

Optical properties of Au nanoparticles embedded in ZrO₂ thin films prepared by dip-dry technique

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Au-ZrO₂ thin film samples of around 150 nm thick were prepared by means of sol-gel and dip-dry techniques on glass substrates, from a transparent sol containing ZrOCl₂ and HAuCl₄. After drying, solid films were obtained. TEM studies showed Au nanoparticles embedded in our films, with sizes in the range from 5 to 20 nm. Also, X-ray diffraction patterns showed Au diffraction peaks corresponding to metallic nanoparticles with sizes in the same range, as calculated from the Debye-Scherrer broadening formula. We also studied the optical absorption of our samples. Optical absorption spectra, shown as a surface plasmon resonance band (SPR), displays a shifting of the SPR peaks for our samples, in two opposite directions, depending on the initial treatment. It is showed as a red shifting for thermally treated samples and a blue shifting for samples with larger Au content. This opposite behavior, and some other possible effects as they could be larger nonlinear optical responses, can be attributed to several possible mechanisms, which include changes in the dielectric constant of the media network. Our results have to be explained not only in terms of the particle size, but also in terms of changes in the dielectric constant of the surrounding media. By means of the Mie model for small colloidal spherical particles, we estimated the corrected refraction index for our films, which in turn, can shed light on our results.

Keywords: Zirconium oxide; Sol-Gel; Thin films; Nanoparticles; Optical properties

1. Introduction

Metallic colloids embedded into glassy matrices, exhibit a variety of interesting optical properties, and they are very attractive as the material for optical devices. Metal nanoparticles isolated in a variety of insulating materials, show an enhanced third-order nonlinear optical susceptibility. Conventional melting methods used to obtain these composite materials limits the amount of metal incorporated into the glass matrix. The sol-gel technique solves the problem, and provides a simple way to obtain these materials. Moreover, the optical response of metallic clusters reveals information about their electronic structure. The main feature in this case, is the surface plasmon excitation, SPR (collective oscillation of the conduction electrons), resulting in a resonance band in the absorption spectra. For gold (as well as for other noble metals), the plasmon resonance occurs in the near UV-VIS region. The SPR peaks for Au nanoparticles have been reported to be located at 556 nm [1]. Also, Au nanoparticles embedded in a dielectric matrix display a high-enhanced third order nonlinear susceptibility χ^3 , which could have potential applications in optical communication [2-4]. Moreover, X-

ray diffraction as well as transmission electron microscopy (TEM) provide information about the film morphology, and crystalline structure.

The central task of this paper is focused on the optical absorption of the samples, which can reveal factors driving the optical behavior. The red shift, as well as the blue shift in the SPR, are related with both, the increasing particle size and changes in the value of the dielectric constant of the surrounding media. TEM and X-ray measurements were carried out to fully interpret such optical behavior.

2. Experimental

Solid films of Au-doped ZrO₂ were obtained by dip-dry process, from a precursor sol prepared by a mixture of ZrOCl₂·8H₂O and ethanol stabilized with acetylacetone (CH₃COCH₂COCH₃). Aqueous HAuCl₄ solution was added, and the resultant solution was stirred for 30 min and aged for one day. Thin films of about 150 nm thickness were obtained by dipping standard glass substrates into this yellow-red clear solution. Films were dried at 60°C, and finally heated at 300-500°C in air, holding this terminal temperature for 30 min. XRD were obtained with a JEOL

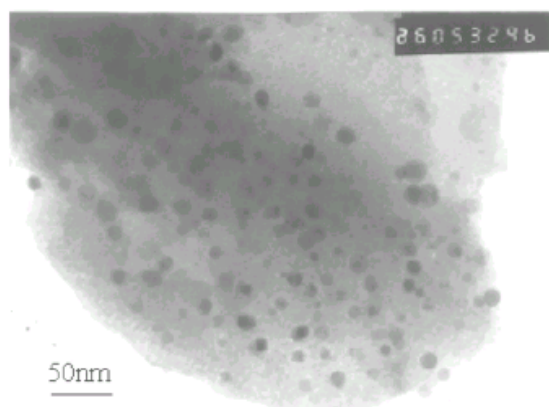


Figure 1. TEM photograph of Au/ZrO₂ film.

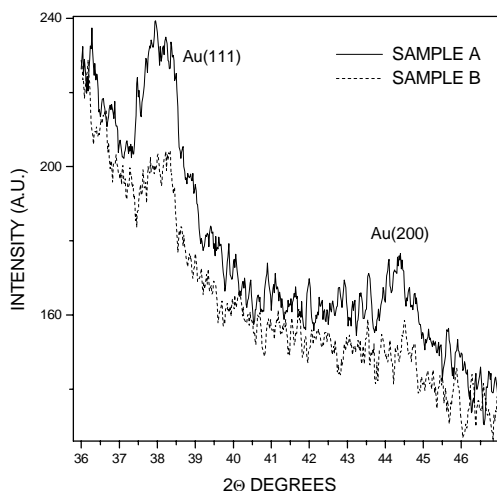


Figure 2. XRD diffraction of two Au/ZrO₂ film samples. Sample A has higher amount of gold than sample B.

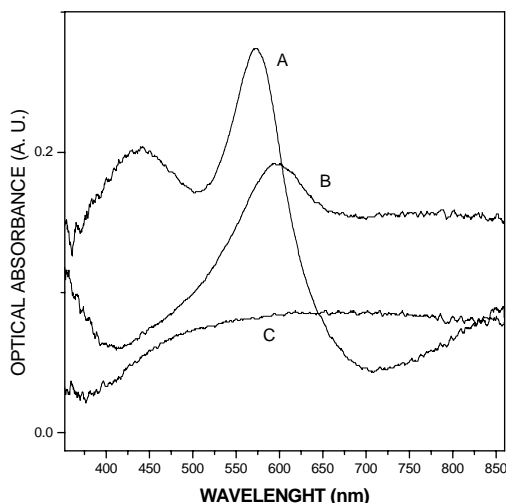


Figure 3. Optical absorbance of samples A and B thermally annealed at 300°C. Sample A has a larger gold volume fraction than sample B. Sample C corresponds to ZrO₂ matrix.

JXD-85D XRD meter (Rigaku co., Tokyo) using CuK radiation operated at 50kV and 140 mA. Optical absorption was made with an Ocean Optics S2000-UV-VIS optical fiber spectrophotometer. TEM photographs were taken with a Hitachi H-800 electron microscope (Hitachi Co., Tokyo).

3. Results and Discussion

The films showed good adherence and changes in color from blue to light purplish blue, depending of the amount of Au salt into the initial mixture. It is well known that colors of noble metal fine particles depend on their size [5].

In Fig. 1 we show a TEM image of our films. It confirms the formation of nearly spherical gold nano-particles immersed in the ZrO₂ matrix, visible as dark spots, with sizes in the range from 5 to 15 nm. These particles are uniformly dispersed and isolated from each other.

X-ray diffraction patterns of the composite films prepared with different Au contents are shown in Fig 2. These samples were thermally annealed at 300° C for 30 min. Sample A has a larger gold volume content than sample B. Two peaks are visible in this figure, at $2\theta = 38.03^\circ$ and 44.3° , which correspond to (111) and (200) planes of metallic gold respectively. As calculated with the Debye-Scherrer broadening formula, the (111) peaks gave 9 and 7 nm for the gold particle size in samples A and B respectively. This result is in good agreement with the gold nanoparticle size observed in Fig. 1.

The optical absorption spectra of these same samples A and B, are shown in Fig. 3. It is observed a blue shift on the SPR peak position from sample B (595 nm) to sample A (573 nm). Thus, for samples treated at the same temperature (300° C), it is observed that a larger volume of gold fraction into the initial sol, results in larger gold particle size, as it was estimated from the X-ray diffraction peaks with the Debye-Scherrer formula. The SPR peaks are blue shifted, as the particle size increases from sample B to sample A, as it is shown in Fig. 3. This optical behavior is opposite to those observed for Au particles fully embedded in glasses, and will be discussed later [6].

Optical absorption spectra of thermally treated samples with the same amount of gold volume content is shown in Fig. 4. Their SPR absorption bands are red-shifting from 565 nm (300°C), to 583 nm (400°C) and 589 nm (500°C).

Plasmon resonances of nanometer-size noble metal particles dispersed in a dielectric medium are given by the Mie-Drude equation [6]. It predicts a red shifting for larger Au particles. The opposite behavior observed in Fig. 3 for larger gold particles, should be explained not only in terms of changes in the distribution of particle size, but also in terms of changes in the dielectric constant of the media. Some reported works show that thermal treatments induce enlargements of Au particles fully embedded in dielectric glasses, giving as a result a red shift in the position of the SPR peaks, as it is shown in Fig. 4 [6-8].

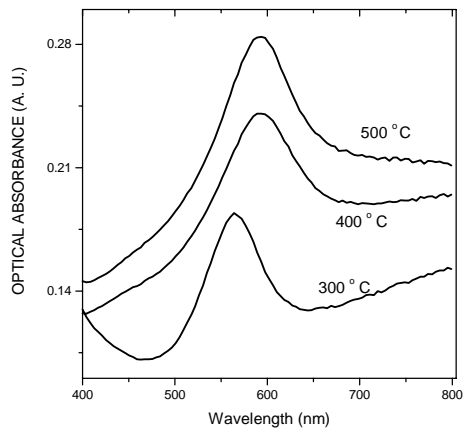


Figure 4. Absorption spectra of thermally annealed samples.

The size dependence of plasmon absorption band has been investigated in several studies [6-11]. Both, blue and red shifts have been reported depending on the matrices. According to the Mie theory [12], the red shift in Fig. 4 results from larger values of the dielectric constant ϵ_m of the matrix. Kreibig and Zacharias [12] also found that the increasing of the dielectric constant ϵ_m , results in shift to longer wavelengths for noble metals.

The refractive index n depends on $\epsilon^{1/2}$. Then, we estimated the changes in the dielectric constant of the matrix, by a numeric calculation of the refractive index. Applying the Mie model [13] for small isolated spherical particles, and considering a gaussian distribution function $f(\lambda, n_g)$ for the refractive index $n_g(\lambda)$ of these matrices, the expected absorption coefficient can be expressed by

$$\alpha(\lambda) = K \int_1^{\infty} \left(\frac{Q_{scat}(\lambda, n, n_{Au}, K_{Au})}{Q_{abs}(\lambda, n, n_{Au}, K_{Au})} + 1 \right) f(\lambda, n) dn \quad (1)$$

where K is a constant of proportionality, which depends on the effective area of colloidal particles, $Q_{scat}(\lambda, n, n_{Au}, K_{Au})$ and $Q_{abs}(\lambda, n, n_{Au}, K_{Au})$ are the absorption and scattering coefficients respectively [14]. These coefficients are functions of wavelength λ , refractive index of the matrix, n_g , and complex refractive index of gold particles (n_{Au}, K_{Au}). Then, we can fit Eq. (1) to experimental data, and obtain the average of the particle size, a , the average refractive index of the matrix, $\langle n_g \rangle$, and the wide of the distribution, σ . Optical properties of ZrO_2 were obtained through a database from the atomic scattering factors from CXRO and LLNL (http://www-phys.llnl.gov/V_Div/scattering/asf.html). Fittings to experimental data of Fig. 4 are shown in Fig. 5. These fittings allowed us to evaluate both, the Au particle size as well as the refractive index of each annealed sample. Results are given in Table 1. An increase in refractive

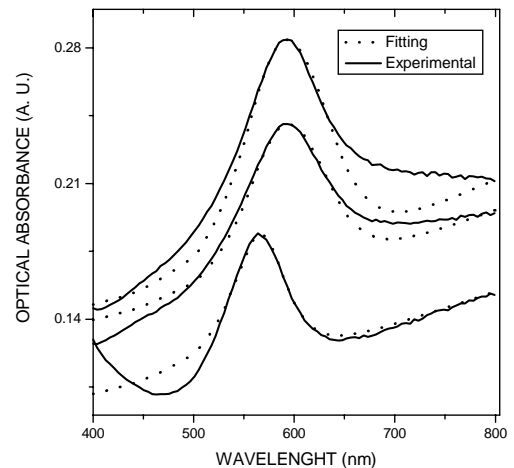


Figure 5. Fitting of the experimental curves displayed in Fig. 4.

index of the matrix is observed as the temperature of annealing is increased. Therefore, with the increasing temperature, the red shift in the SPR peak positions can be explained in terms, not only of an increase of the particle size, but also, in terms of a higher refractive index, which in turn, induces a larger dielectric constant for our annealed samples.

The opposite optical behaviour displayed in Fig. 3 has been found in other reported works, for samples with increasing gold particle size [15,16]. In this case, the influence of the metal-glass interface should be responsible for this blue shifting, by spilling out the metal valence electrons beyond the positive ion region of the matrix. The surface in contact with the metal particle, acts as electron acceptor. This phenomenon causes a decrease of the electron density of the metal, giving rise to this blue shift of the absorption peak. On the other hand, through the heat treatments at least for temperatures below 500°C, an structural evolution of the matrix is induced [17], ϵ_m is enlarged, and a red shift in the SPR peaks position is obtained.

4. Conclusions

We have prepared thin solid films of Au/ZrO_2 by sol-gel and dip-dry methods. As TEM photographs show, gold nanoparticles with sizes in the range 5 – 20 nm are obtained immersed in the ZrO_2 dielectric matrix. The shift in the SPR absorption peaks show two opposite behaviors which can be attributed not only to the metallic grain size evolution, but also to changes in the dielectric constant of the matrix. For thermally treated samples, we have a red shift in their SPR absorption spectra when the size of the particles grow, as it is predicted by the Mie-Drude equation. A blue shift in the SPR peak positions is obtained for samples treated at the same annealing temperature, when the amount of gold content is increased. The Mie theory explains the red shifting, by considering an

Table 1. Calculated Refractive Index for the matrix, in terms of the annealing temperature.

Temperature (° C)	Size (nm)	$\langle n_g \rangle$	σ
300	9	1.75	0.18
400	10	1.93	0.35
500	10	1.91	0.38

increasing dielectric constant with the temperature, and the blue shifting could be explained by mechanisms of interaction between the metallic particle and the surrounding media. Therefore, we can see that the two combined effects of grain size and dielectric constant, drive the optical behavior of gold nanoparticles embedded in a dielectric network [18]. However, this aspect, although intuitively reasonable, needs more detailed investigation.

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