Nanocrystal size dependence of the third-order nonlinear optical response of Cu:Al_2O_3 thin films

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Metal nanocomposite thin films formed by Cu nanocrystals embedded in an amorphous Al_2O_3 host have been synthesized by pulsed laser deposition. The mean nanocrystal diameter d was varied in the range 3.0 ± 0.6 to 6 ± 1 nm. The linear and nonlinear optical properties of the films were studied in the vicinity of the surface plasmon resonance and the size dependence of the third-order nonlinear optical susceptibility of the metal nanocrystals has been determined. The observed dependence $(1/d^3)$ indicates that in the studied diameter interval, the nonlinear response is due to quantum confinement effects in which the major contribution is associated with electronic intraband transitions. © *1999 American Institute of Physics.* [S0003-6951(99)01719-2]

The nonlinear optical properties of nanocomposites formed by metal or semiconductor nanocrystals (NCs) embedded in dielectric hosts have been intensively studied since the middle eighties as these materials might become an attractive alternative for the development of all-optical switching devices in waveguides.[1] They exhibit strong optical nonlinearities derived from dielectric and quantum confinement effects, the latter being usually considered less important in the case of metal NCs.[2] Nevertheless, quantum confinement effects have been reported for Cu NCs with diameters from 5 to 10 nm.[3] Such effects are expected to be more important the smaller the NCs size. The lack of solid state systems with NCs small enough and with a sufficiently sharp size diameter distribution has prevented, to our knowledge, to observe such effects in systems with potential for real applications.

Several techniques have been used to synthesize metal nanocomposite materials such as quenching and heat treatment,[4] sol-gel[5] sputtering[6,7] and ion implantation,[3,8,9] most of them providing size distributions too broad to perform reliable studies as a function of the NCs size. In an earlier work, we have shown that alternate pulsed laser deposition (PLD) in vacuum provides a single step means to produce high quality Cu:Al_2O_3 nanocomposite thin films.[10,11] The synthesized films, containing NCs with a mean diameter of 3.0 ± 0.6 nm, showed an effective third-order optical nonlinear susceptibility value among the higher ones reported in the literature for dielectric matrices doped with metal NCs.[3–6,8–10,12,13] In this letter we report the dependence of the nonlinear response of Cu NCs embedded in an Al_2O_3 host on the NCs mean diameter in the range of 3–6 nm. The analysis of the results allows us to discuss the physical mechanism responsible for the nonlinear response. This has been made possible due to the sharp diameter distribution of the NCs synthesized by PLD, and to an improvement of the experimental procedure used to measure the effective third-order nonlinear susceptibility which allowed to decrease the thermal contribution to the nonlinear response of the films.

The 200-nm-thick Cu:Al_2O_3 films were grown in vacuum (10^{-7} Torr) onto 0.1-mm-thick Corning glass substrates using an ArF excimer laser focused alternately on high purity Al_2O_3 or Cu targets at a fluence of 2 J/cm^2. The deposition sequence involved a fixed number of pulses on the matrix target followed by a number of pulses on the Cu target to obtain an Al_2O_3/Cu structure that was repeated up to ten times. The top layer was always Al_2O_3 in order to avoid the oxidation of the NCs by atmospheric exposure. Further details about film synthesis can be found elsewhere.[11] The whole procedure leads to a composite with well isolated Cu nanocrystals and with a controlled mean diameter d which increases linearly in the range of 3–6 nm as the number of pulses on the Cu target increases from 160 to 320. This can be seen in Fig. 1(a), which shows data

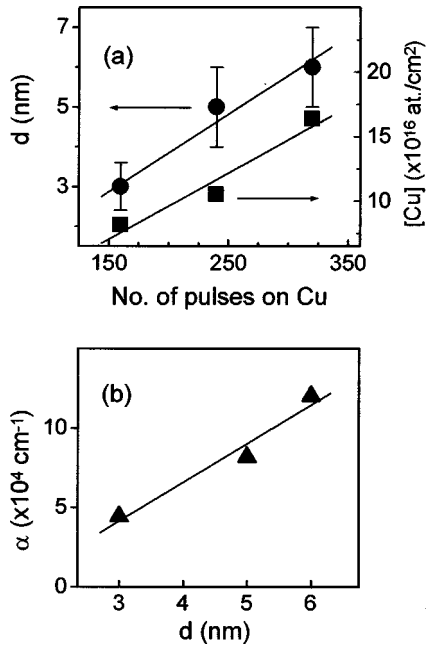

FIG. 1. (a) NCs mean diameter (d) (●) and areal density of Cu atoms [Cu] (■) as a function of the number of pulses on the Cu target during growth of Cu:Al_2O_3 films. The error bars for the d data correspond to the standard deviation of the NCs diameter distribution. (b) Linear optical absorption α of the composite (▲) as a function of the NCs mean diameter (d). The solid lines are linear fits of the experimental data.

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obtained through the analysis of high resolution transmission electron microscopy (HRTEM) images of the films.[11] Notice that the diameter distribution is very sharp (width ± 0.6 nm) in the sample having the smallest mean NCs diameter. The same figure also includes the areal density of Cu atoms determined by Rutherford backscattering spectrometry (RBS). As expected, an increase in the number of pulses in the Cu target leads to a proportional increase in the areal density of Cu atoms in the film.

The presence of the NCs inside the matrix is also evidenced in the linear absorption spectra of the composite films by the appearance of a characteristic peak at 578 ± 4 nm, associated to the surface plasmon resonance (SPR) of the Cu nanocrystals and related to dielectric confinement effects.[8,10] Figure 1(b) shows that the linear absorption coefficient α of the composites at the SPR wavelength follows a linear dependence on the mean NC diameter (d).

The effective third-order optical susceptibility of the films $\chi^{(3)}_{\text{eff}}$ was determined by means of z-scan measurements.[14] Provided that the thermal contribution (n_{2th}) to the nonlinear refractive index (n_2) is sufficiently reduced by choosing a low enough repetition rate for the pump laser beam, this technique allows to obtain separately the thermal (n_{2th}) and electronic (n_{2e}) contributions to the nonlinear refractive index ($n_2 = n_{2th} + n_{2e} \propto \text{Re}[\chi^{(3)}_{\text{eff}}]$).[8,10,13] The z-scan measurements were performed using a cavity-dumped synchronously pumped, mode-locked Rhodamine 6G laser tuned at 590 nm (slightly off the SPR) and providing 30 ps laser pulses at a repetition rate of 400 kHz. Notice that this repetition rate is one order of magnitude lower than that used in the z-scan measurements earlier reported[10] in order to reduce further the thermal contribution to the nonlinear refractive index. This reduction of n_{2th} increases the resolution of the experiment and allows a much more accurate determination of n_{2e}. The laser beam is focused on the sample with a 150 mm focal length lens, leading to a measured beam waist of 30 μm and a maximum irradiance of 2.8×10^7 W/cm^2 at focus, the Rayleigh range (5.4 mm) being much higher than the film plus substrate thickness. During each scan, the sample is moved over a distance of 400 mm centered at the lens focus while its far field transmission is measured by a small aperture detector connected to a lock-in amplifier. Each scan was automatically obtained in approximately 180 s during which each point of the spectrum was averaged 1000 times.

A typical result of the z-scan measurements is shown in Fig. 2 that corresponds to the far field transmission of a composite film containing NCs with a mean diameter of 6 ± 1 nm as a function of its distance (z) to the lens focus. The solid line is a fit of the experimental data using a thin lens approximation.[8,10,13] The agreement between the fit and the experimental data is excellent and both the electronic and thermal contributions can therefore clearly be resolved through their different functional dependence on z.[13] Films synthesized with no Cu show, in contrast, flat z-scan spectra evidencing that the nonlinearity is caused by the presence of the Cu nanocrystals.

Figure 3(a) shows the evolution of both n_{2th} and n_{2e} as a function of the mean NC diameter d for the PLD Cu:Al_2O_3 composite films. It is important to notice that the increase of the NCs diameter is accompanied by an increase of the overall absorption of the film near the SPR [Fig. 1(b)] due to the simultaneous increase in the volume fraction of Cu in the films [Fig. 1(a)]. Therefore, as the absorption at the pump wavelength becomes higher, the laser energy absorbed by the film and thus the thermal load of the medium also increases. Hence, n_{2th} increases as it is experimentally observed in Fig. 3(a). The same figure also shows that n_{2e} increases from 8×10^{-10} to 1.4×10^{-9} cm^2/W, as the NCs diameter is decreased. For the film with the smallest NCs, this number leads to a purely electronic third-order nonlinear susceptibility $\chi^{(3)}_{\text{eff}} \approx 1 \times 10^{-7}$ esu, which is about one order of magnitude higher than the one we have earlier reported.[10] This difference is related to the higher resolution achieved due to the improvement in the conditions used during the z-scan measurements as mentioned above.

The clear dependence of n_{2e} on the mean diameter of the Cu nanocrystals [Fig. 3(a)] allows us to investigate the origin

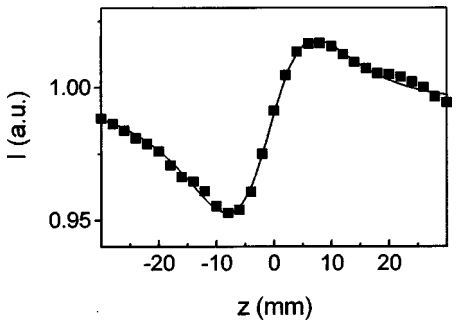

FIG. 2. z scan from a Cu:Al_2O_3 film with NCs of a mean diameter of 6 ± 1 nm. Both the experimental data (■) and the best fit using a thin lens approximation (solid line) are included.

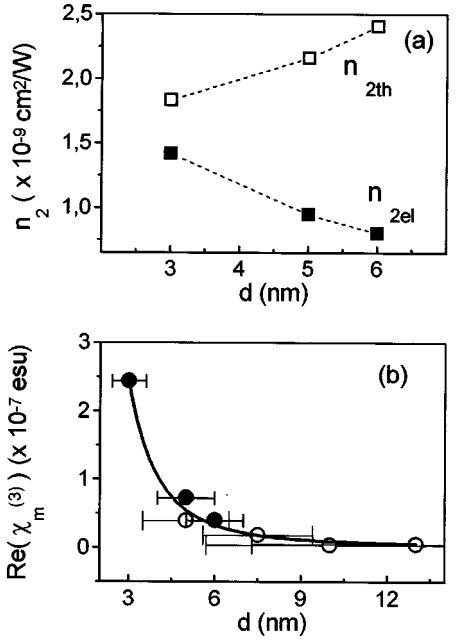

FIG. 3. (a) Evolution of the thermal n_{2th} (□) and electronic n_{2e} (■) contributions to the nonlinear refractive index of Cu:Al_2O_3 films as a function of the NCs diameter. (b) Intrinsic nonlinear optical susceptibility of the metal NCs reported in this work for Cu:Al_2O_3 films (●) and reported in Ref. 3 for Cu:SiO_2 (○) as a function of the NCs diameter. The solid line is a $1/d^3$ fit of the experimental data. The error bars in the d data correspond to the standard deviation of the NCs diameter distribution.

of the nonlinear response of the composite films. When the diameter of the metal NCs is reduced, the conditions imposed by its finite volume modify the wave functions of the electrons, since they get confined in a volume that can become smaller than their mean free path in the bulk material.[2] As a result of this quantum confinement, an isolated metal NC with a diameter below ~10 nm shows an intrinsic nonlinear optical third order susceptibility $\chi_m^{(3)}$ arising from three different possible carrier transition contributions:[2,3] intraband transitions, interband transitions, and ''hot-electron'' transitions. Among these three contributions only the first one is expected to be diameter dependent ($\propto 1/d^3$), since it is originated by electronic transitions between discrete levels in the conduction band of the NCs which appear due to the finite diameter of the metal.

When the metal NCs are embedded in a dielectric matrix, the experimentally measured effective optical susceptibility of the composite material $\chi_{\text{eff}}^{(3)}$ is related to $\chi_m^{(3)}$:[2,3]

$$\chi_{\text{eff}}^{(3)} = p \cdot f^2 \cdot |f|^2 \cdot \chi_m^{(3)}, \tag{1}$$

where p is the volume fraction of NCs, and $f = 3\epsilon_0/(\epsilon + 2\epsilon_0)$ is the local field effect (with ϵ_0 and ϵ being the dielectric constants of the matrix and metal, respectively). Near the SPR, $\epsilon + 2\epsilon_0 = 0$, f becomes resonant and $\chi_{\text{eff}}^{(3)}$ is thus enhanced by local field effects.

From Eq. (1) it is clear that $\chi_{\text{eff}}^{(3)}$ depends both on the NCs diameter (through $\chi_m^{(3)}$) and on the metal volume fraction, (p). In order to discriminate the effect of the NCs diameter from the effect of the metal volume fraction, it is possible to obtain an expression for $\chi_m^{(3)}$ as a function of the experimentally measured parameters. Taking into account the Mie relation,[2] which relates α with f and p, $\chi_m^{(3)}$ can be expressed as a function of α and $\chi_{\text{eff}}^{(3)}$:

$$\chi_m^{(3)} = \frac{2\pi}{\lambda} \cdot \frac{\epsilon_2}{f^2 \cdot \sqrt{\epsilon_0}} \cdot \frac{\chi_{\text{eff}}^{(3)}}{\alpha}, \tag{2}$$

where λ is the laser wavelength (590 nm) and ϵ_2 is the imaginary part of the dielectric constant of the metal. The values of both α and $\chi_{\text{eff}}^{(3)}$ are obtained experimentally through linear absorption and z-scan measurements, respectively. The values for ϵ_2 and f were calculated from the data reported elsewhere.[4] These values together with those of α and $\chi_{\text{eff}}^{(3)}$, allowed us to determine the evolution of $\chi_m^{(3)}$ as a function of the NCs diameter. The results are shown in Fig. 3(b) along with the data reported in Ref. 3 for ion-implanted $Cu:SiO_2$ nanocomposites in which $\chi_m^{(3)}$ was determined by a similar method.

The solid line in Fig. 3(b) is the best fit of the experimental data to a $1/d^3$ dependence. The excellent agreement of the fit with the experimental results shows that the third order nonlinear optical susceptibility of the isolated metal NCs indeed follows a $1/d^3$ dependence at a wavelength slightly off resonance. Notice that the observed dependence is independent of the host material (Al_2O_3 or SiO_2), as expected. This result shows that for NCs with mean diameters from 3 to 10 nm, the main contribution to the metal third order susceptibility comes from intraband transitions between discrete levels in the metal conduction band. This has not earlier been addressed for solid state systems with NCs with mean diameters as small as 3 nm and has only been possible due to the sharper diameter distribution of the NCs produced by PLD when compared to other synthesis methods like sol-gel[5] or ion implantation.[3,13]

In summary, the good quality of the $Cu:Al_2O_3$ nanocomposite films synthesized by PLD has allowed us to address clearly the origin of the nonlinear response of nanocomposite films formed by metal NCs with mean diameters below 6 nm in the vicinity of the surface plasmon resonance. The results clearly demonstrate that the nonlinearity is caused by quantum confinement effects whose larger contribution is associated to intraband electronic transitions.

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