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Role of surface-to-volume ratio of metal nanoparticles in optical properties of Cu:Al$_2$O$_3$ nanocomposite films

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We report on the role of the surface-to-volume ratio of Cu nanoparticles (NPs) both in the linear and nonlinear optical properties of Cu:Al$_2$O$_3$ nanocomposite films. The results show that when the shape of the NPs deviates sufficiently from that of a sphere, the increase of the fraction of metal atoms present at the surface (N_S) with respect to the total amount of atoms (N_T) in the NP leads to a substantial reduction of the enhancement of the local field. As a consequence, for N_S/N_T values above a certain threshold (≈ 0.4–0.5), the surface–plasma resonance is smeared out and the nonlinear optical response of the nanocomposite film becomes very weak and independent of the dimensions of the NPs or their volume fraction in the matrix. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1923198]

Nanocomposite materials made out of metal nanoparticles (NPs) embedded in a dielectric matrix have been the subject of ever-growing interest since the late 1980s due to the fact that the optical properties of these composites greatly differ from those of their components. Many applications for these materials have been proposed, including enhanced fluorescence spectroscopy,[1] biosensors,[2] or all-optical switching devices.[3] The latter application relies on the large third-order optical nonlinear response of such nanocomposite materials, which is characterized by the effective third-order susceptibility. Since the size and shape of the metal NPs as well as their volume fraction and concentration in the matrix are considered to play an essential role in the nonlinear optical response of the nanocomposite,[4,5] these materials hold great promise for technology based on the feasibility of engineering their optical properties through the material design.

To date, a large number of the experimental and theoretical studies on the optical properties of these nanocomposites have been focused on the very low volume fraction of the NPs (p) regime,[6–9] i.e., $p \ll 1$. It has recently been shown though that a sufficient increase of the volume fraction of NPs results in a nonlinear response much higher than that predicted by effective medium theories[10–12] that are valid for $p \ll 1$. Increased p values can be achieved for NPs with shapes that deviate from that of a sphere. It is thus unclear what is the role played by the different morphological parameters (volume fraction, particle shape, and size) in the nonlinear response of high concentration metal nanocomposites. The aim of this work is to answer this question by analyzing the linear and nonlinear optical properties of Cu:Al$_2$O$_3$ nanocomposite films with high volume fraction of NPs ($p > 0.10$) and with NP shapes that deviate largely from that of a sphere.

Films were synthesized by alternate pulsed laser deposition (PLD) that provides a very suitable method to embed the metal NPs in a dielectric oxide matrix, organized in layers and achieving a degree of control on their shape. The experimental procedure has been described previously[13] and uses an ArF laser ($\tau_{FWHM}=20$ ns, $\lambda=193$ nm) to alternately ablate high-purity Al$_2$O$_3$ and Cu targets. The films were grown either in vacuum or in an Ar environment, the latter being used to reduce surface mobility of the incoming species and thus lead to elongated NPs. First, an amorphous Al$_2$O$_3$ layer on a transparent glass substrate was deposited as reported elsewhere.[13] Five Cu layers alternated with pure Al$_2$O$_3$ layers were subsequently grown. The metal NPs were always grown on the same surface (Al$_2$O$_3$) and an Al$_2$O$_3$ layer was always protecting the films against oxidation. The sample can be thus seen as a sequence of Cu:Al$_2$O$_3$ nanocomposite layers each of them having a height equivalent to that of the metal NPs and separated by ≈ 10 nm thick Al$_2$O$_3$ spacing layers. This distance is large enough to ensure that no electromagnetic interaction between adjacent layers of NPs occurs.[14]

Films were characterized by rutherford backscattering spectrometry (RBS), grazing incidence small-angle x-ray scattering (GISAXS), and high resolution transmission electron microscopy (HRTEM) as reported elsewhere.[13] Table I summarizes some of the morphological data that are relevant for the present study: the metal content per layer ([Cu]) as determined by RBS, and the average in-plane major axial dimension (a) and in-plane axial ratio (a/b) determined by HRTEM, where b is the in-plane average shorter dimension. The volume fraction of NPs, p, which is the parameter commonly used to describe the properties of nanocomposites (e.g., Refs. 6–12) has been calculated by assuming the NPs are ellipsoids and using the in-plane dimensions determined

TABLE I. Morphological characteristics of the nanocomposite films studied in this work: [Cu]=number of Cu atoms/cm^2 per NPs layer; a=average in-plane longer dimension of the NPs; a/b=in-plane aspect ratio of NPs; p=fraction of NPs per layer; N_S/N_T=number of atoms at the surface to total number of atoms constituting the NPs.

Environment during growth	[Cu] (10^{15} atoms/cm^2/layer)	a (nm)	a/b	p	N_S/N_T
Vacuum	5.1	4.0	1.3	0.11	0.5
Vacuum	7.7	5.1	1.4	0.17	0.4
Vacuum	11.5	7.2	1.4	0.25	0.3
Ar	8.5	5.9	1.9	0.25	0.5
Ar	12.0	12.4	3.4	0.50	0.5

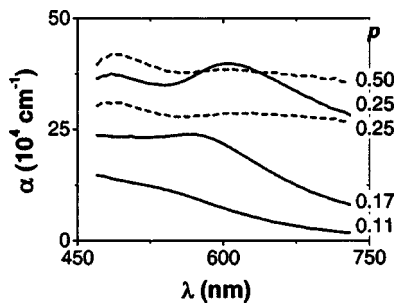[a]Electronic mail: j.solis@io.cfmac.csic.es

FIG. 1. Absorption spectra for the films synthesized in vacuum (solid line) and in an Ar pressure (dashed line) for different volume fractions (p) of the metal NPs.

FIG. 2. (a) Third order nonlinear susceptibility and (b) N_S/N_T as a function of the volume fraction of metal NPs, p, for the films grown in (●) vacuum and (■) Ar. The lines are a guide for the eyes.

by HRTEM and the average dimension h along the direction perpendicular to the film plane determined by GISAXS that was in all cases 3.0 ± 0.5 nm.

The comparison of these data and the images reported elsewhere[13] shows that for the films grown in vacuum an increase of the amount of metal leads to NPs with approximately constant in-plane aspect ratio but an increased p. For the films grown in Ar, an increased amount of metal leads instead to an increase in both p and the in-plane aspect ratio of each of the NPs. When comparing films that have a similar p, films grown in Ar show NPs with higher ellipticity than those grown in vacuum; for those films that have similar [Cu], it is clear that the NPs grown in Ar have a substantially higher p than those grown in vacuum.

Measurements of the reflectance and transmittance optical spectra in the visible spectral region at normal incidence have been performed to determine the linear refractive index, the absorption coefficient and the spectral position of the surface-plasma resonance (SPR). Linear refractive indices were determined by taking into account the effects of the substrate and the interference of multiple reflections caused by the layered configuration of the films. Similar values were determined in all the films, the value $n_0 = 2.1 \pm 0.2$ at 590 nm being significantly higher than that of the Al_2O_3 matrix as reported earlier.[15]

Figure 1 shows the absorption spectra of all studied samples. The spectra of films grown in vacuum exhibit a characteristic resonance at $\lambda \approx 590$ nm, associated to the SPR of Cu NPs, except for the film having the lowest p. The SPR is redshifted and the overall absorption increases as the volume fraction of NPs p is increased. In contrast, the films grown in Ar exhibit an increased and broad absorption across the whole studied spectral range with no clear evidence of a SPR in the spectral windows from 450 to 750 nm even though the HRTEM images reported in Ref. 13 showed that they indeed contain Cu NPs. The number labeling each curve is the volume fraction of the NPs, p, is included in order to strengthen the fact that the presence of SPR does not exclusively depend on p (compare, for instance, the two samples with $p=0.25$ that were grown at different environmental pressure).

Nonlinear optical characterization was performed by degenerate four wave mixing (DFWM) to determine the modulus of the third order susceptibility, $\chi^{(3)}(\omega;\omega,\omega,-\omega)$. The laser source used was a mode-locked Rhodamine 6G cavity dumped dye laser, synchronously pumped by an actively mode-locked Ar^+ laser, providing typically 12 ps laser pulses at the working wavelengths (580–620 nm). Detection was
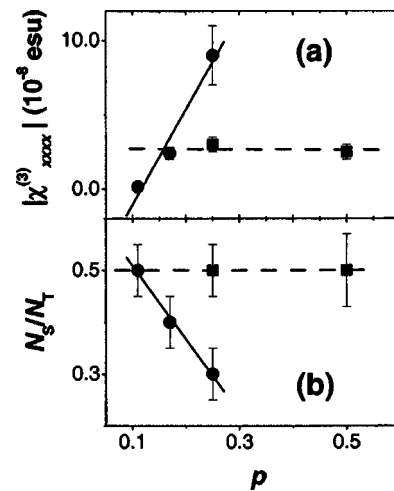
carried out with standard phase lock-in techniques. The repetition rate that offered the best signal-to-noise ratio while avoiding cumulative thermal effects under these conditions was experimentally determined to be 400 kHz.[16] The DFWM experiment was set up in the forward (BOXCARS) scheme.[17] The use of half-wave plates in the beams allowed independent selection of their polarizations so as to measure the different components of the third-order nonlinear optical tensor $\chi^{(3)}_{ijkl}(\omega;\omega,\omega,-\omega)$. The conjugated signals were measured as a function of the pump intensity both for the films and a CS_2 cell used as a reference, the latter showing a value for $|\chi^{(3)}_{xxxx}(\omega;\omega,\omega,-\omega)| = 2 \times 10^{-12}$ esu when excited with ps pulses in the visible.[17] Across the whole pumping intensity interval used (10^7–10^8 W/cm^2), the conjugated signal of both the CS_2 sample and the $Cu:Al_2O_3$ nanocomposites gave the expected cubic dependence for a nonsaturated third-order nonlinearity. It was also found that the symmetry conditions for a macroscopically isotropic system were verified, as well as the intrinsic permutation symmetry for the degenerate case.[18] It was also checked that the component $ijij$ was negligible and $|\chi^{(3)}_{iiii}(\omega;\omega,\omega,-\omega) = 2\chi^{(3)}_{ijij}(\omega;\omega,\omega,-\omega)|$. Henceforth we will refer from now on to the component $iiii$ measured in the nanocomposites, denoted as $|\chi^{(3)}_{xxxx}|$.

The third-order nonlinear optical response of the films was studied in the spectral region centred in the SPR wavelength of the $Cu:Al_2O_3$ films (580–620 nm). No significant variation of the effective third-order susceptibility of the films was observed over the wavelength interval of 580–620 nm. We have therefore chosen $\lambda = 590$ nm to present the results that follow. Figure 2(a) shows the variation of $|\chi^{(3)}_{xxxx}|$ with the volume fraction of NPs p for the samples grown both in vacuum and in Ar. Figure 2(a) clearly shows that whereas $|\chi^{(3)}_{xxxx}|$ strongly increases as p increases for films grown in vacuum, it is essentially constant and thus independent of p for the films grown in Ar. A value of $|\chi^{(3)}_{xxxx}|$ as high as $\approx 10^{-7}$ esu is reached for the film grown in vacuum having the highest p, whereas the film having the lowest p shows a conjugated signal close to the resolution limit ($<10^{-8}$ esu) of the technique.[16] The films grown in Ar have instead similar $|\chi^{(3)}_{xxxx}|$ values even when p values are very different.

In a recent work,[10] a strong enhancement of the nonlinear optical response of $Cu:Al_2O_3$ nanocomposites has been reported as p was increased and discussed in terms of electromagnetic interactions among neighboring NPs that appear for metal contents higher than the one corresponding to the coalescence threshold. Those nanocomposite films were grown in vacuum and thus the morphological features of the NPs were very similar to those produced in vacuum studied in this work. The films grown in Ar show, instead, NPs with a significant departure from the spherical shape. These morphological changes might bring into play new factors. One obvious factor related to these shape changes is the increased surface-to-volume ratio of the nonspherical NPs when compared to the quasispherical ones. Besides, atoms at the dielectric matrix–metal NPs interface will have a strong bond asymmetry and, hence, the electrons belonging to these atoms might not contribute to the SPR the same way as electrons from the atoms at the core of the NPs.

We have computed the number of atoms at the surface, N_S, to the number of atoms constituting the NPs, N_T, ratio assuming that the NPs are ellipsoids and using the in-plane dimensions determined by HRTEM (and included in Table I) and the out-of-plane dimension determined by GISAXS. The computed values are also included in Table I, and plotted in Fig. 2(b) as a function of p. It can be seen that whereas N_S/N_T decreases as p is increased for the films grown in vacuum, it remains constant for those films grown in Ar. This different trend shows that films containing similar [Cu] (i.e., 12.0×10^{15} and 11.5×10^{15} atoms/cm^2/layer for films synthesized in Ar and vacuum, respectively) have instead totally different p and N_S/N_T [Fig. 2(b)]. As a result, half of the Cu atoms of the NPs of films synthesized in Ar are located on the surface of the NPs, whereas when they have been synthesized in vacuum, only one third of the Cu atoms are on the surface of the NPs for the film with the highest [Cu]. When comparing the features of the two films grown in Ar, it can be seen that it has been possible to strongly increase p while keeping N_S/N_T approximately constant.

The comparison of the absorption spectra plotted in Fig. 1 to the data in Table I shows that, irrespective of p, a distinct SPR cannot be identified when $N_S/N_T \sim 0.50$. Further, Figs. 2(a) and 2(b) show that samples with high NS/NT ($\approx 0.4-0.5$) present a nonlinear optical response that is either independent of p or negligible, while $|\chi^{(3)}_{xxxx}|$ is significantly enhanced if N_S/N_T is kept sufficiently low (0.30). In the latter case, which corresponds to a film grown in vacuum, the enhancement of the nonlinear optical response would be due to the appearance of a SPR at the measuring wavelength and possibly to the electromagnetic coupling among neighboring clusters for [Cu] due to the high metal volume fraction, as discussed in Ref. 10. In contrast, for the samples grown in Ar, the SPR would be smeared out, due to the low number of electrons contributing to the collective oscillation. Therefore there would be no SPR-related enhancement of the nonlinearity of the composites and, in addition, the likely electromagnetic coupling among neighbouring clusters for high-concentration composites would be less efficient since the local fields are much weaker.

We note that strong shape-related SPR shifts have been clearly observed for larger NPs (for instance, tens of nanometers as reported in Ref. 19), and thus, N_S/N_T ratios much smaller than the ones in our case. We cannot totally discard that the departure from the spherical shape of the NPs in the films grown in Ar might have lead to a substantial shift in the spectral position of the SPR outside the 450–750 nm window and that this would in turn result in a SPR-related enhancement of $|\chi^{(3)}_{xxxx}|$. However, we believe that a shift of the SPR of more than 150 nm is unlikely given that the maximum shift of the SPR found in $Cu:Al_2O_3$ films with larger NPs grown in vacuum is less than 50 nm.[10]

In summary, we have shown that the linear and nonlinear optical properties of nanocomposite films formed by Cu NPs embedded in a dielectric matrix are strongly influenced by the morphology of the NPs through the ratio of atoms present at the surface to the total number of atoms constituting each NP. When this ratio is larger than 0.4–0.5, the number of electrons that effectively contribute to the surface–plasma resonance and thus promote the enhancement of the local field is significantly decreased. This decrease in the local field is mirrored both by the linear and nonlinear optical properties of the nanocomposite film.

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