Spectral density analysis of the optical properties of Ni-Al₂O₃ nano-composite films.

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ABSTRACT

Thin films consisting of transition metal nanoparticles in an insulating oxide exhibit a high solar absorptance together with a low thermal emittance and are used as coatings on solar collector panels. In order to optimise the nanocomposites for this application a more detailed understanding of their optical properties is needed. Here we use a highly efficient recently developed numerical method to extract the spectral density function of nickel-aluminum oxide (Ni-Al₂O₃) composites from experimental data on the dielectric permittivity in the visible and near-infrared wavelength ranges. Thin layers of Ni-Al₂O₃ were produced by a sol-gel technique. Reflectance and transmittance spectra were measured by spectrophotometry in the wavelength range 300 to 2500 nm for films with thicknesses in the range 50 to 100 nm. Transmission electron microscopy showed crystalline Ni particles with sizes in the 3 to 10 nm range. The spectral density function shows a multi-peak structure with three or four peaks clearly visible. The peak positions are influenced by particle shape, local volume fraction distributions and particle-particle interactions giving rise to structural resonances in the response of the composite to an electromagnetic field.

Keywords: nanocomposite, thin films, optical constants, spectral density, structural resonances, sol-gel deposition

1. INTRODUCTION

Nanocomposite thin films consist of a mixture of two or more materials, which are present as separate phases. The simplest ones are two-phase composites, where at least one of the phases is present as nanoparticles or in nanocrystalline form, while the other can be nanocrystalline or amorphous. The composite can be designed so that its physical properties will take any value between those of the constituents, by properly tailoring the volume fractions of the constituents, as well as the nanostructure. Hence nanocomposites are of much interest for a variety of applications and this has led to a large interest in the theoretical description of their structure as well as their effective physical properties^{1,2}.

The use of nanocomposite films can also give a large freedom in the design of optical thin film systems, because they can exhibit a large variety of optical properties. Nanocomposite films can be treated in the same way as homogeneous thin films as long as the diameter of the nanoparticles or nanocrystallites is much smaller than the wavelength of the incident electromagnetic field. In this so called quasistatic limit, the optical properties can be conveniently described by an effective dielectric permittivity. The calculation of the effective dielectric permittivity, or equivalently the effective electrical conductivity, of composites have occupied researchers for more than a century, at least since the calculation of Maxwell³ of the effective conductivity of spherical particles dispersed in a homogeneous matrix. A number of reviews trace the history of the subject⁴ as well as summarize the state of the art⁵⁻⁸. The subject gained considerable interest due to the development of selective solar absorbing coatings for solar collectors during the 1970's and 1980's^{9,10}. These coatings exhibit a high solar absorptance together with a low thermal emittance, thereby diminishing thermal radiative losses from the collector plate. Indeed, today most commercial solar absorbing coatings, produced by thin film deposition methods such as electrodeposition, sputtering and sol-gel deposition, employ nanoparticulate or nanocomposite coatings¹¹. A thorough understanding of the relationship between optical properties and nanostructure is very important for designing coatings for this application.

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The effective dielectric permittivity is a function of the dielectric permittivities of the constituents and their volume fractions, as well as the details of the nanostructure. It was realized quite early that effects of particle shape can be treated by introducing depolarization factors and the case of an ellipsoidal particle was studied¹². It follows that the optical properties of ellipsoidal particles with random orientation in a matrix can be described by using a triplet of depolarization factors, which sum up to unity. A continuous distribution of ellipsoidal shapes was sometimes assumed in order to describe the optical properties of complex nanoparticle aggregates¹³. During the 1970's this formalism was extended to treat dipole-dipole and multipole interactions between particles by introducing a distribution of depolarization factors to describe the structural resonances of a nanoparticle system¹⁴⁻¹⁶. Computations of these resonances for a number of geometries, for example cubes¹⁴, pairs of spheres¹⁶, a number of chains and clusters¹⁷, as well as spheres on a lattice¹⁸ were carried out. The theoretical basis of this description was further developed by Bergman¹⁹, and later used by him and Milton to derive rigorous bounds on the dielectric permittivity^{20,21}. They showed that it is possible to describe the structural effects on the effective dielectric permittivity in terms of a spectral density function (SDF), in the case of a two-phase composite. This has a number of important consequences: (1) An exact description of the optical properties of nanocomposites would require an exact description of their nanostructure – something which is seldom possible in practise. (2) The nanostructure can be described by the spectral density function, but there exist no simple relation between them. (3) The spectral density function can in principle be determined from experimental data, provided that the volume fractions and effective dielectric permittivities of the constituents are known.

The progress in this field of research has been slow. Computations of the spectral density for model systems are of interest mainly in cases, where experimental samples are well characterized, or exhibit an ordered structure. In the majority of cases nanoparticles are distributed in a disordered structure and detailed comparison with theory is a challenge. Progress has also been hampered by the difficulty to invert experimental optical data to obtain the SDF. The mathematical inversion is known as an ill-posed problem, and efforts to compute the SDF from experimental optical data have been intermittent. The Aachen group fitted mostly infrared data for a number of materials including metal-insulator composites, porous materials and insulator composites using the SDF formalism. Much of this work has been summarized in a longer and a short review^{7,22}. Day and coworkers developed a nonlinear least square fitting technique with imposed constraints²³ and used it to analyze far infrared data for insulator composites²⁴. More recently, Tuncer²⁵ has developed a numerical Monte-Carlo method for computing the SDF from experimental dielectric permittivity data. This method is very promising even in cases where experimental data do not show sharp features, and it was applied to the optical properties of Co-Al₂O₃ metal-insulator composite films in a recent work of ours²⁶. In the present paper we apply the method to sol-gel deposited Ni-Al₂O₃ thin films. We think that transition metal-insulator nanocomposites constitute a good test case for our method. It is true that their experimental optical spectra do not show the sharp peak structures of noble metal composites. On the other hand, noble metal nanoparticles exhibit a size dependence of their dielectric permittivity, which makes the evaluation of their SDF more uncertain. In section 2 below, we review briefly the spectral density formalism as well as the computational techniques that we use. Section 3 describes the preparation and experimental optical data of the samples. We obtain the effective dielectric permittivity of the samples from transmittance and reflectance measurements in the wavelength range 300 to 2500 nm. In section 4 we present the computed SDF's for Ni-Al₂O₃ thin films and discuss the interpretation of the results. We discuss different frameworks for interpretation and point out difficulties with the SDF approach, as well as presently unclear features. Our conclusions are summarized in section 5.

2. THEORY

2.1 Spectral density formalism

In order to give an introduction to the spectral density formalism, we consider the classic Maxwell Garnett^{27,28} effective medium theory and show how it can be generalized by introducing a SDF. The Maxwell Garnett (MG) theory is considered to be a good approximation for a mixture of separated nanoparticles in a continuous host material^{6,29,30}, as long as the particles are not close to touching. Consider a sample consisting of aligned ellipsoids where the incident electric field is directed along one of the principal axes. The effective dielectric permittivity, ε , can be written as

$$\varepsilon = \varepsilon_m \frac{1 + 2f\alpha/3}{1 - f\alpha/3}, \quad (1)$$

where f is the volume fraction of particles, ε_m is the dielectric permittivity of the host material and α is proportional to the polarisability of a single particle. It is given by

$$\alpha = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L(\varepsilon_p - \varepsilon_m)}, \quad (2)$$

where ε_p is the dielectric permittivity of the particle material and L is the depolarization factor pertaining to the pertinent ellipsoid axis. It is seen that the single particle polarisability exhibits a resonance when $\varepsilon_p = (1 - L)\varepsilon_m / L$. The MG theory takes into account dipole-dipole interactions between particles in an average sense and the MG resonance will shift and depend on f in addition to L . This can be seen by rewriting Eq. (1) in the following way:

$$\varepsilon = \varepsilon_m \left(1 + f \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L(1 - f)(\varepsilon_p - \varepsilon_m)} \right). \quad (3)$$

It is realized that the MG theory exhibits a structural resonance when the denominator in the second term is zero, and it is obtained from the single particle resonance by the replacement $L \rightarrow L(1 - f)$. In the case of ellipsoids with the same shape, but random orientations, the second term must be summed over the triplet of depolarization factors pertaining to the three principal axes of the ellipsoid. Furthermore distributions of particles of different shapes, as well as multipolar interactions when particles are close to touching, lead to a variety of structural resonances, that can be described by general distributions of a parameter, which reduces to $L(1 - f)$ in the MG case. By integrating the second term in Eq. (3) over a SDF, $g(x)$, one obtains a completely general effective medium theory, which separates the properties of the constituents from the effects of the nanostructure. The latter effects are described by the spectral density function $g(x)$.

$$\varepsilon = \varepsilon_m \left(1 + \int_0^1 \frac{g(x)}{((\varepsilon_p / \varepsilon_m) - 1)^{-1} + x} dx \right). \quad (4)$$

It is customary to treat the resonance with $x=0$ separately, since that is the percolation strength¹⁵, which specifies the dc conductivity of the nanocomposite. In addition we write Eq. (4) in normalized form by introducing the “scaled” permittivity^{25,26} $\xi = (\varepsilon - \varepsilon_m) / (\varepsilon_p - \varepsilon_m)$, and obtain

$$\xi = (\varepsilon - \varepsilon_m) / (\varepsilon_p - \varepsilon_m) = \xi_s + \int_{0^+}^1 g(x) [1 + ((\varepsilon_p / \varepsilon_m) - 1)x]^{-1} dx, \quad (5)$$

where ξ_s is the percolation strength. This equation is basically the same as that of Fuchs¹⁵ and equivalent to the expression obtained by Bergman¹⁹. All realistic effective medium theories can be rewritten in this form and the function $g(x)$ depends only on the nanostructure of the nanocomposite. The mathematical properties of $g(x)$ are expressed by the sum rules,

$$\xi_s + \int_0^1 g(x) dx = f; \quad \int_0^1 x g(x) dx = (1 - f) / d, \quad (6)$$

where d is the effective dimensionality of the system and f is the volume fraction of the particle phase. The validity of the first sum rule is easily realized by comparing Eqs. (3) and (4). From the discussion above it is seen that the MG theory can be described with the simple SDF,

$$g(x) = f \delta(x - L(1 - f)), \quad (7)$$

which is a fair description for materials consisting of nanoparticles in a continuous amorphous matrix material^{29,30}. For the so called aggregate topology²⁹, consisting of a random mixture of nanocrystals of the two component, the Bruggeman theory³¹ is often used. It can also be put in the form of eq. (5), although with the considerably more complex SDF^{16,32},

$$g(x) = [-9x^2 + 6(1+f)x - (3f-1)^2]^{1/2} / 4\pi x. \quad (8)$$

The MG theory displays one sharp resonance, while the Bruggeman theory gives rise to a broad featureless spectrum of resonances.

2.2 Computational method

Performing an inversion from the experimental dielectric permittivity to $g(x)$ is a difficult problem that needs advanced computational techniques. The numerical method that we use is based on a Bayesian statistics approach, in which spectral parameters (x_i) are selected randomly, and the SDF estimates are computed many times with a new set of x_i -values in each step. The spectral density expression is solved with the Monte Carlo integration hypothesis such that by randomly selecting x values we solve the following expression in each step,

$$\xi = \xi_s + \sum_{i=1}^n g_i(x)(1 + ((\varepsilon_p / \varepsilon_m) - 1)x_i)^{-1} \quad n \leq M, \quad (9)$$

where M is the number of data points and n is the number of unknowns used in each summation step. This converts the non-linear problem to a linear one, with g_i being the unknown weights of the randomly selected x_i values. A constrained least-squares algorithm is applied to get the corresponding g -values and ξ_s .^{25,33} A detailed description of the method was presented previously^{25,33}. A large number of summation steps yield a continuous spectral density x axis, which would not be possible with other non-linear curve fitting schemes. Examples of the numerical procedure and its utility have been shown on simulated and experimental data previously^{25,26,33,34}.

In the present investigations, the spectral parameter space is chosen to be in a logarithmic scale. The pre-selected random x values are taken from a log-linear distribution $-3 \leq \log_{10} x \leq 0$, then the percolation strength ξ_s is obtained from an integral over $-\infty \leq \log_{10} x \leq 3$. However, in the present study the percolation strength was not significantly different from zero.

3. EXPERIMENTAL PROCEDURES

In this section we summarize the sol-gel method for the sample preparation of Ni-Al₂O₃ nanocomposite films, as well as some results on their structural and optical characterization. A more detailed account of these matters can be found in previous works³⁵⁻³⁸.

3.1 Sample preparation

It is only in the last few years that solution-chemistry or sol-gel science was found to be a suitable method to produce nano-particles appropriate for thermal solar absorber applications. The solution-chemistry method investigated in this work was invented by Gunnar Westin, Uppsala University³⁵. It is at present under a patenting process and can therefore not yet be described. However some basic information about the solutions can be found below.

3.2 Chemical solutions

An alumina precursor solution was prepared. The concentration of aluminum ions in the alumina solution was gravimetrically determined as per amorphous alumina; an exact amount of solution was dried in air and subsequently heated to 800°C in a platinum crucible to yield pure amorphous alumina. The formed alumina was accurately weighed and thus the Al ion concentration could be calculated. The time until the alumina solution precipitated varied from 48 hours to two weeks. The most important parameter that determines the stability of the alumina solution seems to be the temperature. The stability of the alumina solution is substantially prolonged if refrigerated.

Nickel precursors were dissolved in solvents to make a nickel precursor solution. The dissolution was complete and no gravimetric determination of the concentration was necessary. The nickel solution is long-term stable.

Mixing precursor solutions of Ni and Al₂O₃ in different proportions controlled the nickel to alumina ratio of the absorbing films. The mixed alumina and nickel solution was stable for at least 24 hours. The stability could be increased up to one week if the solution was diluted with methanol. Coatings were prepared from precursor solutions containing Ni relative volume percentages between 20 and 80 %^{36,37}.

larger particles in films with a higher Ni concentration. The particles seem to be separated from each other, even at the highest nickel contents.

Heavy ion Elastic Recoil Detection Analysis (ERDA) is a well suited method to measure the composition of light and heavy elements simultaneously³⁷. A beam of 45 MeV $^{127}\text{I}^{9+}$ ions were used as projectiles in a forward elastic recoil configuration to produce target recoils. The signals for each recoiling ion were recorded, and the recoil energy spectrum was converted to elemental composition. The results showed that the relative volume percentages of Ni and Al in the film were almost the same as in the precursor solutions. However, the oxygen contents found by ERDA are larger than the estimated ones from the stoichiometric composition Al_2O_3 . The most likely explanation is that the Ni particles are partly oxidized and it was inferred³⁷ that about 15 % of the Ni atoms are bound in the form of NiO, probably as a surface layer on the nanoparticles.

3.6 Optical measurements and optical constants

Reflectance and transmittance spectra were measured by a Perkin-Elmer lambda 900 spectrophotometer in the wavelength range 300 to 2500 nm for semitransparent Ni- Al_2O_3 films with thicknesses in the range 50 to 100 nm. The films were coated on Corning glass and the volume percentages of nickel, uncorrected for the presence of NiO, ranged from 20 to 80%.

Dispersion analysis was carried out on the reflectance and transmittance data by a fitting program (CODE)³⁹. The program fits a mathematical model of the dielectric permittivity of the film to the experimental data by a routine that utilizes a downhill simplex algorithm. It should be noted that the nanoparticles are much smaller than the wavelength of the light in the considered wavelength interval. We chose the Bruggeman effective medium model in order to describe the dielectric permittivity, using literature data for the dielectric permittivity of Ni⁴⁰ and a generalized Cauchy model³⁸ for the dielectric permittivity of Al_2O_3 . Good fits could be obtained to the experimental reflectance and transmittance by this model, but the fitting parameters do not necessarily correspond to physical values. In particular the volume fraction of Ni in the model does not correspond to the experimental one³⁸. Hence this model was used only as a mathematical tool to fit spectra in order to obtain good values of the dielectric permittivity of the composite film by dispersion analysis. We do not regard the Bruggeman model as physically realistic for the present nanocomposite films. Indeed as shown in the next section, the SDF is very far from the broad and featureless Bruggeman behavior. Figure 2 shows the complex refractive indices for pure Al_2O_3 , as well as for Ni- Al_2O_3 nanocomposites, that were obtained from experimental data. The complex dielectric permittivity is the square of the complex refractive index.

Figure 2. The real part (left panel) and the imaginary part (right panel) of the effective refractive index, for pure alumina (A) as well as for different nickel-alumina composite (up to 65%nickel-35%alumina (N65A35)) thin films. The compositions are given in the insets. The grey lines represent the standard deviations of the data.

4. SPECTRAL DENSITY FUNCTIONS

It is not straightforward to apply the spectral density formalism to experimental samples, something which is well illustrated by the present study. The SDF is strictly valid for two-component composites, but it is seldom that experimental samples are strictly two-component ones. The Ni-Al₂O₃ nanocomposites contain some NiO, as inferred from ERDA, and in addition, we cannot exclude porosity. The porosity is not known for the present coatings, but the low refractive index of pure Al₂O₃ points to a porosity of roughly 15% for this film. However, the dielectric permittivity of a metal is very different from the permittivity of an insulator like Al₂O₃ and NiO. Hence we consider the present samples as consisting of metal particles in a homogeneous insulator phase, and neglect the differences in dielectric permittivity between the oxides. The dielectric permittivity of Ni was taken from available tabulations⁴⁰, while the dielectric permittivity of Al₂O₃ was obtained from an alumina film prepared in the same way as the composite samples, as described before³⁸. The volume fraction of Ni nanoparticles is denoted by f and was obtained by correcting the nominal Ni content for the presence of NiO.

Figure 3. Left panel: Spectral density function for a Ni-Al₂O₃ film with nominal Ni content 40 %, corresponding to a volume fraction of Ni nanoparticles of $f=0.34$, on (a) a linear scale and (b) a logarithmic scale. Right panel: Imaginary vs. real part of the scaled dielectric permittivity for this film, Points denote experimental data, while the line is calculated from the SDF in the left panel.

In figure 3, the scaled permittivity, ξ , is plotted in the complex plane for a film with nominally 40 %Ni. It is seen that our computed SDF, shown in the left panel, can accurately reproduce the experimental dielectric permittivity data. A similar agreement was found for all the other samples. In figure 4 we present the SDF for five Ni-Al₂O₃ films with nominal Ni volume fractions from 20 % to 80 %. The SDF is given in arbitrary units and the curves have been displaced along the y-axis for clarity. The SDF displays a multi-peak structure with three or four peaks clearly visible. A similar behaviour has been observed in earlier work of ours on evaporated Co-Al₂O₃ nanocomposite films²⁶. The peak situated at the highest x might possibly give information on the average particle shape but the others are evidently due to particle-particle interactions giving rise to structural resonances in the response of the composite to the electric field. Each peak is characterized by the peak x -value, x_i , and a peak strength, q_i , that add up to give the total volume fraction by the first sum rule in Eq. (6). It should be noted that the logarithmic scale in fig. 4 tends to make the differences in peak strength less apparent. This is also apparent from the left panel of figure 3. Actually the peak at highest x is the largest one with always more than twice the strength of the others.

Figure 4. Logarithm of spectral density function $g(x)$ (in arbitrary units) is shown as a function of the spectral parameter x for five compositions of $\text{Ni-Al}_2\text{O}_3$ thin films. From bottom to top the nominal compositions were 20%, 40%, 60%, 65 % and 80% nickel. The curves have been displaced along the y-scale for clarity.

Now we consider the implications of the first sum rule in Eq. (6). A problem of applying this sum rule is that the percolation strength is not known since the electrical conductivity of the samples was not measured. However since the particles look well separated on TEM micrographs, we assume that the percolation strength is small and compute the volume fraction from $f_{\text{calc}} = \sum q_i$. In figure 5, the experimental volume fraction is compared to the one obtained from the integral over the SDF. The experimental f is different from the nominal one, because we have corrected for the presence of NiO. It is seen that the f_{calc} is systematically lower than the experimental one. The deviation is consistent with the presence a porosity of 0.1 to 0.15, at least for the films with volume fractions below 0.5 .

Figure 5. The volume fraction computed from the SDF is plotted as a function of the experimentally determined volume fraction. The full line depicts the situation that the volume fractions are equal and the dashed line is a fit to the three points at $f \leq 0.50$.

At the highest Ni contents the computed volume fraction from the SDF, seem to flatten out at a value of 0.3 to 0.4. This curious behaviour is consistent with recent results for Co-Al₂O₃ nanocomposites²⁶. It must be remembered that the spectral density formalism is derived from a purely electro(quasi)static theory and that other mechanisms giving rise to absorption in some frequency range are excluded. In particular tunnelling of electrons between particles will occur at high volume fractions, where the particles are nearly touching. This mechanism will certainly affect low frequency electrical properties and gives rise to a power-law quasi-dc electrical conductivity of a nanocomposite⁴¹. This effect can conveniently be treated by the model SDF for a power-law permittivity given by Stroud et al.⁴². It gives an enhancement of the percolation strength by less than an order of magnitude, but this is insufficient to explain the discrepancies observed for Co-Al₂O₃. The influence of tunnelling charge transfer phenomena on infrared and/or optical absorption has to our knowledge, not been studied. Recently it has been suggested that the infrared properties of nanocomposites should be described using concepts used for transition metal oxides⁴³, implying that a purely electrostatic theory may be insufficient. It is conceivable that such processes could “steal” resonance strength from the SDF, thus leading to a lower computed than experimental volume fraction of a nanocomposite.

Now we discuss some possible reasons for the observed multi-peak structure in the SDF. Spheroidal or ellipsoidal particle shapes would give rise to two and three resonance peaks, respectively. However, this explanation is unlikely because of the lack of resonances in $g(x)$ for $x > 0.4$. Such resonances would have to be present for the majority of our samples in order for triplets of depolarisation factors to sum up to unity. The peak structure of the SDF is reminiscent of the behaviour of fractal equivalent circuit models⁴⁴ of optical properties of percolating composites. Indeed acceptable fits to $g(x)$ by this type of model are possible²⁶, but a problem is that these models also have resonances at high x , which we do not observe in the SDF derived from experimental data.

Determining local density distributions is a very general way to characterize the nanostructure of composite materials⁴⁵. It is conceivable that the structural resonances correspond to local regions with different volume fractions of Ni nanoparticles in the sample. The relatively sharp resonances seen in fig. 3 suggests an interpretation in terms of MG ones, but with different values of f in eq. (7). Resonances at low x would then correspond to local regions with high f . In fig. 5 we compare the weighted average of the resonance peak positions with their expected position from eq. (7), using the total volume fraction of particles. The weighted average of the peak positions was obtained from $\langle x_i \rangle = \sum q_i x_i / f_{\text{calc}}$, and is plotted as a function of the experimental volume fraction in fig. 6. It is seen that data for three of the samples fall close to the prediction of eq. (7) for spherical particles ($L=1/3$), while the other two points requires the assumption of non-spherical particles with $L=1/2$. Similar tendencies can be observed for the case of Co-Al₂O₃ nanocomposites, using our previously published data²⁶.

Figure 6. The average resonance peak positions for Ni-Al₂O₃ nanocomposite films are plotted as a function of experimental volume fraction. The lines denote the predictions of the Maxwell-Garnett theory (Eq. (7)) for spheres with $L=1/3$ and for moderately non-spherical particles with $L=0.5$.

The correlations seen in fig. 6 suggest that local density distributions should be looked into as a way to characterize nanocomposite samples and to predict their optical and electrical properties. Significant work along these lines have been done in the field of geophysics by Hilfer and coworkers⁴⁵, but only little attention has been devoted to optical properties of nanoparticle films⁴⁶ using closely related concepts⁴⁷.

5. CONCLUSIONS

We have determined the spectral density function of a series of nickel-alumina nanocomposites by an accurate numerical technique. The composites were prepared by sol-gel deposition and consisted of nickel particles in an oxide matrix. The spectral density exhibited an unexpected multi-peak structure with three to four structural resonances clearly visible. The weighted mean of these resonance positions can be reconciled with the position of the resonance predicted by the Maxwell Garnett theory for spherical or moderately non-spherical particles. However, the detailed interpretation of the SDF is still very uncertain. We have pointed out some problems with the SDF as well as a few possible interpretations. The possible existence of quantum mechanical absorption mechanisms at frequencies lower than those considered in the present study cannot be treated within an electromagnetic theory. Possible interpretations of multi-peak SDF's include fractal networks of particles and local density distributions.

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