

Surface plasmons in granular Ag-SiO₂ films*

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We report the first observation of surface plasmons in a granular metal. The plasma frequency ω_p in the Ag-SiO₂ system is determined from plasma resonance absorption measurements over the entire range of composition from the continuous-metal-film limit to the isolated-metal-particle limit. The observed decrease in ω_p with increasing insulator concentration is understood within the framework of the phenomenological Maxwell-Garnett theory.

Surface plasmons¹ have been studied extensively both in continuous-metal films²⁻⁸ and in isolated-metal particles.⁹⁻¹³ However, there have been no reported experimental studies of surface plasmons in particulate systems for which the isolated-particle approximation breaks down. Granular metals¹⁴ are ideal materials in which to study surface-plasmon behavior, because the interparticle distance can be varied by varying the volume fraction x of the insulator component. When x is small the metal grains coalesce, forming a metallic continuum with dielectric inclusions. In the limit $x \rightarrow 1$, the inverse structure is obtained with isolated crystalline metal grains dispersed in a dielectric matrix. A transition between these structures occurs in the intermediate range of composition.

In this paper we report the first observation of surface plasmons in a granular metal. We have studied the Ag-SiO₂ system for $0 \leq x \leq 0.85$ using the plasma resonance absorption technique.⁸ This is the first material for which the evolution of the plasma frequency has been followed from the continuous-metal-film limit to the isolated-metal-particle limit. Our results agree well with the predictions of the Maxwell-Garnett theory.

Granular Ag-SiO₂ films were prepared as described in Refs. 15 and 16. The weight fractions of Ag and SiO₂ (determined spectroscopically) together with the measured film density, were used to determine the volume fraction x of insulator in the granular metal to an accuracy of $\pm 5\%$. While the densities of the sputtered silver and SiO₂ films were found to be equal to those of the bulk materials (within an experimental uncertainty of $\pm 3\%$), the densities of the granular metals were substantially lower than would be expected from a void-free composite of silver and vitreous silica. In view of the extreme immiscibility of Ag and SiO₂, it is likely that the silica does not completely fill the space between the Ag particles, and the resulting voids are responsible for the observed density depression. We concluded that the silver in our Ag-SiO₂ samples did have the bulk density since electron diffraction and electron microscopy showed

it to be in the form of crystalline grains with a lattice constant equal to that of bulk silver. The voids produce an average insulator density S_i lower than that of bulk SiO₂. When plotted against total volume fraction x of insulator, the void concentration is a bell shaped function which is zero at $x=0, 1$ and which reaches a maximum near $x=0.5$ (the composition at this point, expressed as volume fractions, is 0.5 Ag, 0.3 SiO₂, and 0.2 voids).

Transmission electron micrographs, shown in Fig. 1, were obtained from 300-Å-thick films sputtered onto carbon film substrates supported by a fine copper mesh. Coalescence of the silver particles due to heating by the microscope electron beam¹⁵ was suppressed by overcoating the granular metal films with a thin layer of carbon.

Polarized absorption measurements were made in the wavelength range 3000–5000 Å on 400-Å-thick films supported by quartz substrates. The samples were oriented so the incident light impinged at an angle of 60° to the film normal. Measured spectra for films with $x=0.08$ and 0.61 are shown in Fig. 2. The p -polarized wave is absorbed at a wavelength corresponding to the plasma frequency, whereas the s -polarized wave does not couple to the surface plasmon and no absorption is observed. In metal-rich films (small x) the absorption peak was well resolved [Fig. 2(a)]. However, in the dilute limit the absorption was quite small [Fig. 2(b)] and identification of a peak in the p -polarized spectrum was difficult. Since the s -polarized wave does not excite plasmons, the spectrum observed with this polarization of light represents a background absorption level in the vicinity of the plasma resonance peak. Therefore, the s -polarized spectrum was subtracted from the p -polarized spectrum to enhance the absorption peak.

We have analyzed our results in terms of the phenomenological Maxwell-Garnett theory, generalized to include nonspherical particles.¹⁵ The theory takes into account the modification of the incident electromagnetic \vec{E} field by the dipole fields of the individual polarizable silver grains and provides a relationship between the frequency depen-

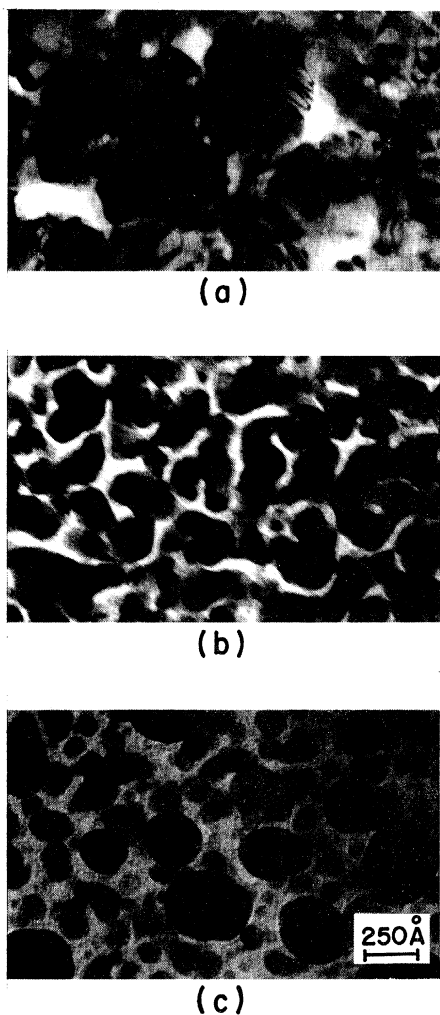


FIG. 1. Electron micrographs of three representative samples having different volume fraction x of insulator: (a) $x=0.25$, (b) $x=0.5$, and (c) $x=0.7$.

dent dielectric constant $\epsilon(\omega)$ of the composite material and the dielectric constants $\epsilon_m(\omega)$ and $\epsilon_i(\omega)$ of its metal and insulator constituents, namely,

$$\frac{\epsilon(\omega) - \epsilon_i(\omega)}{L_m \epsilon_m(\omega) + (1 - L_m) \epsilon_i(\omega)} = (1 - x) \times \frac{\epsilon_m(\omega) - \epsilon_i(\omega)}{L_m \epsilon_m(\omega) + (1 - L_m) \epsilon_i(\omega)}, \quad (1)$$

where L_m is the depolarization factor corresponding to the shape of the metal particles. Equation (1) is not valid in the metal-rich limit since the material then consists of dielectric inclusions in a continuous metal matrix and the dielectric constant is properly described by inverting the roles of the metal and insulator components. This is accomplished by performing the transformation

$\epsilon_m \leftrightarrow \epsilon_i$, $(1 - x) \rightarrow x$, and $L_m \rightarrow L_i$ in Eq. (1).

The plasma frequency is defined as that frequency for which $\text{Re}[\epsilon(\omega)] = 0$.¹⁷ Substituting values¹⁸ for $\epsilon_i(\omega)$ in Eq. (1), we solved for the values of $\epsilon_m(\omega)$ that satisfied this condition, and subsequently determined ω_p using the dielectric constant data for bulk silver published by Ehrenreich and Philipp.¹⁹ Following Cohen *et al.*¹⁵ we have also determined the dependence on x of λ_A , the wavelength for which $\epsilon_2(\omega)$ of the granular metal reaches a local maximum due to the singularity in the expression for the local field. Our experimental measurements of the dependence of $\lambda_p (= 2\pi c/\omega_p)$ and λ_A on x , together with the behavior predicted by Eq. (1) for spherical ($L_m = \frac{1}{3}$) and cylindrical ($L_m = \frac{1}{2}$) particles, are shown in Fig. 3.

For $x > 0.45$, a good fit to the data is obtained by treating L_m as an adjustable parameter with a value of 0.385, corresponding to prolate spheroids having an axial ratio of ~ 1.2 . This is consistent with the particle shapes observed in the electron micrographs [Fig. 1(c)]. However, the value of L_m for nonspherical particles depends upon their orientation relative of the \vec{E} vector of the excited mode. Since our samples are composed of randomly oriented particles (Fig. 1), it is not strictly meaningful to characterize a sample by a single depolarization factor. It is interesting, nonetheless, that the data can be fit rather well over a large range of composition with a single parameter

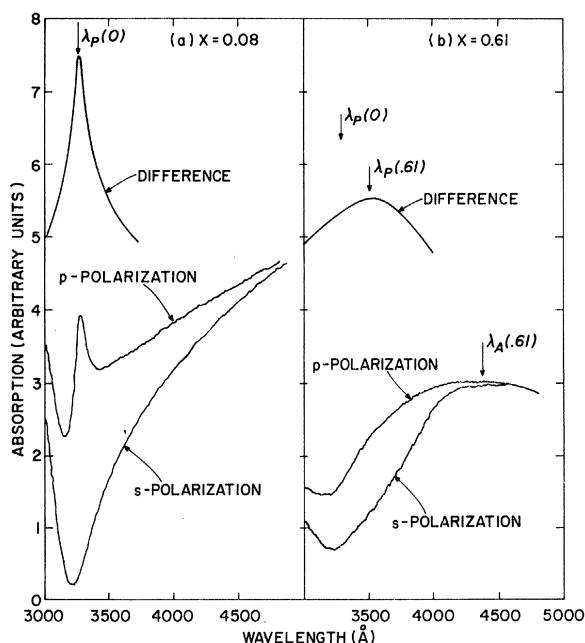


FIG. 2. Absorption spectra for the two polarizations of incident light: (a) $x=0.08$ volume fraction and (b) $x=0.61$ volume fraction insulator. Also shown is the difference between the s - and p -polarized spectra.

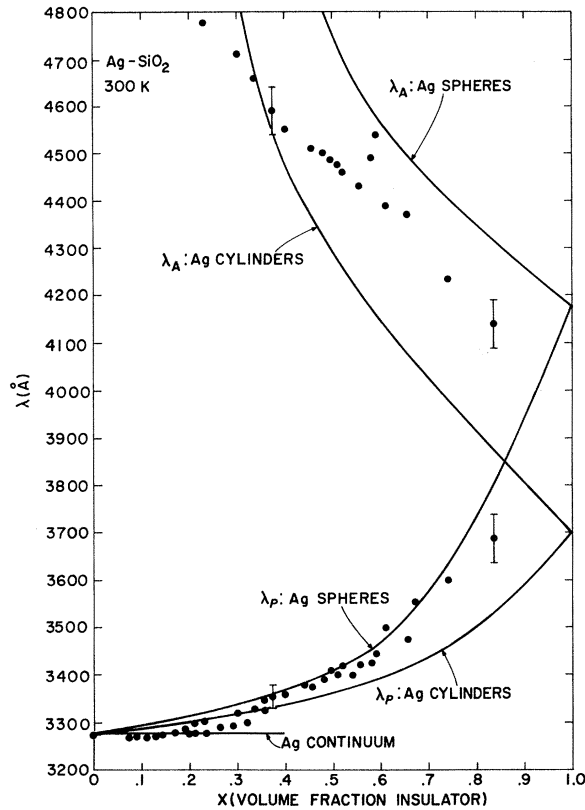


FIG. 3. Plot of the experimental data points for λ_p and λ_A as a function of volume fraction insulator. Also included are curves calculated using a generalized Maxwell-Garnett theory for spherical and cylindrical silver particles.

L_m . As x is reduced below 0.6 the Ag particles begin to coalesce and their shapes become complex [Fig. 1(b)]. This structural transition is manifested in the optical measurements as a gradual change from near-spherical to near-cylindrical particles (the change is not as evident in the λ_p data as it is in the λ_A data because the effect of particle shape on λ_p is smaller than it is on λ_A). In contrast to this gradual change in the optical properties, the dc electrical resistivity (Fig. 4) indicates an abrupt transition from nonmetallic to metallic behavior near $x=0.6$. This difference is not unreasonable if one considers the physical processes involved. At the percolation threshold^{16,20,21}

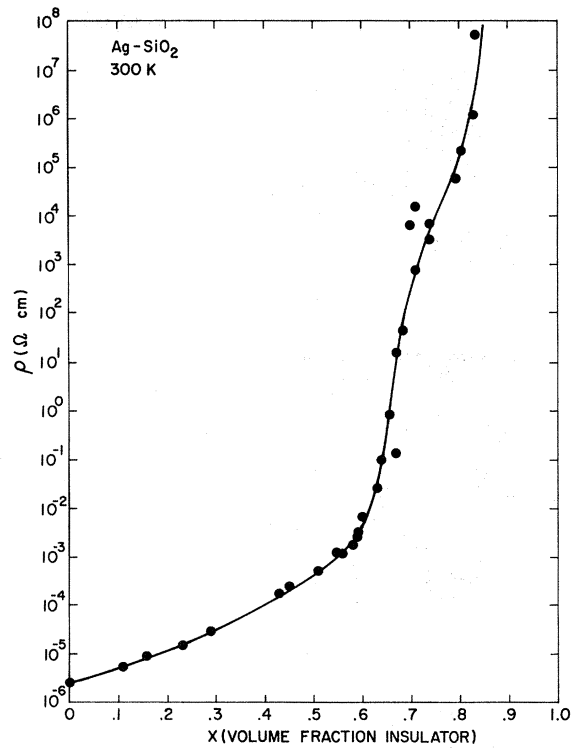


FIG. 4. Plot of the measured resistivities as a function of volume fraction insulator.

it takes very few conductive channels to produce the observed abrupt change in resistivity. Thus, the electrical transition occurs at concentrations for which the Ag particles have just begun to coalesce. On the other hand, it requires a much greater degree of coalescence to alter the optical behavior appreciably, and the optical transition occurs for smaller values of x and over a broader range. In the very metal rich samples [$x \lesssim 0.2$, Fig. 1(a)], the observed plasma frequency is independent of composition, in agreement with the theory when the roles of the metal and insulator are inverted.¹⁵

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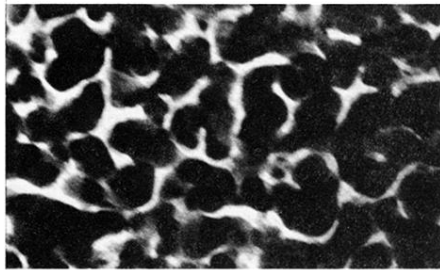
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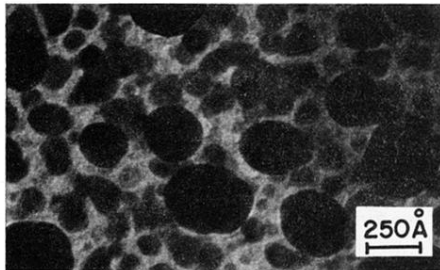
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(a)



(b)



(c)

FIG. 1. Electron micrographs of three representative samples having different volume fraction x of insulator: (a) $x=0.25$, (b) $x=0.5$, and (c) $x=0.7$.