

Metal nanoparticle-doped coloured films on glass and polycarbonate substrates

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Abstract. In a program on the development of metal (e.g. Au, Ag, Cu and their alloy) nanoparticles in sol-gel derived films, attempts were made to synthesize different coloured coatings on glasses and plastics. The absorption position of surface plasmon resonance (SPR) band arising from the embedded metal nanoparticles was tailored by controlling the refractive index of the matrix for the development of different colours. Thus different coloured (pink to blue) coatings on ordinary sheet glasses were prepared by generating Au nanoparticles in mixed SiO₂-TiO₂ matrices having refractive index values ranging from about 1.41 to 1.93. In another development, *in situ* generation of Ag nanoparticles in the inorganic-organic hybrid host leads to the formation of different abrasion resistant coloured coatings (yellow to pink) on polycarbonate substrates after curing. As expected, the SPR peak of Ag or Au is gradually red-shifted due to the increase of refractive index of the coating matrices causing a systematic change of colour.

Keywords. Au and Ag nanoparticles; coloured coatings; silica-titania; silica-titania-epoxy composite films and nonlinear optical material.

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1. Introduction

The optical absorption position of metal nanoparticles (e.g. Au, Ag, Cu etc.) that are much smaller than the wavelength of light can be tailored by controlling several factors like size, shape, concentration of the nanoparticles [1–4] and the refractive index (n) of the embedding medium [5,6]. All these phenomena can be explained using the classical theory of Mie [7]. The optical absorption α of metal nanoparticles embedded in a medium of refractive index n is [7,8]

$$\alpha = \frac{18\pi Q n^3 \varepsilon_2 / \lambda}{(\varepsilon_1 + 2n^2)^2 + \varepsilon_2^2},$$

where Q is the volume fraction of nanoparticles. ε_1 and ε_2 are cluster-size dependent dielectric constants and are function of radius (r) and wavelength (λ). If the size effect of the nanoparticles is not considered, the position of SPR arising from

the metal nanoparticles can be tailored by changing the refractive index of the embedding matrices. In this work we have studied the effect of the matrix refractive index (n) on the optical properties of metal (Au and Ag) nanoparticles. Our result shows that using this approach, the position of SPR band can be controlled systematically and different coloured coatings on glass and plastic substrates can be prepared. As such coatings are also promising nonlinear optical materials [9,10], work is in progress for nonlinear and optical limiting characterizations.

2. Experimental

The Au and Ag nanoparticle doped coatings were prepared from SiO_2 and $\text{SiO}_2\text{-TiO}_2$ hybrid sols using silicon, titanium and substituted silicon alkoxides, $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$, AgNO_3 , n-butanol and water, by the sol-gel dip-coating technique followed by thermal annealing (in the case of glass substrates) or UV curing (in the case of polycarbonate substrates). The $\text{SiO}_2 : \text{TiO}_2$ molar ratios (nominal) were varied from 1 : 0 to about 1 : 4. The molar ratio of Au to oxide ($\text{SiO}_2 + \text{TiO}_2$) was kept constant in all the coatings, being 3 equivalent mol% Au : 97% oxide ($\text{SiO}_2 + \text{TiO}_2$). In the cases of inorganic-organic composites, 3 equivalent mol% Ag was incorporated into the hybrid matrix ($\text{SiO}_2 + \text{epoxy} + \text{TiO}_2$). Coatings were deposited on clean soda-lime silica glass and polycarbonate substrates by dip-coating employing a lifting speed of 2–4 inches/min. The resulting films deposited on glass substrates were dried at 60°C for 60 min followed by annealing at 500°C for 30 min. The coatings deposited on PC were first dried at 90°C followed by curing using a conveyerized UV curing machine. The coating thickness, estimated by a profilometer, was in the 200–1000 nm range. Undoped coatings were also prepared for the measurement of matrix refractive index values. The refractive index values were measured using J.A. Wollam Co. M44 spectroscopic ellipsometer and Gaertner (model L116B) ellipsometer. Refractive index values are reported at 632.8 nm. UV-visible spectra were recorded using a Cary 50 scan spectrophotometer. The pencil hardness values of the coated and uncoated polycarbonate surfaces were measured following ASTM D3363 specification.

3. Results and discussion

Although we have investigated several systems in both inorganic and inorganic-organic hybrid hosts [1–6,11,12], we are reporting here two systems keeping in view the preparation of different coloured coatings: (i) Au in ($\text{SiO}_2 + \text{TiO}_2$) and (ii) Ag in ($\text{SiO}_2 + \text{epoxy} + \text{TiO}_2$). The former is applicable for glass and latter is for plastic substrates. In both the systems, the mole ratios of SiO_2 and TiO_2 were varied in order to obtain different refractive index values of the coating matrices.

3.1 Au in ($\text{SiO}_2 + \text{TiO}_2$)

The as-prepared coatings are transparent and colourless and show absorption peak at about 312–320 nm region due to the presence of AuCl_4^- inside the coatings [11]. This peak is due to the charge transfer between Au and chloride ligands [11].

The formation of Au nanoparticles have been started when the coatings are dried at 60–90°C, and as a result, the intensity of AuCl_4^- peak is gradually weakened and SPR peak due to Au nanoparticles gradually intensified. The evolution of Au nanoparticles in the coating matrices is monitored using UV–visible spectroscopy. Two representative samples of compositions $\text{SiO}_2:\text{TiO}_2 = 1:0$ and $2:3$ (nominal) are shown in figures 1 and 2 respectively. In the case of pure silica ($\text{SiO}_2:\text{TiO}_2 = 1:0$) the Au-SPR peak (figure 1) is observed at 543 nm during drying even at 60°C and this position is retained even after heat treatment at 500°C. This observation suggests that the refractive index values of the dried gel and densified films remain more or less similar ($n = 1.41$). The formation of Au nanoparticles in the film having composition $\text{SiO}_2:\text{TiO}_2 = 2:3$ (nominal) is observed at 90°C (figure 2). It is interesting to note that in the gel film (dried at 90°C) the Au-SPR is observed at about 543 nm (refractive index of matrix remains low at this stage because of porosity) but in the densified film (after heat treatment at 500°C) this band has been shifted to about 580 nm due to the increase of refractive index of the matrix ($n = 1.848$). We therefore observed a clear shifting of Au-SPR from 543 nm to about 600 nm on going from $\text{SiO}_2:\text{TiO}_2 = 1:0$ to about $1:3$ (nominal) due to the systematic increase of the matrix refractive index values. As a consequence, coatings of different colours (pink, magenta, violet, royal-blue and blue) are obtained on glass substrates. One question might be raised at this point: whether this systematic shifting of Au-SPR is caused only due to the change of the refractive index of the matrix or other factors like size, shape etc. are also playing significant roles. To find this answer, we performed X-ray diffraction (XRD) and transmission electron microscopy (TEM) of the heat-treated (500°C) films. XRD analysis showed the presence of broad Au FCC peaks in all the coatings. TEM of two representative coating samples having compositions $\text{SiO}_2:\text{TiO}_2 = 1:0$ and $2:3$ clearly showed the presence of Au nanocrystals of radius from 6 to 15 nm (average particle radius ~ 9 nm). This observation confirms that the shifting of Au-SPR is caused mainly due to the change of matrix refractive index.

3.2 Ag in ($\text{SiO}_2 + \text{epoxy} + \text{TiO}_2$)

In this case the sol is prepared using silicon alkoxide, epoxyalkyl trimethoxysilane, titanium tetraisopropoxide, water, silver nitrate and organic solvents. Silver nitrate is found to be decomposed during thermal or UV curing, and as a result, Ag nanoparticles are formed inside the coatings. The $\text{SiO}_2:\text{TiO}_2$ mole ratio is varied from $1:0$ to about $1:2.3$ in order to obtain matrix refractive index values ranging from 1.48 to 1.71. The as-prepared coatings are colourless and transparent. It has been observed that in the absence of TiO_2 , AgNO_3 is decomposed to metallic Ag even at 60°C and Ag-SPR is observed at about 420 nm. However, in the presence of TiO_2 , AgNO_3 is decomposed to metallic Ag nanoparticles after UV curing. In fact, during thermal ($<100^\circ\text{C}$) followed by UV curing of these films, three reactions occurred simultaneously: (i) polymerization of epoxy groups into polyethylene oxide, (ii) reduction of Ag ions into Ag nanoparticles and (iii) strengthening of inorganic ($\text{SiO}_2/\text{TiO}_2$) network. As a result, the cured coatings became more abrasion resistant (pencil hardness $\sim 3\text{H}$) compared to the uncoated polycarbonate (pencil

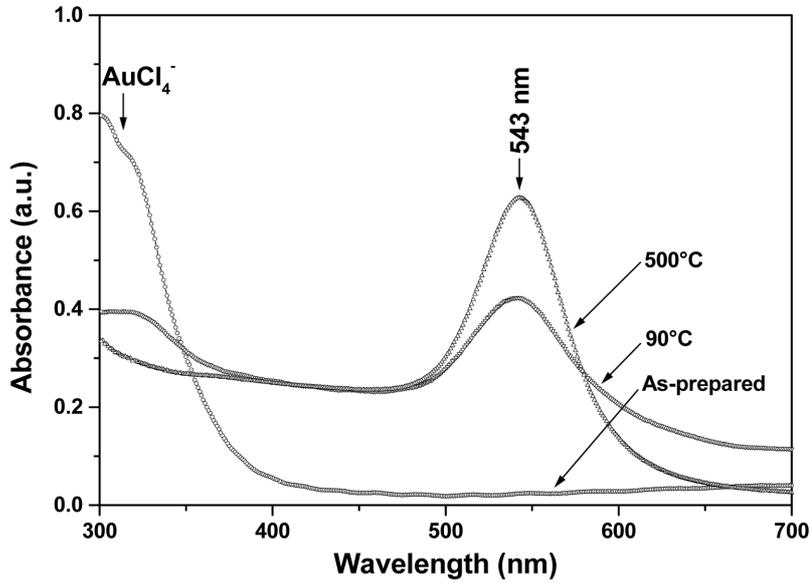


Figure 1. Optical absorption spectra of Au-doped films ($\text{SiO}_2 : \text{TiO}_2 = 1 : 0$) after heat treatment at different temperatures.

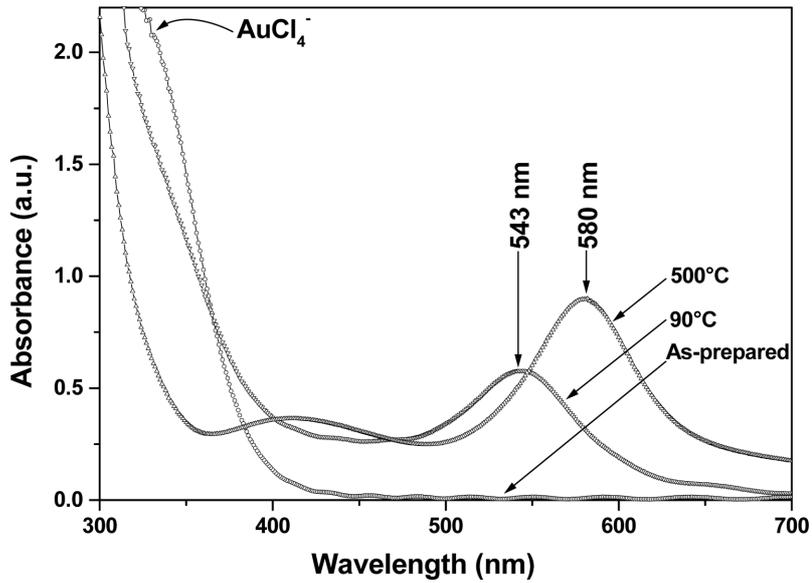


Figure 2. Optical absorption spectra of Au-doped films ($\text{SiO}_2 : \text{TiO}_2 = 2 : 3$) after heat treatment at different temperatures.

hardness \sim HB) and coloured due to the formation of Ag nanoparticles. In this system also we observed a clear shifting of Ag-SPR from about 420 nm ($n = 1.48$) to 500 nm ($n = 1.71$). As a result, different coloured coatings (yellow to pink) are

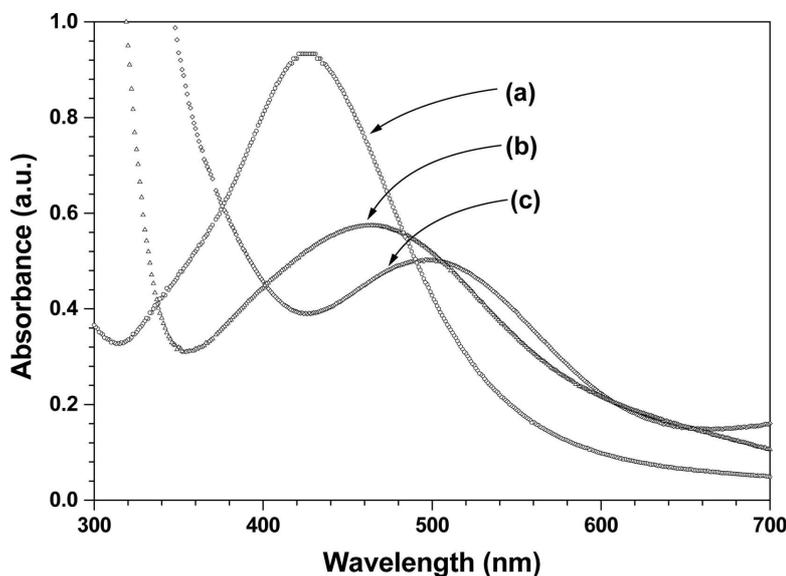


Figure 3. Optical absorption spectra of Ag nanocluster-doped inorganic-organic hybrid coatings (UV cured) deposited on polycarbonate substrates having different refractive index values: 1.48 (a), 1.65 (b) and 1.71 (c).

obtained on polycarbonate substrates. Figure 3 shows shifting of Ag-SPR on going from matrix refractive index values 1.48 to 1.71.

TEM studies of Ag-nanoparticle doped inorganic-organic hybrid coatings showed different particles size distributions in cases of coatings (a) and (c) as marked in figure 3. The average particle size distribution in cases (a) and (c) are about 9 and 2 nm (radius) respectively. This observation suggests that although the shifting of Ag-SPR is mainly governed by the matrix refractive index, the size effect has contribution as well. In fact, the shifting of Ag-SPR in case (c) is more than expected. This can be explained due to the formation of smaller particle size distribution ($r \approx 2$ nm). When the size is smaller ($r \sim 2$ nm) an obvious red-shifting of SPR is expected to appear due to the free path effect of electrons [8].

4. Conclusions

Shifting of the Au- and Ag-SPR absorption positions in the visible wavelength of light can thus be successfully tailored by changing the refractive index of the embedding medium, leading to the generation of different coloured coatings on glass and plastic substrates.

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