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Nanoscale color control of TiO_2 films with embedded Au nanoparticles

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A B S T R A C T

We demonstrate an efficient nanoscale control of the optical properties of TiO_2 films by tuning the Surface Plasmon Resonance (SPR) in the embedded Au nanoparticles. The films were grown by reactive magnetron sputtering. SPR tuning was achieved by different annealings, which affected the shape and size of the Au nanoparticles, and also the phase of the dielectric matrix. These changes promoted the variations on the optical properties. As shown by the modeling of the effective dielectric function of the TiO_2/Au in the SPR region, the variation of their optical absorption spectra correlates with morphological changes.

1. Introduction

The interest in composite materials containing metal nanoparticles (NPs) embedded in dielectric matrices is related to their potential application in a wide range of technological applications, such as colored coatings [1], solar cells [2], sensors [3,4], antibacterial [5] photocatalysis [6–8], and nonlinear optics [2,9,10]. TiO_2 is a transparent semiconductor material with a wide band gap $E_g = 3.2$–3.4 (eV) and high refractive index ($n = 2.5$–2.9) used for metal-dielectric composites designed for obtaining desired optical properties in the visible range.

The brilliant colors of composites containing noble metal inclusions are due to SPRs in the metallic phase [11]. Films with well-separated embedded metallic NPs with dimensions significantly smaller than the wavelength of the exciting light are characterized by a peak in the visible range of the absorption spectra. The band width, intensity, and position of the absorption maximum depend on the surrounding dielectric matrix, the size, distribution and especially on the shape of the NPs. This fact allows to tune the optical properties of the composite, (i) by changing the refractive index of the matrix (n_h) and (ii) by modifying the morphology and distribution of the metallic inclusions changing the aspect ratio of metallic NPs [12].

2. Experimental details

TiO_2/Au composite films were deposited on glass/quartz substrates, and *in-situ* Au doped by one step reactive magnetron sputtering process, at a constant temperature of 150 °C [13]. The deposited films were annealed in order to promote changes in the morphology, distribution and structural features of *in-situ* grown gold NPs. The doping leads to an average Au volume fraction, f_{Au}, of about 12 at.% as determined by the Rutherford backscattering spectrometry (RBS).

The crystalline structure of as-grown and annealed films was investigated by X-ray diffraction (XRD), using a Philips PW 1710 diffractometer (Cu-K_α radiation) operating in a Bragg-Brentano configuration. The XRD studies allowed to study the film structure concerning both the Au NPs and the TiO_2 matrix. Transmission electron microscopy (TEM) employing a Hitachy 800H apparatus was used to characterize the shape, size and spatial distribution of NPs. Color coordinates and absorption spectra were measured using a commercial MINOLTA CM-2600d and a UV–vis–NIR spectrophotometer (UV-3101) respectively [4,13].

3. Results and discussion

According to the RBS data, there were no measurable changes in the Au doping profiles across the 300 nm of the entire films' thickness during the annealing. The SPR-mediated color control has been achieved by means of annealing of TiO_2/Au composite films grown by reactive magnetron sputtering. Fig. 1 shows the color coordinates (L^*, a^*, b^*) and the change after annealing at different temperatures. Concerning the TiO_2 matrix, the XRD studies revealed that it is amorphous in as-grown and at low temperature annealed conditions. At 500 °C the TiO_2 dielectric matrix starts to crystallize in an anatase-type structure, transforming to rutile above 700 °C. Simultaneously, the Au atoms are organized in crystalline nanoparticles (revealing a fcc-type structure, with the (111) preferential growth orientation) [4,13].

Optical spectra, together with the corresponding morphological data, are depicted in Fig. 2. As it can be seen the SPR related absorption of light occurs only in the films annealed at 400 °C or higher

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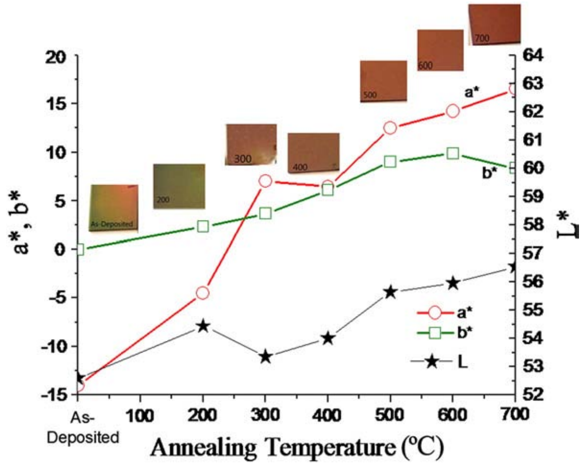

Fig. 1. Color coordinates (L^*, a^*, b^*) and the appearance of TiO_2/Au composite films annealed at different temperatures.

temperatures. The intensity of the resonance absorption increases with the annealing temperature and so does the NP size, as revealed by the TEM images of the same figure. At higher annealing temperatures the SPR band shifts to longer wavelengths and changes its shape. From the theoretical result obtained for a perfectly spherical metallic particle, often referred to as the Mie theory [14] the SPR condition is:

$$\varepsilon_s + 2\varepsilon_h = 0 \qquad (1)$$

where $\varepsilon_h = n_h^2$ is the dielectric constant of the host (matrix) and ε_s denotes the metal-dielectric function. In the simple Drude model,

$$\varepsilon_s(\omega) = \varepsilon_\infty \left[1 - \frac{\omega_p^2}{\omega\left(\omega + i\Gamma_p\right)}\right] \qquad (2)$$

where ε_∞ is a constant, ω_p is the plasma frequency and Γ_p is a damping parameter. Assuming $\Gamma_p << \omega_p$, it follows from Eqs. (1) and (2) that the SPR frequency for a sphere is given by

$$\omega_{SPR} = \frac{\omega_p}{\sqrt{1 + 2\varepsilon_h / \varepsilon_\infty}}. \qquad (3)$$

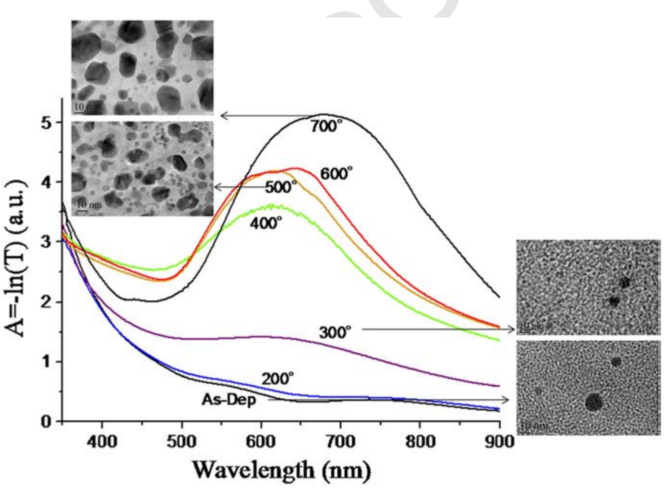

Fig. 2. Optical transmittance spectra (plotted in logarithmic scale) of a set of TiO_2/Au composite films annealed at different temperatures. TEM images of four representative films are also shown.

The width of a single SPR is determined mostly by the plasmon damping which depends on the NP size. For spherical Au NPs the following expression has been proposed [15].

$$\hbar\Gamma_p(R) = \hbar\Gamma_p(\text{bulk}) + g_s v_F / R = 0.0244 + 0.922 g_s / R \quad [\text{eV}], \qquad (4)$$

where v_F is the Fermi velocity, g_s is a geometrical factor of the order of unity and the NP radius R is in nanometers (For the geometrical factor, a value of $g_s \approx 0.7$ has been suggested) [16]. The intensity of the resonance is inversely proportional to Γ_p and directly proportional to the particle volume (R^3). Thus, the theory predicts that the intensity of the SPR band decreases and its broadening increases with the decrease of the NP size. It is experimentally demonstrated when samples annealed at 300 °C and 400 °C are compared (Fig. 2). However, for higher temperatures the absorption band becomes broader and its shape changes suggesting that perhaps there are more than one resonance involved.

The single SPR defined by Eqs. (1)–(3) is split if the particles are not spherical [17]. Axial-symmetric nanorods are supposed to produce two SPRs,

$$\omega'_{SPR} = \frac{\omega_p}{\sqrt{1 + \left(\eta_{||}^{-1} - 1\right)\varepsilon_h / \varepsilon_\infty}}; \quad \omega''_{SPR} = \frac{\omega_p}{\sqrt{1 + \left(\eta_{\perp}^{-1} - 1\right)\varepsilon_h / \varepsilon_\infty}} \qquad (5)$$

where $\eta_{||}$ and $\eta_\perp$ are so called depolarization coefficients [18], which are some geometrical factors, non-negative numbers obeying the relation $\eta_{||} + 2\eta_\perp = 1$. The first resonance takes place for electromagnetic wave polarized along the nanorod axis while the second one corresponds to the perpendicular polarization. If nanorods are embedded in a matrix in a random-orientation fashion, then one should expect to observe both SPRs. If we approximate nanorods by elongated (prolate) spheroids with excentricity e, the depolarization coefficients are given by [18]:

$$\eta_{||} = \frac{1 - e^2}{e^3}\left(\frac{1}{2}\log\frac{1 + e}{1 - e} - e\right) \le \frac{1}{3}; \quad \eta_\perp = \frac{1 - \eta_{||}}{2} \ge \frac{1}{3}. \qquad (6)$$

Using these relations one can see that $\omega'_{SPR} < \omega_{SPR} < \omega''_{SPR}$. The two resonances corresponding to Eq. (4) merge into a single one determined by Eq. (3), when $\eta_{||} = \eta_\perp = 1/3$ (spherical NPs).

Another effect clearly seen in Fig. 2 is the red shift of the absorption band. This is related to a change in the phase composition of the matrix. As already demonstrated, the transition temperature of the anatase-rutile TiO_2 has been reported on a wide range of temperatures, depending on the structure and morphology of the film growth process [19,20], and occurs typically between 700 and 800 °C for the studied samples, as it is reported in previous publications [13]. The two phases have different values of the refractive index, $n_{anatase} = 2.5$ and $n_{rutile} = 2.9$ at $\lambda = 550$ nm proposed [21]. As the annealing temperature was increased, the matrix became more crystalline, increasing the refractive index, but some amorphous TiO_2 phase remains. Anatase is the main crystalline phase until 700 °C, and at higher annealing temperatures the TiO_2 matrix is richer in rutile and the value of ε_h is even higher [4,13].

A model of the optical properties of the TiO_2/Au composite films was performed in order to quantify the arguments. The effective dielectric function of the composite material was calculated using the previously developed modified Maxwell-Garnett (MMG) formalism, which takes into account the dipole–dipole interaction between polarized particles [22,23]. As in the classical Maxwell-Garnett approach, the (complex) effective dielectric function (ε^*) of the composite is related to the particle's polarizability (α) through the equation:

$$\frac{\varepsilon^* - \varepsilon_h}{\varepsilon^* + 2\varepsilon_h} = \frac{4\pi}{3} N\alpha \qquad (7)$$

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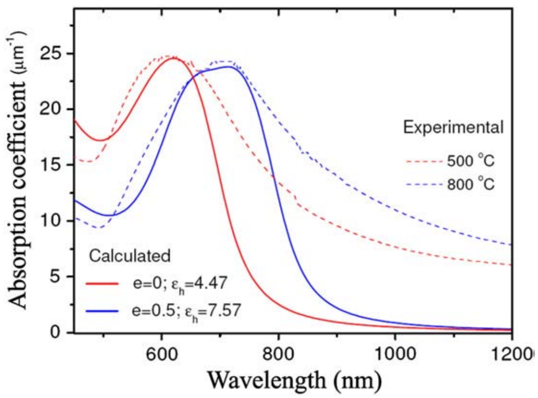

Fig. 3. Calculated and experimental optical absorption spectra of two TiO_2/Au films annealed at 500 and 800 °C, respectively (Au NPs 12 at.%).

where N is the particle number per unit volume. However, in the MMG the polarizability is renormalized due to the dipole–dipole interactions between the particles and therefore this approach is valid for higher volume fractions of inclusions (see Refs [4,23] for further details). For the modeling purposes, the complex dielectric function of gold is used, where two extra contributions representing inter-band transitions have been included in addition to the Drude term (2) as proposed in the bibliography [24]. Dispersion of the refractive index of the TiO_2 matrix was taken into account according to the semi-empirical relations of Ref [25]. The value of $n_h(\lambda = 550\ \text{nm})$ was fitted by assuming a certain percentage of the amorphous and crystalline TiO_2 phases and voids.

Fig. 3 shows the modeling results of two representative spectra demonstrating the effects of the refractive index of the matrix (SPR band position) and NP's shape (band splitting). It is clearly seen that there are two separate resonances already for moderately elongated NPs ($e = 0.6$ corresponds to the aspect ratio of approximately 1.25). These changes in the position and shape of the absorption band result in the variation of the film color coordinates (Fig. 1). The experimental spectra of Fig. 3 also show a long absorption tail extending to the near-infrared, not reproduced by the modelling. This absorption is attributed to more complex shapes gold inclusions. This assumption is supported by the TEM micrographs of Fig. 2 and it is known that metallic fractal clusters indeed can produce broad absorption spectra [26].

4. Conclusions

In conclusion, we have shown that the tuning of the Surface Plasmon Resonance is possible through the nanoscale control of the nanoparticle shape and the refractive index of the matrix, both being achieved by means of annealing treatments at appropriate temperatures.

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