Controlling the transmission at the surface plasmon resonance of nanocomposite films using photonic structures

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The transmission of nanocomposite thin films formed by Cu nanocrystals embedded in an amorphous aluminum oxide (Al_2O_3) matrix has been enhanced in the vicinity of the surface plasmon resonance wavelength, by the design of one-dimensional photonic structures. The nanocrystals are distributed in layers, whose separation and periodicity are used to control the optical response of the films. It is found that at the SPR a transmission enhancement up to 36% can be achieved with respect to a film with an homogeneous distribution of the nanocrystals. These photonic structures have been successfully produced by pulsed laser deposition. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605797]

Nanocomposite thin films formed by metal nanocrystals (NCs) embedded in a dielectric matrix show attractive optical properties at the surface plasmon resonance (SPR) wavelength due to dielectric and quantum confinement effects.[1] In the vicinity of this wavelength, the linear optical response exhibits a strong absorption band and the nonlinear optical response shows an enhancement that has been broadly reported.[2–4] Many applications of these metal nanocrystal composite materials have been proposed taking advantage of the optical response at the SPR, including their use in surface enhanced Raman spectroscopy,[5] surface enhanced second harmonic generation,[2] and for the development of sensors[6] and all-optical switching devices.[7] The features of the SPR essentially depend on the optical properties of both the metal NCs and the dielectric host material. The modification of the dimensions and shape of the NCs also induces changes in the intensity and width of the SPR absorption band, which have been extensively studied.[1] Nevertheless, there are no studies regarding the modification of the optical response around the SPR as a function of the NCs distribution in the matrix.

The aim of this work is to design and synthesize thin films containing metal NCs with a controlled transmission around the SPR wavelength region, using the one-dimensional photonic structure concept. A similar idea has been considered to produce *metal–dielectric* multilayered structures with a spectral range of increased transmittance, as for the case of thin films of Cu/SiO_2 (Ref. 8) and Ag/MgF_2 (Refs. 9 and 10) multilayers. So far, NCs have been only included as "defects" in a dielectric–dielectric multilayer photonic structure to enhance the nonlinear optical response.[11,12] In this work, it will be shown that the metal NCs can be the building blocks of the photonic structure, and how the transmission around the SPR wavelength can be enhanced by controlling their distribution. This result will have impact on the performance of metal–dielectric nanocomposite devices, such as NCs based nonlinear optical switches,[7] in which the nonlinear behavior induced by the presence of the NCs has to be preserved. The present ap-

proach will improve the light throughput of the device.

The thin film system selected to model and produce the structures consists of Cu NCs embedded in an amorphous aluminum oxide (a-Al_2O_3) matrix, since in previous works this kind of thin films has been successfully produced exhibiting excellent linear and nonlinear optical properties.[13,14] The thin films were grown on glass substrates by pulsed laser deposition (PLD) technique. An ArF excimer laser was used to alternately ablate high purity Al_2O_3 and Cu targets, in order to grow films with the in depth structure Al_2O_3/Cu NCs/Al_2O_3. The Cu NCs formed in each deposit are distributed on the plane of the film, and their in-depth separation is controlled by modifying the Al_2O_3 deposition conditions. Further details on the deposition procedure and structure of the films can be found elsewhere.[15,16] First, it has been grown a film with the NCs layers homogeneously spaced, whose absorption spectra shows a broad SPR band at 600 nm.[13,14] This film will be used as a reference, and will be referred thereafter as sample A. The film is formed by six NCs deposits equally spaced by a-Al_2O_3 layers of 7 nm thickness, as determined from Rutherford backscattering spectrometry (RBS) measurements. This thickness is large enough to ensure that there is no electromagnetic interaction between NCs belonging to different layers. The Cu content is 9×10^{15} at cm^{-2} per layer, corresponding to the development of ellipsoidal NCs with in plane mean diameter of ~ 5 nm and average center to center separation of ~ 12 nm, and a mean height $\leqslant 4$ nm.[15,16]

In order to optically model the one-dimensional photonic structures, the thin film is assumed to be formed by alternating a-Al_2O_3 and Cu–nanocomposite layers. A Cu–nanocomposite layer is defined as the deposited Cu NCs in each layer plus the a-Al_2O_3, which fills in the in-plane space between NCs. The thickness of the nanocomposite layer is assumed to be equal to the mean height of the NCs (4 nm). Since the mean size of the Cu NCs is much smaller than the wavelength in the visible range, this material can be considered optically as an homogeneous effective medium. The effective refractive index of the defined Cu–nanocomposite layer has been determined by ellipsometry and transmission measurements in sample A. A spectroscopy rotating analyzer

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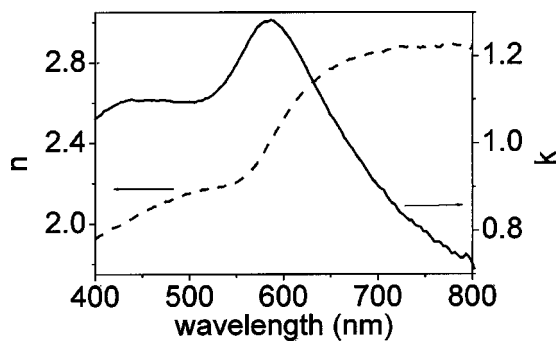[a)Electronic mail: asuarez@io.cfmac.csic.es

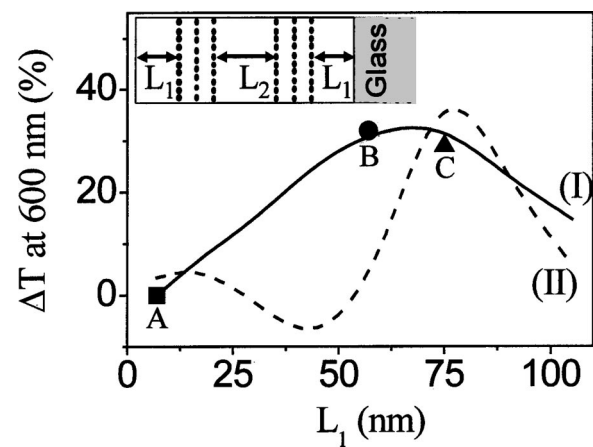FIG. 1. Effective refractive index, n (- - -) and k (—), of the Cu–nanocomposite layer.

FIG. 2. Calculated relative change $[\Delta T = (T_{ps} - T_r)/T_r]$ of the photonic structure transmission (T_{ps}) respect to the transmission of the reference film (T_r) at 600 nm as a function of L_1 for a photonic structure of type I: $L_2 = 7$ nm (—) and type II: $L_2 = L_1/2$ (- - -). Experimental values obtained for samples A (■), B (●), and C (▲), are also plotted. Inset schematically shows the structure of the films. Dark dots represent the Cu NCs and the white background represents the a-Al_2O_3. Each block of three layers of Cu NCs forms a photonic unit. L_1 and L_2 are the thicknesses of a-Al_2O_3 that are considered as parameters for the design of the photonic structures.

ellipsometer (model VASE, J. A. Woollam Co., Inc.) has been used to measure the ellipsometry parameters tan Ψ and cos Δ in the range 400–800 nm using steps of 3 nm, for incidence angles 61° to 75° at steps of 7°. The transmission has been measured at normal incidence for the same wavelength range. The measured optical response has been modeled as that corresponding to a multilayer structure formed by a-Al_2O_3 layers with a thickness of 7 nm, alternated with Cu–nanocomposite layers of 4 nm for six periods. Since the refractive index of the a-Al_2O_3 deposited by PLD has been determined in a previous work,[17] the complex refractive index of the Cu–nanocomposite layers is the only parameter in the optical model. It has been directly determined using a standard iterative procedure that follows the Marquardt–Levenberg algorithm to achieve the best fit of the data simulated for the optical model to the experimental data from both ellipsometry and transmission measurements.[18] Figure 1 shows the obtained complex effective refractive index of the Cu–nanocomposite layer. The imaginary part of the refractive index shows a band with a maximum at 586±3 nm, which is close to the SPR broad absorption band reported for films with Cu NCs embedded in a dielectric matrix.[13,19] The real part shows the corresponding anomalous dispersion phenomena in the vicinity of the SPR wavelength.[1]

Once the effective refractive index of the Cu–nanocomposite is known, the one-dimensional photonic structures with an enhanced transmission at 600 nm have been designed. The inset in the Fig. 2 shows a schematic diagram of the photonic structures. The six Cu–nanocomposite layers have been organized in two sets of three layers. This set of three layers separated by 7 nm of a-Al_2O_3 is defined as a "photonic unit." It is convenient to use the three layers of nanocomposite instead of one since, in this way, the optical contrast with the a-Al_2O_3 is enhanced, i.e., the reflectivity at a single Cu–nanocomposite/Al_2O_3 interface is only of 11%, whereas a 18% is obtained when the Cu–nanocomposite layer corresponds to the first layer of the defined photonic unit. The parameters selected to design the photonic structures are then the thickness of the a-Al_2O_3 layers that separate the photonic units from the substrate and the film surface (L_1) and between them (L_2). In terms of these parameters, two types of structures, I and II, have been considered in the modeling. Type I has a fixed $L_2 = 7$ nm and a variable L_1. Structure type I differs only in the a-Al_2O_3 thickness L_1 in respect to the reference sample, which corresponds to the particular case $L_1 = L_2 = 7$ nm. Structure type

II has a resonator like configuration, described by $L_1 = L_2/2$. In this way, both structures can be described in terms of a single parameter, L_1.

Figure 2 shows the relative change in the transmission of structures of types I and II at 600 nm with respect to that of sample A, calculated as a function of L_1. The results show that the changes in transmission are very different for the two types of studied structures. Nevertheless, a relative increase above 30% in the transmission with respect to the reference film is achieved in both cases. For type I the increment is of 32% for L_1 equal to 67 nm, whereas for type II the increment is of 36% for L_1 equal to 77 nm.

Finally, two thin films, B and C, have been synthesized for the L_1 values corresponding to the maximum of transmission for types I and II, respectively. They have been grown by PLD, under the same deposition conditions than those used for sample A. They have been subsequently characterized by RBS and ellipsometry, leading both techniques independently to the determination of the Al_2O_3 thicknesses L_1 and L_2. Table I shows that the results obtained by both techniques are in good agreement and they are also very close to the intended ones.

Figure 3 shows the transmission spectra measured at normal incidence for the three samples [A(reference), B, and C]. Sample A exhibits the typical attributes of a spectrum of Cu NCs homogeneously distributed in a dielectric medium, showing a decrease of the transmission for a band centered at 600 nm, which corresponds to the SPR.[13] Samples B and C

TABLE I. Thickness of the a-Al_2O_3 layers obtained by ellipsometry (L_1, L_2) and RBS (L_1', L_2') for the three synthesized samples. Data are given in nm.

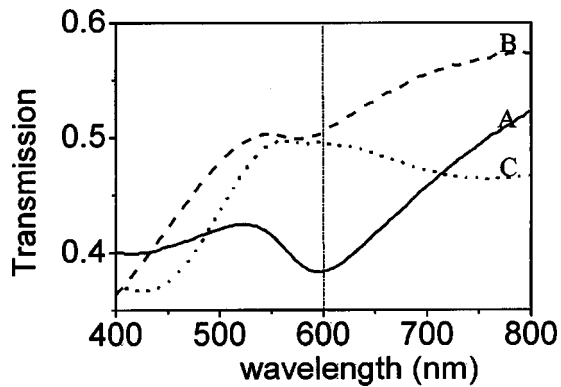| Sample	L_1	L_2	L_1'	L_2'
A	7±1	7±1	7±1	7±1
B	57±6	7±1	66±4	7±1
C	75±8	150±15	79±4	158±8

FIG. 3. Transmission spectra of the synthesized samples A (—), B (- - -), C (· · ·), as a function of wavelength. A continuous vertical line marks the SPR wavelength.

exhibit a considerable enhancement of the transmission not only at the SPR wavelength, but also in a wide range around it. Sample B shows a reminiscence of the SPR absorption band, while the transmission of sample C has almost no dependence on the wavelength in this region. These results evidence that it is possible to compensate the typical low transmission at the SPR band by distributing the metal NCs in a one-dimensional photonic structure.

The experimental values of the relative increase in transmission for samples B and C with respect to sample A at 600 nm have been included in Fig. 2. The increments are 32% and 29% for samples B and C, respectively. The slight difference observed with respect to the model calculations is in part due to the small variation that exits in between the thicknesses obtained in the grown films, L_1 and L_2, (see Table I) and the intended values. In addition, the ellipsometry measurements have shown that the effective refractive index of the Cu–nanocomposite layers for each sample shows relative variations within 13% from sample A to C. In spite of these slight differences, the experimental transmission enhancements are very close to the optimum values that can be achieved according to the model calculations.

In conclusion, one-dimensional photonic structures containing Cu NCs have been modeled. First, the layers containing the metal NCs have been optically characterized using an effective refractive index. Subsequently, by means of an appropriate selection of the distribution of the Cu–nanocomposite layers, photonic structures have been designed and optimized to achieve an enhancement in the transmission at the SPR wavelength up to 36%, respect to the film in which the Cu NCs are homogeneously distributed. The photonic structures have been finally produced by PLD, exhibiting an optical response in good agreement with that predicted from the models.

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).

[2] R. Antoine, M. Pellarin, B. Palpant, M. Broyer, B. Prével, P. Galleto, P. F. Brevet, and H. H. Girault, J. Appl. Phys. **84**, 4532 (1998).

[3] K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A. J. Ikushima, T. Tokizaki, and A. Nakamura, J. Opt. Soc. Am. B **11**, 1236 (1994).

[4] D. Ricard, P. Roussignol, and C. Flytzanis, Opt. Lett. **10**, 511 (1985).

[5] S. Nie and S. R. Emory, Science **275**, 1102 (1997).

[6] A. J. Haes and R. P. Van Duyne, J. Am. Chem. Soc. **124**, 10596 (2002).

[7] G. I. Stegeman and E. M. Wright, Opt. Quantum Electron. **22**, 95 (1990).

[8] R. S. Bennink, Y. Yoon, R. W. Boyd, and J. E. Sipe, Opt. Lett. **24**, 1416 (1999).

[9] M. Bloemer and M. Scalora, Appl. Phys. Lett. **72**, 1676 (1998).

[10] M. Scalora, M. J. Bloemer, A. S. Pethel, J. P. Dowling, C. M. Bowden, and A. S. Manka, J. Appl. Phys. **83**, 2377 (1998).

[11] N. Tsurumachi, M. Abe, M. Arakawa, T. Yoda, T. Hattori, J. Qi, Y. Masumoto, and H. Nakatsuka, Jpn. J. Appl. Phys., Part 2 **38**, L1400 (1999).

[12] N. Tsurumachi, S. Yamashita, N. Muroi, T. Fuji, T. Hattori, and H. Nakatsuka, Jpn. J. Appl. Phys., Part 1 **38**, 6302 (1999).

[13] J. M. Ballesteros, R. Serna, J. Solis, C. N. Afonso, A. K. Petford-Long, D. H. Osborne, and R. F. Haglund, Jr., Appl. Phys. Lett. **71**, 2445 (1997).

[14] R. de Nalda, R. del Coso, J. Requejo-Isidro, J. Olivares, A. Suarez-Garcia, J. Solis, and C. N. Afonso, J. Opt. Soc. Am. B **19**, 289 (2002).

[15] R. Serna, C. N. Afonso, C. Ricolleau, Y. Wang, Y. Zheng, M. Gandais, and I. Vickridge, Appl. Phys. A: Mater. Sci. Process. **71**, 583 (2000).

[16] R. Serna, J. Gonzalo, A. Suarez-Garcia, C. N. Afonso, J. P. Barnes, and A. K. Petford-Long, J. Microsc. **201**, 250 (2000).

[17] R. Serna, J. C. G. de Sande, J. M. Ballesteros, and C. N. Afonso, J. Appl. Phys. **84**, 4509 (1998).

[18] C. M. Herzinger, P. G. Snyder, B. Johs, and J. A. Woollam, J. Appl. Phys. **77**, 1715 (1995).

[19] R. H. Magruder, L. Yang, R. F. Haglund, Jr., J. E. Wittig, and R. A. Zuhr, J. Appl. Phys. **76**, 708 (1994).