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Topological considerations in the optical properties of granular composite films

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Extensive measurements have been made on the optical properties of two gold-dielectric composite systems which exhibit distinctly different topologies. The agreement between optical data, topological observation, and simple composite media theories demonstrates the dominant effect of topology in determining the optical response of heterogeneous materials.

Since Faraday[1] there has been strong interest in the development of a satisfactory description of the electromagnetic properties of heterogeneous materials. Recently, there has been an upsurge in activity in this field,[2–4] with the optical properties of composite media becoming a particular concern. This interest has been sparked in part by the possibility of new technological applications of composite materials,[5,6] and in part by the availability of new theoretical approaches.[2,7] Until now, however, the experimental data[8–11] available to test rigorously the various theoretical models have been very limited, and previous investigations did not include correlations of optical data with topological observations.

In this Communication we briefly report on the results of extensive measurements of the intrinsic optical properties of dielectric-metal (cermet) composite films in the dielectric rich regime. These results conclusively demonstrate that there are at least two general classes of optical behavior that can be encountered in composite media; that these two classes of behavior are unambiguously correlated with the particular microtopology of the composite; that previously reported[10,11] "anomalous behavior" of certain composite films is a result of differences in topology, and that the simple mean-field approaches to the problem provide adequate descriptions of the phenomena.

To substantiate these conclusions, we present data on two different gold composites, Au-Al_2O_3 and Au-MgO. These samples were produced in uniform composition, thin film form by controlled evaporation from individually controlled Au and dielectric sources, as described elsewhere.[12] Films were produced with metallic volume fraction ranging from 0.02 to 1.0. Transmission electron microscopy studies[12] of the two composite systems reveal radically different microstructures. The Au-Al_2O_3 system displays grains of gold randomly dispersed in an amorphous oxide matrix with the grain size varying from $\lesssim$50 to $\sim$200 Å as the metal fill fraction is increased. This topology is typical of that exhibited by metal-Al_2O_3 and metal-SiO_2 composites. The Au-MgO cermet exhibits small ($\sim$50 Å) indistinguishable and interspersed crystallites of the two constituents. This topology is exhibited by most composites having a MgO or alkali-halide dielectric components. A basic aspect of essentially all cermet composites is the formation of thin $\lesssim$10-Å insulating coatings onto the metallic grains during deposition. The existence of such stabilizing coatings on both gold composites was verified by our studies[12] of spatially graded composition films which showed that even in areas of high ($\gtrsim$50 at.%) Au concentrations, growth of individual grains is favored over establishment of percolation paths. As shown below, these coatings must be included in a proper analysis of the optical behavior of composite films.

The intrinsic optical constants, n and k, of the Au composites were obtained from computer inversion of the results of transmittance and reflectance measurements.[12,13] The intrinsic optical constants are much more sensitive to the nature of the films than are simple transmittance measurements as presented in the past[2,4,14] and thus our data facilitate a much more exacting test of the theoretical descriptions than has previously been possible.

Two different theoretical models have been commonly used in attempts to describe the optical response of composite materials. One is the approach popularized by Maxwell Garnett (MG), the other, the Bruggeman self-consistent theory (BSC) as recently discussed, for example, by Lamb *et al.*[15]; these two theories should be appropriate for topologically distinct cases. In its form of interest here, the MG theory considers cermet composites to consist of metallic inclusions imbedded in a dielectric matrix; the BSC theory considers the cermet constituents to be on a topologically equivalent basis. The obvious assumption is then that the MG theory should be most appropriate for composites of the Au-Al_2O_3 type, while the BSC theory should be applicable to Au-MgO-type systems. This is the case.

In its simplest form the MG theory yields, for the polarizability of small spherical particles (we assume spherical particles throughout this paper),

$$\epsilon_{MG}=\epsilon_0\frac{2\epsilon_0(1-f)+\epsilon_1(2f+1)}{\epsilon_0(f+2)+\epsilon_1(1-f)}\ ,$$

where ϵ_0 is the dielectric constant of the host medi-

um, $\epsilon_1=\epsilon_1(\omega)$ is the dielectric function of the metal, and $f=v_m/(v_m+v_d)$ is the volume fraction of metal in the composite. This theory is applicable only for fairly low ($f<0.35$) fill fraction cermets, and cannot be expected to predict a percolation threshold, as it is based on the long-range dipolar interactions between particles.

The BSC theory is a mean-field approach to the dielectric response of a composite medium. For the case where the two components are treated symmetrically, the response ϵ_B is defined by

$$\frac{3f}{2+\epsilon_1/\epsilon_B}+\frac{3(1-f)}{2+\epsilon_0/\epsilon_B}=1 \ .$$

Wood and Ashcroft[7] have extended this theory to describe a "correlated three component system" where the metal particles are coated with a thin layer of dielectric. The coated particles are then treated symmetrically with the bulk of the oxide. In this system, the dielectric response is described as before, except that ϵ_1 is replaced by

$$\epsilon_1'=\epsilon_0\frac{2Q^3(\epsilon_1-\epsilon_0)+(2\epsilon_0+\epsilon_1)}{(2\epsilon_0+\epsilon_1)-Q^3(\epsilon_1-\epsilon_0)} \ ,$$

where $Q=1-t/R$; t is the coating thickness, and R is the sphere radius including the coating.

These two theories predict different behavior for the two composites as the fill fraction of metal is increased. For low fill fractions, the predictions are nearly identical, since there is a little topological distinction between the two descriptions. At intermediate fill fractions, the MG theory exhibits a sharp peak in the extinction coefficient k, owing to the small particle resonant absorption. (Here we are assuming a free-electron-like metal.)

The BSC theory shows a much broader absorption spectrum peaked at longer wavelengths. At high fill fractions, the MG theory is no longer applicable, and the BSC theory predicts an increasing k in the long-wavelength region. For the simple BSC theory, this threshold occurs at $f=\frac{1}{3}$. With a thin stabilizing coating, the onset of the positive slope in k at large λ occurs at higher fill fractions.[7]

In comparing theoretical predictions to experiments, the experimentally determined values of the dielectric constant for the bulk metal[16] were modified to take into account surface and impurity scattering.[12] The best results were obtained assuming a scattering time of $\tau=0.37$ fsec for the Au-MgO composites and $\tau=0.7$ fsec for Au-Al_2O_3. The choice of this one parameter is not critical; somewhat different values would not change the conclusions of this paper. The dielectric constants of the oxides were taken to be real and constant over the range of the measurements ($\epsilon_0=3.0$ for MgO, $\epsilon_0=2.56$ for Al_2O_3). These values are measured dielectric constants for the pure evaporated oxides. In all cases the coating parameter Q was taken to be 0.98, in accord with transmission electron microscopy observations. The precise choice of Q is also not critical to the comparison with experiment.

Comparisons between calculations and the representative experimental results for the optical constants n and k are displayed graphically in Figs. 1–3. Figure 1 shows n and k for low-fill-fraction films of both cermets, along with calculations of the MG and BSC theories. There is good agreement between the experiment and theory, except in the short-wavelength region of the Au-Al_2O_3 composite, where the experimental value of k is greater than either theoretical prediction and exhibits only one peak. This behavior has been seen before[13] in transmittance measurements. Electron diffraction studies of Au-Al_2O_3 composites in the low-f regime show that, unlike the case for Au-MgO, the small Au particles are highly disordered or amorphous. Consequently, the two peaks in k predicted from the interband transitions in pure bulk Au are not observed, as these transitions are modified by the disorder. Calculations (to be presented elsewhere) made using the optical constants for liquid gold[17] show the single-peak structure we observe. Only as f (and particle size) increase do good crystalline order and the bulklike interband optical absorption develop.

Figure 2 shows the intermediate regime, where both theories should be applicable, and where the topology makes a significant difference in the predictions for the two systems. The AuMgO cermet does not exhibit the so-called dielectric anomaly[2,10,11] or

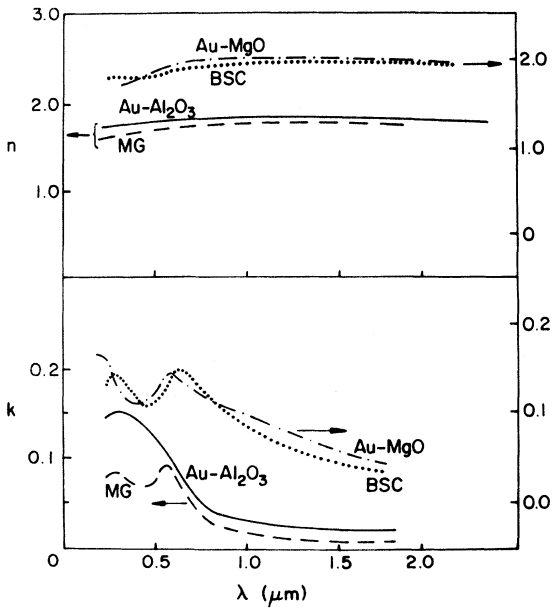

FIG. 1. Low-fill-fraction composites. Au-Al_2O_3 and MG calc, $f=0.04$; Au-MgO and BSC calc, $f=0.07$.

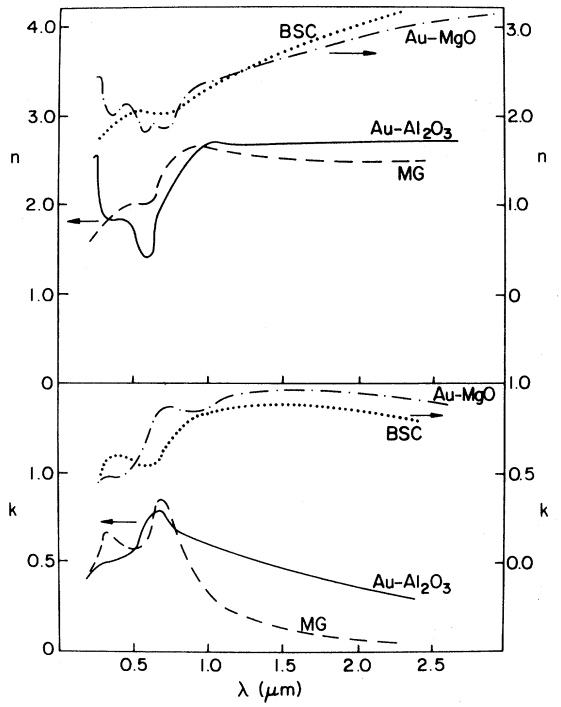

FIG. 2. Intermediate fill fraction; $f=0.3$ for all curves.

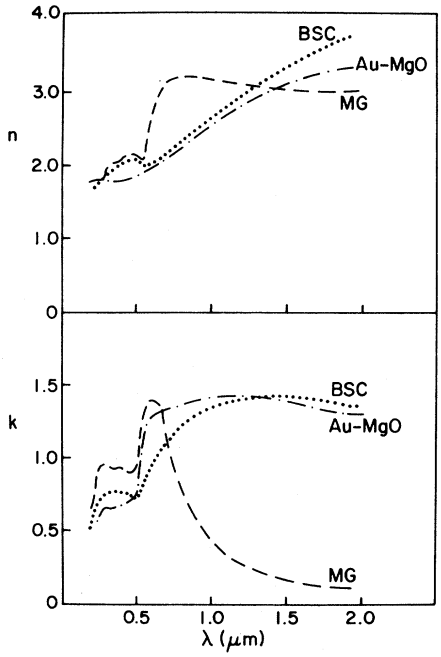

FIG. 3. High fill fraction; $f=0.4$ for all curves.

absorption peak near 5000 Å shown by Au cermets with the inclusion topology. The Au-MgO cermet does reproduce the prediction of the BSC theory. The Au-Al_2O_3 cermets exhibits the absorption peak and aside from an excess infrared (ir) absorption, Au-Al_2O_3 follows the MG prediction. The excess ir absorption is attributed to impurity and defect states in the oxide. The conclusion is based partly on measurements on composites with more reactive metallic components (e.g., Fe, V), where a nearly flat and featureless absorption curve is invariably obtained from the amorphous, partially reacted composites.

Figure 3 shows a higher-fill-fraction regime, near that at which the BSC theory predicts an increasing k at long wavelength. The Au-MgO system clearly displays the behavior predicted by the BSC theory. For Au-Al_2O_3, at $f \gtrsim 0.4$ there is very poor agreement with the MG prediction and thus no comparison is shown. This result is not surprising; the topology of Au-Al_2O_3 as it approaches the percolation limit ($f \approx 0.5$) begins to depart significantly from that assumed by the MG theory, and the long-wavelength assumption is no longer satisfied. For $f \gtrsim 0.5$ the agreement between the BSC theory and Au-MgO results also begin to breakdown. This can also be explained as a result of a change in topology; the dielectric coatings rapidly disappear as f varies in this region and dc conductivity develops, yielding a different optical response.

These data demonstrate the validity of the simple MG and BSC theories when applied to appropriate topological systems in the dielectric-rich regime. Good agreement with experiment is obtained without invoking distributions in particle size or shape. The inclusion of the effect of experimentally observed dielectric coatings on the metal particles extends the applicability of the theory to higher fill fractions for MgO-type composites. The existences of these oxide coats at intermediate fill fractions is demonstrated by the onset of metallic conduction in these and other systems (2) at fill fractions higher than those predicted by the simple theory.

Results essentially identical to those shown here have been obtained with other composite films, including Ag-Al_2O_3, Ag-MgO, and Ni-MgO, and Ni-Al_2O_3 films. In all instances the optical behavior follows the MG prediction in the dielectric-rich regime for composites with amorphous oxide constituents, whereas the behavior of composites with crystalline oxide constituents follows the BSC predictions.

While not of central concern here, the transition from the insulating to metallic regime is an intriguing, and difficult, problem, particularly as it is associated with changes in composite topology. Sheng[2] has proposed a solution for a composite of the Au-Al_2O_3 type by considering the composite to be a mixture of two different topologies (one which predominates at low f, the other at high f) with the relative proportions of the mixture and particle shape changing with f. Good qualitative agreement with transmittance measurements on Au-SiO_2 films (2) is obtained. A similar treatment adapted to composites of the Au-

MgO type is straightforward. Comparison of our optical constant data with such calculations will be presented elsewhere. We note, however, that this dual topology model, while illuminating, contains several additional parameters which make its predictive value somewhat limited. Furthermore, the suitability of any effective medium theory in the metallic regime where the long-wavelength assumption may not be valid is a fundamental concern.

In summary, we have investigated the optical properties of two gold-oxide cermet systems with distinctly different topologies. These two systems are well described over broad spectral and fill fraction ranges by two theories based on different topological assumptions and on the existence of oxide coats. The agreement between optical data, topological observations, and theory clearly establish the dominant effect of topology in determining the optical response of heterogeneous composite materials.

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