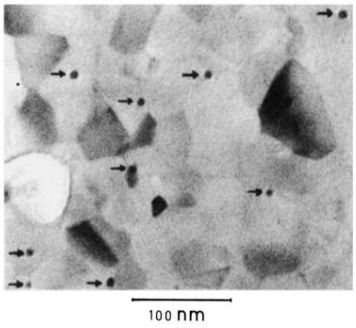

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