Observation of two surface-plasmon modes on gold particles

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Annealed, thin films of gold were studied by electron microscopy and optical transmission. The particles ranged in size from less than 5 to 100 nm (longest dimensions). The observation of two surface-plasmon peaks was analyzed by treating the particles as oblate spheroids in which the average shape, as determined by optical measurements, is governed by the heat treatment and evaporation thickness. The depolarizing effect of the substrate was clearly demonstrated by shifts in the frequencies of the resonance peaks. Two resonances associated with surface-plasmon modes of oscillation were observed for each of the two axes of the model oblate spheroids.

I. INTRODUCTION

It has been known for some time that condensation of metal vapors onto substrates does not produce microscopically uniform thin films.[1] Rather, thin (less than 20 nm) films of many materials appear to grow from nucleation points, often producing islands, so that electrical continuity is disturbed. Although the substrate is well below the fusion point of the evaporant, high surface mobility must be responsible for island formation. Anomolous optical behavior of such films results. Extensive investigations of gold films have been performed[2] with the conclusion that simple application of the three-dimensional Maxwell Garnett theory[3] is inadequate to describe the response of the films. A more sophisticated form of the theory replaced the spherical particles of the Maxwell Garnett theory by spheroids, considerably improving agreement with experiment.[4,5]

Recently, a greatly simplified approach was successfully used to predict the frequency, angular, and polarization dependence of thin, annealed silver films.[6] The theory considers the films to be composed of small, isolated, oblate spheroids which respond in accordance with bulk dielectric properties. Silver is attractive for study because of its low damping in the visible region, allowing the particles to respond in a resonant manner. No consideration was made for the dipolar interaction between particles[7] or interaction with the underlying substrate, although the latter effect appears[8] to be adequate to reconcile the difference between the calculated particle shape and that observed by microscopy on similarly prepared samples.[9]

Gold has also been of high interest because of its chemical inertness and because in particulate form it displays surface-plasmon resonances in the visible, as does silver. Although many studies have been done on gold-particle systems,[2,5,10–12] very little work has included polarization and angular resolution. We present in this paper a study of thin (1–5 nm) evaporated gold films on quartz. Electron microscopy was used to verify the particle nature of the films in successive anneals. Polarized optical transmission of the films from normal incidence to near-grazing are presented. A new calculation[8] of the substrate interaction with the spheroids is used and is shown to have a significant influence on the particle resonances. The present study indicates the sensitivity of the position of optical resonance to particle shape so that the shapes of particles much smaller than the wavelength of light could be determined by optical means.

II. THEORY

The basic elements of the theory have been given previously.[6] Briefly, heat-treated, metal-island films are modeled as isolated oblate spheroids with the minor axes oriented by the underlying substrate. The particles are assumed to obey a frequency-dependent, dielectric function given by bulk optical measurements. For particles small compared to the wavelength of the incident radiation, the solution to Laplace's equation in spheroidal coordinates yields conditions for resonance determined only by the bulk dielectric function and the shape (not the size, such as is evinced in retardation effects) of the particles. The two fundamental modes of dipole oscillation correspond to a surface-plasmon mode along the minor axes ($l=1$, $m=0$) and to a surface-plasmon mode along the major axes ($l=1$, $m=1$).

The substrate underlying the particles can interact with the charge oscillations, sometimes acting to depolarize the particle and thus effect a shift in the resonances. By using analogy with the problem of a thin, uniform, dielectric film on a substrate, which can be calculated exactly, the magnitude of the effect may be approximated for spheroids. The details of the calculation and comparison with experiment will be presented elsewhere.[8] Basically the quantities ϵ_{10} and ϵ_{11}, giving the conditions for resonance, in Eqs. (7) and (8) of Ref. 6, are modified in the same manner as for a continuous thin film, giving new positions and strengths for the resonances. If the particles

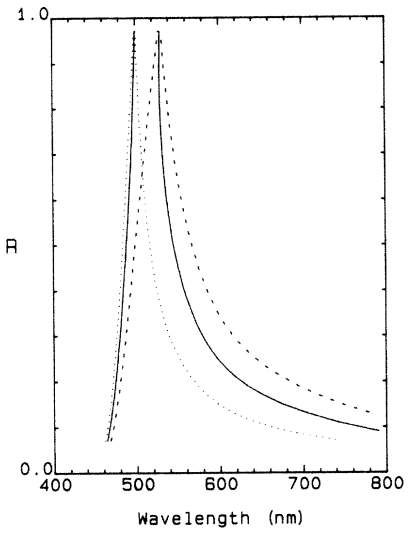

FIG. 1. Calculated position of resonance in gold spheroids as a function of minor- to major-axis ratio (R). Curves extending to short wavelengths describe surface-plasmon oscillations with charge antinodes on the minor axis ($l=1$, $m=0$), while the curves extending to long wavelengths describe oscillations with charge antinodes on the major axis ($l=1$, $m=1$). Dotted curve, particle in vacuum; solid curve, particle on quartz; dashed curve, particle fully surrounded by a medium with an index of refraction of quartz.

are totally immersed in a dielectric, these quantities are simply multiplied by that dielectric function. The results are plotted in Fig. 1 as a function of the minor- to major-axis ratio (R).

The fraction of light which is not transmitted through a film of particles is simply given by the number of particles per unit area times the effective cross section per particle. When a distribution of particle shapes is used, this quantity is the sum of the individual number density for each shape times the corresponding cross sections, assuming no overlap of cross section. Although the distribution of particle shapes could not be measured directly in this experiment, the total volume per unit area (equal to the evaporation thickness) was used as a normalizing factor to obtain the total number density.

III. EXPERIMENT

Thin films of metallic particles were prepared in a manner similar to that described earlier.[6,9] Thin (1–5 nm) metallic films of gold were deposited upon quartz substrates by electron beam evaporation and subsequently heat-treated at 100 to 800 °C for 1–4 min. Although the thickness of the films was monitored by a mass transducer during the evaporation, the exact film thickness is subject to error, especially for the thinner coatings. Desorption of the evaporant was minimized by using high deposition rates (0.2–0.5 nm/sec). The films are electrically discontinuous, having formed gold islands which reshape and coalesce upon heating. This reshaping is obvious by the color of the films which changes from purple to pink or green after annealing. Some color change was noticed even for brief anneals at only 100 °C. For electron microscopy, polished silicon substrates were used as evaporation bases. Both substrates, quartz and silicon, were prepared by evaporating about 50 nm silicon dioxide before the metallic coating in an attempt to present identical surfaces to the gold particles.

Figure 2 shows the results of annealing a 2-nm film of gold. The unannealed sample shows small islands with random shapes and sizes which become circular upon annealing. Increased annealing causes adjacent particles to coalesce, forming larger but similarly shaped particles. A micrograph of an annealed 5-nm silver film on silicon (Fig. 3) shows the oblate nature of such particles with the short axes aligned along the substrate normal. Micrographs of gold films with varying thicknesses reveal particles with major diameters of no more than 5–10 nm for 1-nm-thick films to more than 100 nm for the thicker films or for those subjected to high-temperature annealing.

Optical absorbance data were recorded by using an automatic recording spectrophotometer[13] for both p- and s-polarized light at various angles of incidence. Correction for the absorption and reflection of the substrate was made by placing an identical substrate without particles in the reference beam. The experimental data reported here are shown as recorded by the spectrophotometer.

IV. RESULTS

Figure 4 shows the optical effects of anneals upon the gold films. All films at normal incidence show a broad peak which becomes more narrow and shifts to the blue with increasing temperature of the anneal. This can be understood as a reshaping of the islands from a very flat shape (low R) to the closer sphere (high R). This trend is noticed in Fig. 1 for the ($l=1$, $m=1$) mode which is the only dipole mode activated at normal incidence. For the 800°C anneal the peak shifts slightly to the red, indicating a decrease in the average R of the particles, and broadens, indicating a wider distribution of shapes as would be expected from the micrographs.

The theory including the substrate interaction predicts that the position of resonance response is already substantially shifted from that of the particles in vacuum, particularly for the ($l=1$, $m=1$) mode of dipole oscillation. In fact, this mode is shifted at least half the difference between the unshifted case and the fully surrounded case (refer to Fig. 1). This was tested by applying xylene to the particle surface and covering with another quartz slide. The index of refraction of xylene closely matches that of the quartz and fully wets the surface. Thus the particles are immersed in an isotropic dielectric medium. The resonance position should then be described by the dashed curve of Fig. 1. For two films with different shapes, this procedure yielded experimental shifts of 32 nm for $R=0.27$ and 24 nm for $R=0.7$. Figure 1 predicts shifts of 41 and 13 nm, respectively. The differences are not too surprising considering that the model would be most accurate for very flat particles (low R) and would probably overestimate the coupling between the more spherical particles and the substrate. Also, the exact value of the bulk

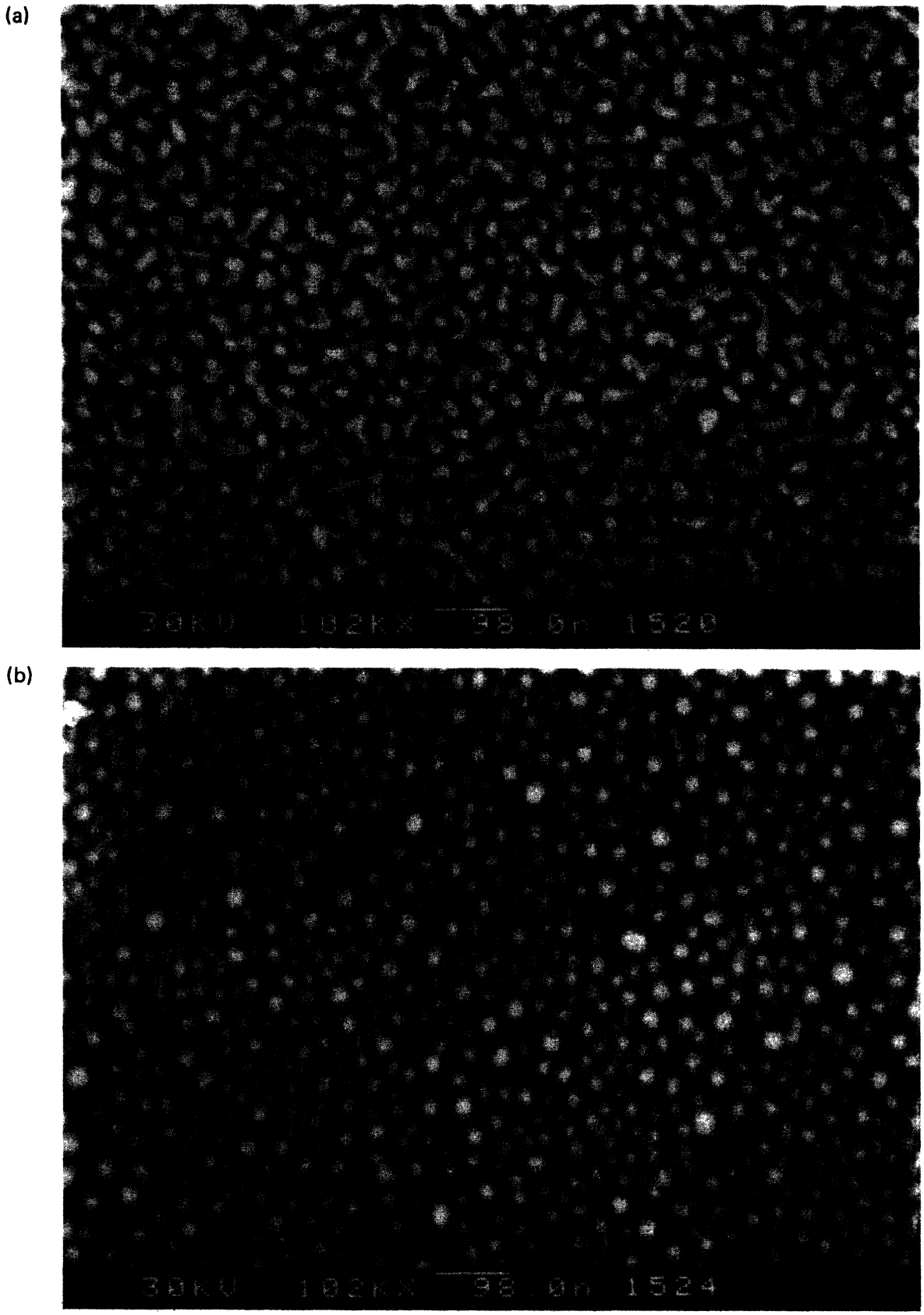

FIG. 2. Scanning electron micrographs of a gold film with an evaporation thickness of 2 nm. (a) Unheated, (b) 200 °C anneal, (c) 400 °C anneal, (d) 800 °C anneal. The duration of each anneal was 4 min. The substrate for these micrographs is silicon (to prevent charging) coated with about 50-nm silicon dioxide by electron-beam evaporation. Samples on quartz used in transmission studies were prepared at the same time. The bar indicates a length of 98 nm.

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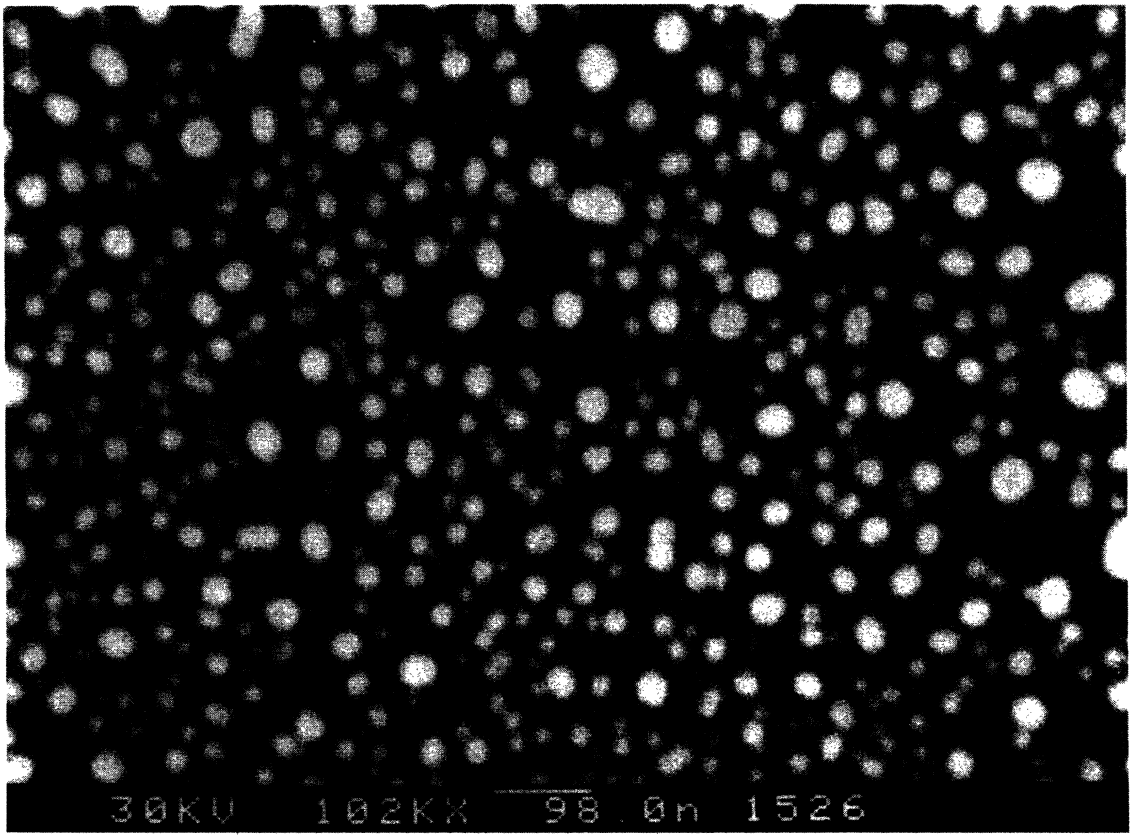

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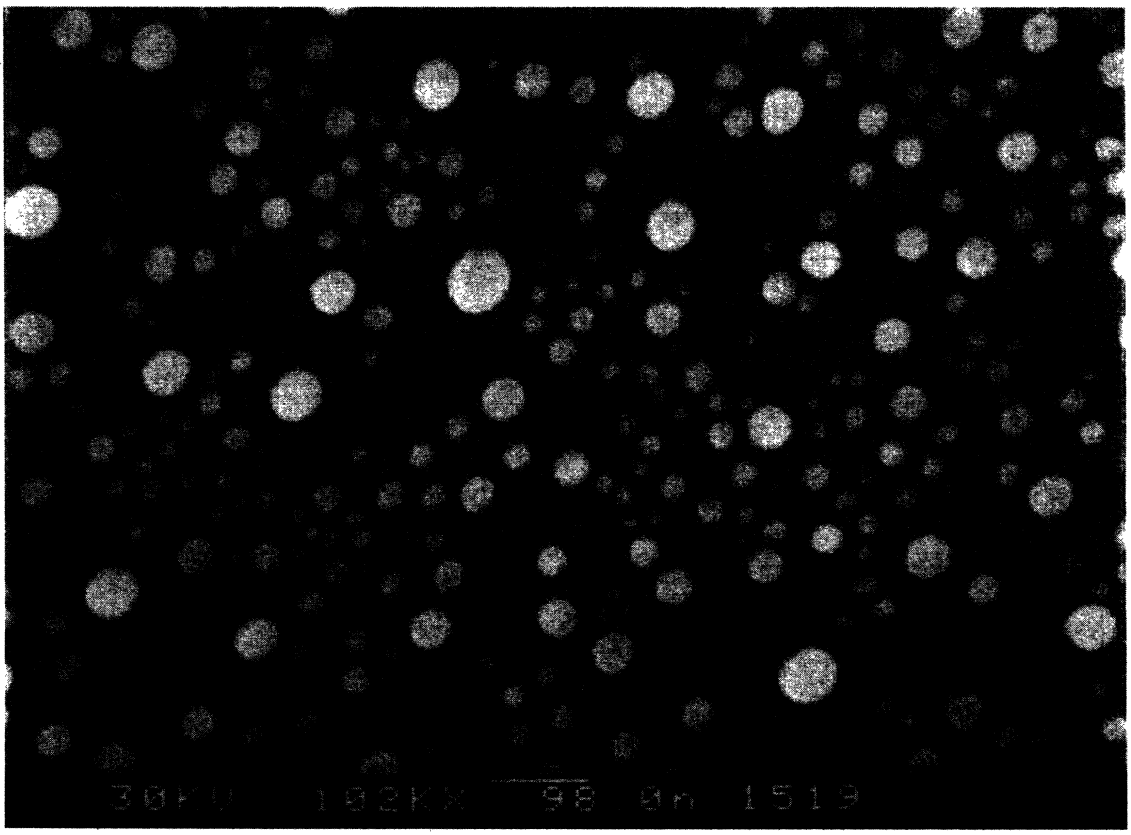

FIG. 2. (*Continued*).

FIG. 3. Scanning electron micrograph of an annealed-silver film with an evaporation thickness of 5 nm. The observation angle is 60° from normal. The oblate nature of the particles is apparent. The bar indicates a length of 32.8 nm.

dielectric function of gold is critical in determining the resonance position and, thus, the predicted shift. The shift in the ($l=1$, $m=0$) oscillation could not be verified by this method on gold, since the internal angle of illumination on the particles is less than about 43° even at grazing incidence on the cover slide, and thus this oscillation would not be clearly seen. This effect also resolves the difference between the reported R's measured by microscopy[9] and by optical transmission[6] for similarly prepared silver samples. The qualitative behavior is verified, pointing out that the particles do interact with the substrate and are shifted from their free positions.

Figure 5 presents typical angular polarized data of a moderately flat particle film produced by a 5-nm evaporation. R was determined to be about 0.25 from the position of the long-wavelength peak. For s-polarization, a single peak is observed at all angles, since the exciting electric vector of the light can only couple to the ($l=1$, $m=1$) charge oscillation of the particle which is along the major axes of the model spheroids. An increasing number of particles is intercepted by the probe beam as the angle is increased. It is not surprising that the absorbance increases with angle.

For p-polarized light, a spectrum identical to the s-

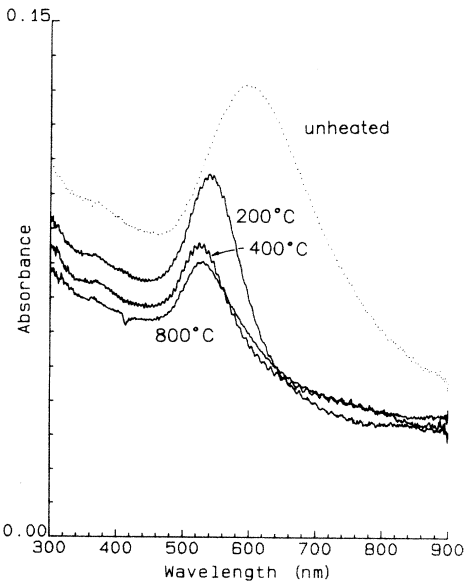

FIG. 4. Experimental absorbance at normal incidence of a thin film of gold with an evaporation thickness of about 2 nm on quartz. Anneals of 4 min at the indicated temperatures are shown.

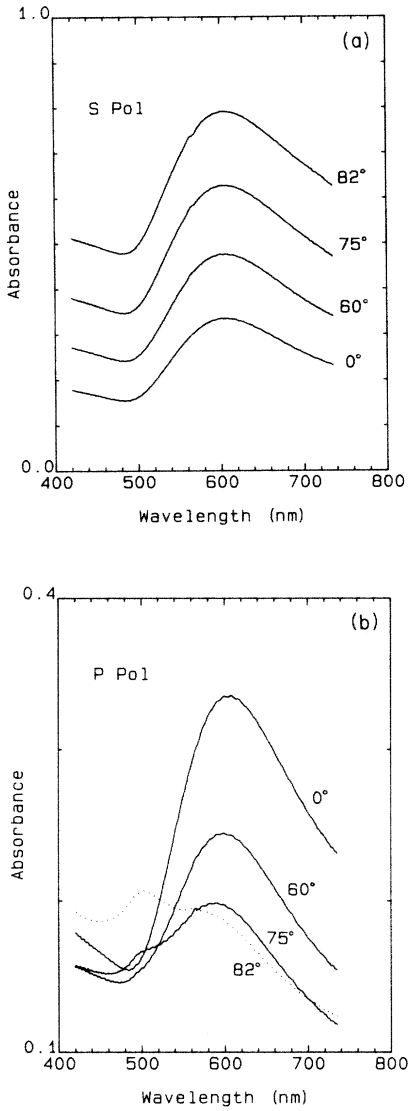

FIG. 5. Experimental absorbance as a function of angle using polarized light for a 5-nm evaporation on quartz. An identical slide at the same angle without gold was used in the reference beam. *s*-polarization is shown in (a) and *p*-polarization is shown in (b).

polarized spectrum is observed at normal incidence. At increasing angles, this peak diminishes, and at extreme angles to the normal, a short-wavelength peak near 500 nm is seen to grow with angle. This short-wavelength peak is characteristic of the ($l=1$, $m=0$) mode of charge oscillation in which the charge antinodes are situated on the minor axes of the model spheroids. This peak is much weaker than in the case of silver[6] because of the increased damping[14] of gold below 550 nm.

Shown in Fig. 6 are theoretical plots of absorbance using the bulk dielectric function for gold[14] and the total cross section,[6] calculated for a 5-nm-thick film with a Gaussian distribution of particle shapes centered at $R=0.25$ with a width of 0.1. Agreement appears to be good, considering the approximation of the particle shape to be spheroidal. Also, the angular discrimination (about

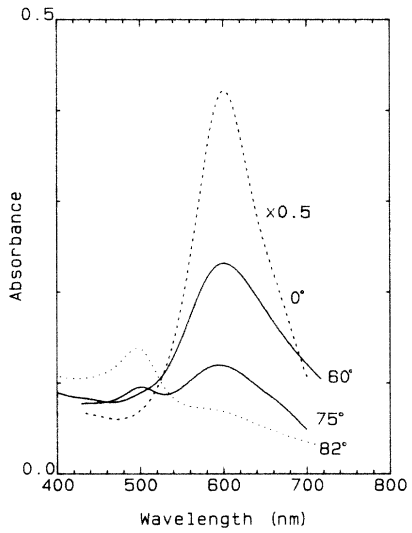

FIG. 6. Calculated *p*-polarized absorbance as a function of angle for a 5-nm gold film composed of particles with a shape given by $R=0.25$ with a width in a Gaussian shape distribution of 0.1.

50 mrad) of experimental measurement is not perfect, which can lead to errors at extreme angles. The most obvious point of disagreement is that the angular dependence of the absorbance is much stronger than the experiment indicates. Although not shown, this is true for *s*-polarized data as well. The theory is based upon single particles which do not interact with neighboring particles. Corrections must be made if, for example, particles are sufficiently close to each other for overlap of cross sections for adjacent particles to occur. The overlap would increase with angle so that the corrected theoretical angu-

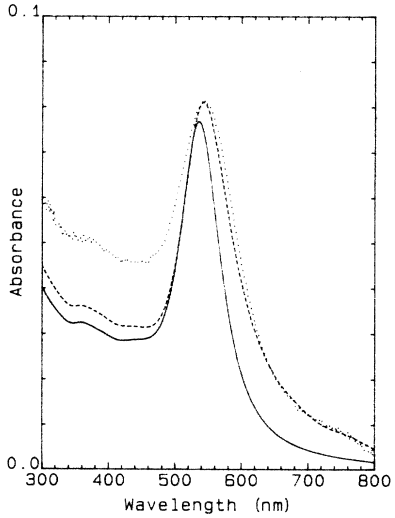

FIG. 7. Comparison of theoretical and experimental absorbance. Dotted curve, experimental absorbance of an approximately 2-nm-thick gold film on quartz annealed at 200°C for 4 min. Solid curve, theoretical absorbance using a 2-nm film thickness using a single-particle shape of $R=0.62$. Dashed curve, same as solid curve, but using a Gaussian shape distribution with a width of 0.22.

lar dependence would be weakened. The same sort of correction appears to be needed to help explain the thickness dependence as well. That is, the effective cross section is not simply proportional to the evaporated thickness. Such a calculation is beyond the scope of the present work.

For films of very small particles produced by evaporating 1—2 nm gold, agreement with theory appears to be considerably improved. For example, Fig. 7 shows a direct comparison of theory and experiment for a 2-nm film illuminated at normal incidence. The addition of a Gaussian distribution of particle shapes provides very close agreement in the Drude region (wavelengths greater than 500 nm). For extended wavelengths into the infrared, bulk optical data would need to be modified because of size-dependent scattering.[15] The experimental data in the region between 300 and 500 nm replicates the structure shown in the theory but has been displaced vertically. The speculation should not be made, however, that the particles do not behave in accordance with dielectric data from bulk measurements. The existing dielectric data on gold in this region have considerable variation according to methods used to produce the samples.[16,17] Such a variation could be used to explain the discrepancy between theory and experiment.

V. CONCLUSION

Optical transmission and electron microscopy have been used to demonstrate that annealed, thin, metallic films of gold behave as oriented oblate spheroids with a dielectric response in agreement with bulk optical properties. The substrate upon which the particles reside affects that response and was most dramatically seen as a shift in the resonance peak in which the antinodes are oriented parallel to the substrate surface. Agreement between theory and experiment is good, especially for films composed of very small particles.

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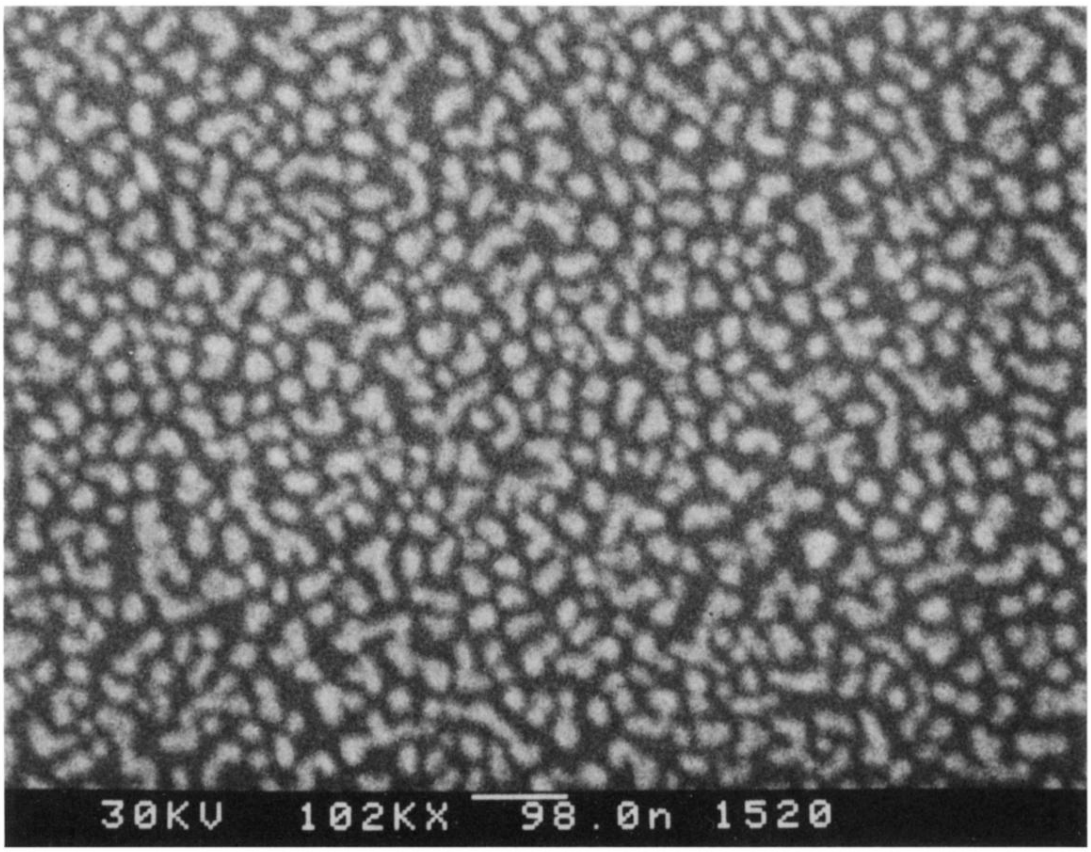

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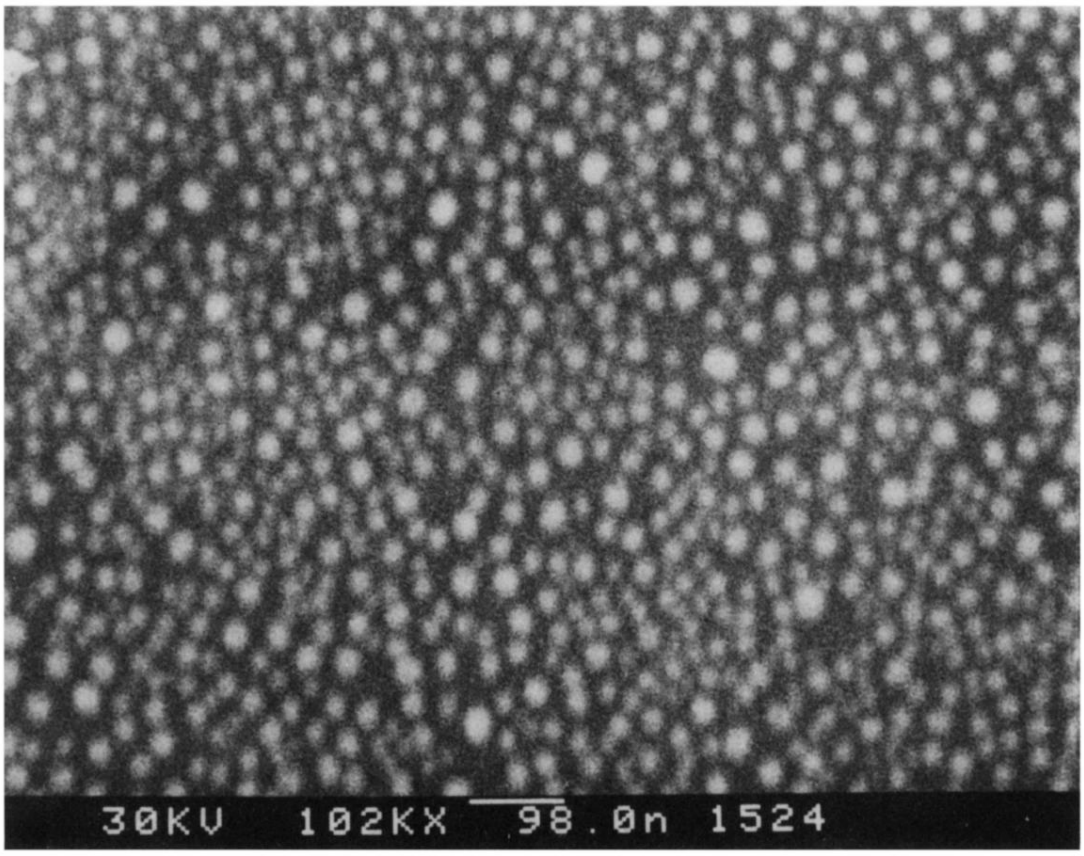

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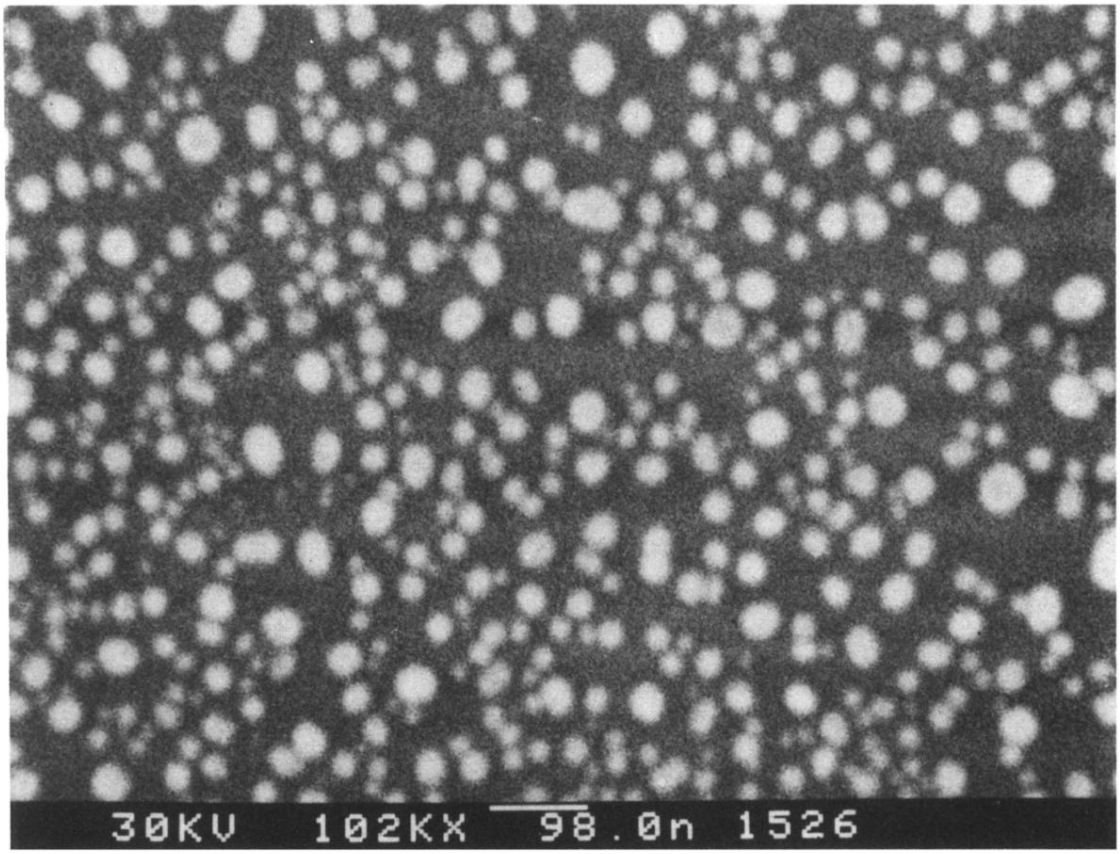

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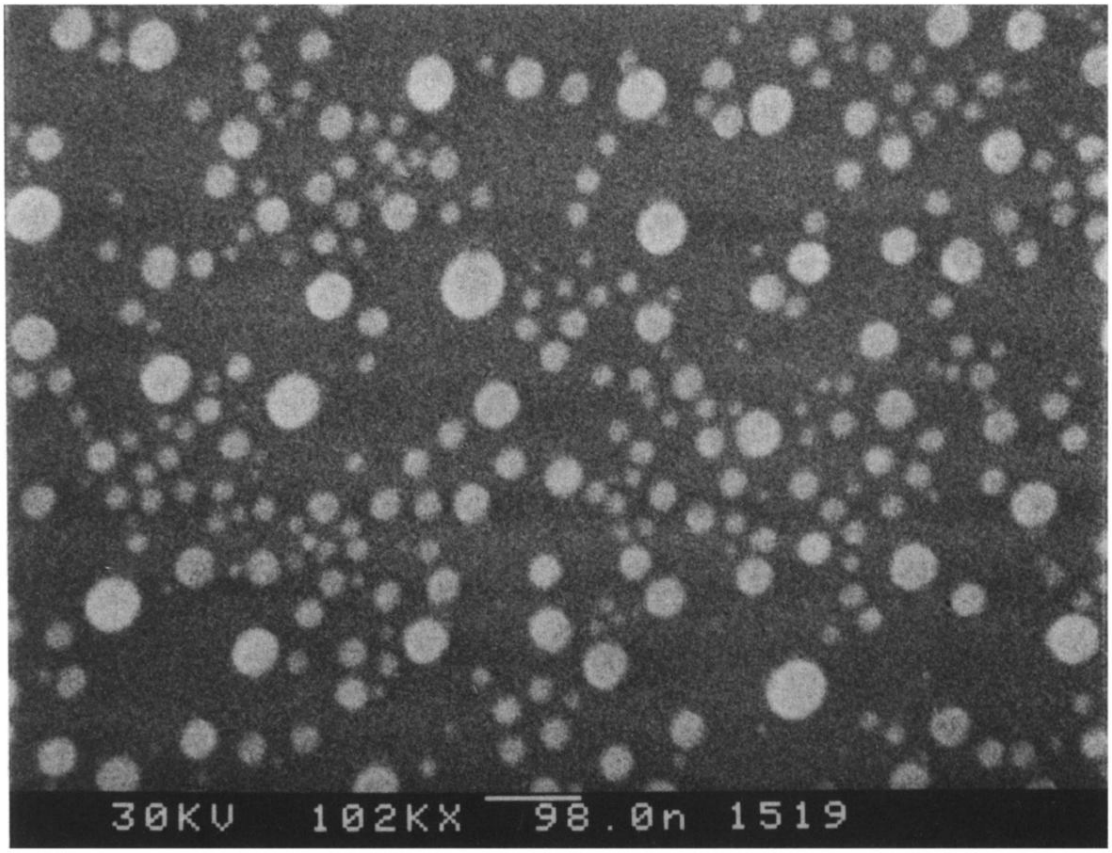

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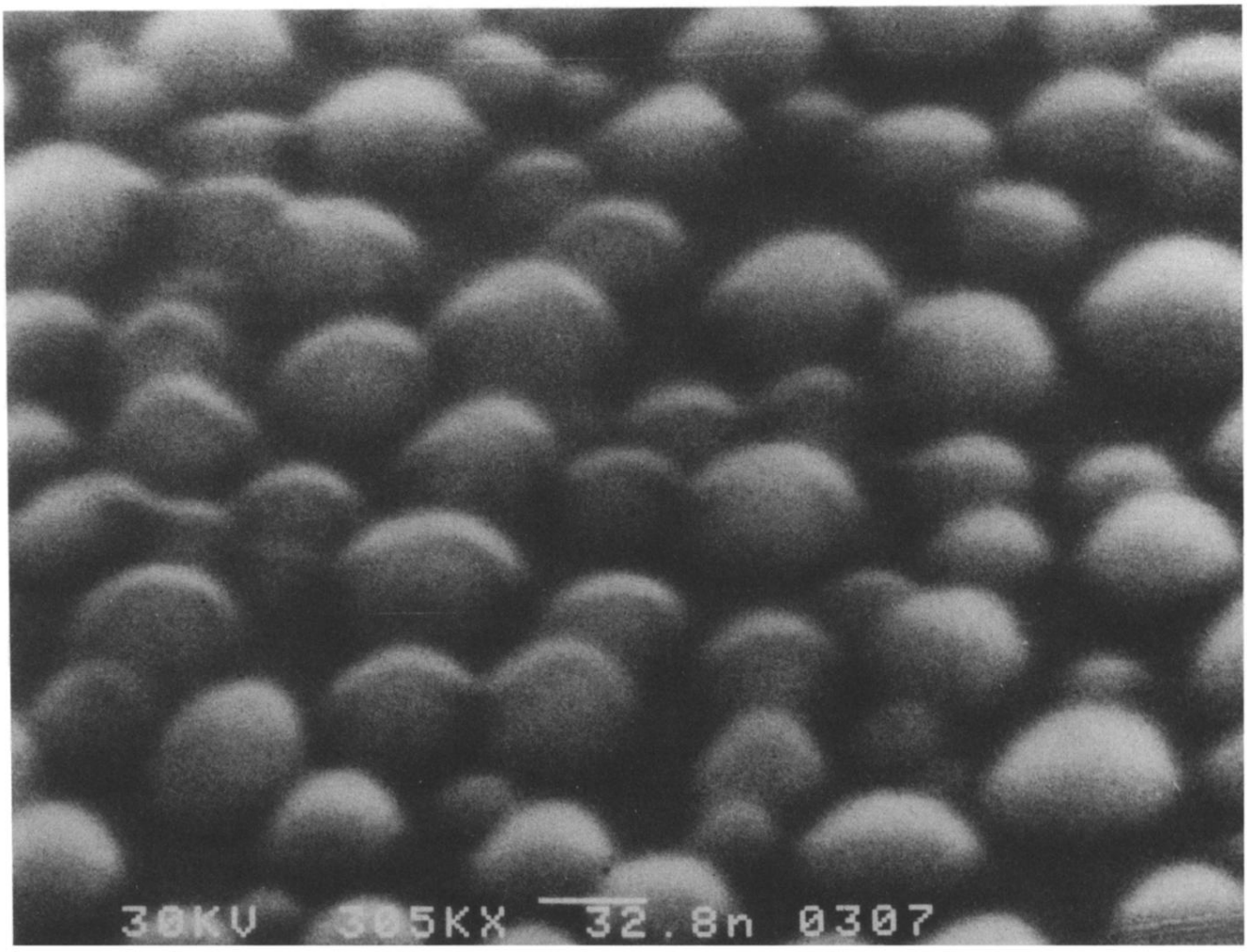

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