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Enhanced nonlinear optical absorption of Au/SiO_2 nano-composite thin films*

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Nano metal-particle dispersed glasses are the attractive candidates for nonlinear optical material applications. Au/SiO_2 nano-composite thin films with 3 vol% to 65 vol% Au are prepared by inductively coupled plasma sputtering. Au particles as perfect spheres with diameters between 10 nm and 30 nm are uniformly dispersed in the SiO_2 matrix. Optical absorption peaks due to the surface plasmon resonance of Au particles are observed. The absorption property is enhanced with the increase of Au content, showing a maximum value in the films with 37 vol% Au. The absorption curves of the Au/SiO_2 thin films with 3 vol% to 37 vol% Au accord well with the theoretical optical absorption spectra obtained from Mie resonance theory. Increasing Au content over 37 vol% results in the partial connection of Au particles, whereby the intensity of the absorption peak is weakened and ultimately replaced by the optical absorption of the bulk. The band gap decreases with Au content increasing from 3 vol% to 37 vol % but increases as Au content further increases.

Keywords: Au/SiO_2 nano-composite film, plasma sputtering, optical absorption spectra
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1. Introduction

Metal-particle-dispersed dielectric matrix composite films have lately received considerable attention, owing to their applications in nonlinear optical devices such as ultrafast optical switches, real time holography and optical computing.[1] The significant optical nonlinearity is induced from the strong surface plasmon resonance (SPR) of metal particles, thereby generating specific optical absorption peaks where the third-order optical nonlinearity is highly enhanced.[2] The SPR frequency depends on the content, size and shape of the metal particles, as well as the dielectric properties of metal particles. In the last decade, much research work has focused on further improving the optical nonlinearity by increasing the content of metal particles. Several techniques such as pulsed laser deposition,[3,4] electrochemical deposition,[5] ion implantation,[6] sol–gel[7−9] and sputtering[2,10−18] have been used. Compared with the above methods, co-sputtering can easily yield high metal-particle dispersed contents and expediently control the size of the metal particles. Liao *et al*[2] have prepared Au/SiO_2 composite films with Au content ranging from 4 vol% to 74 vol% using multitarget magnetron sputtering and studied the dependence of the third-order nonlinear susceptibility ($\chi^{(3)}$) on Au content. However, the influence of microstructure on the properties of thin films has not been described fully. In the present study, perfect spherical Au particles dispersed in SiO_2 composite thin films are prepared by inductively coupled plasma sputtering and later heat-treatment. The microstructure, particle size and optical absorption properties along with the relevant band gap for the Au/SiO_2 composite films are investigated with a special emphasis on the influence of Au content.

2. Experimental procedure

Au/SiO_2 composite thin films were prepared by inductively coupled plasma sputtering (ULVAC, MB95-1010). Au (99.99%, Φ50 mm) and SiO_2 (99.99%, Φ50 mm) targets placed on a copper backing plate were located on the helicon cathodes. The sputtering chamber was initially pumped down to a base pressure of 5×10^{-5} Pa, then argon and oxygen gases were introduced up to a working pressure of 1.6×10^{-1} Pa. The flow rates of argon gas into

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two cathodes were kept at 8.3×10^{-8} m^3/s with an rf power of 200 W. Oxygen gas fed into the chamber by a radical gun equipped with an rf power magnetron was in an active ionic state and maintained at a flow rate of 5.8×10^{-8} m^3/s with an rf power of 50 W. The distance between target and substrate was kept constant at 180 mm. Au and SiO_2 layers were deposited alternately on a quartz substrate by controlling a shutter in front of the targets and substrate. The volume fraction of Au was controlled by changing the deposition time of Au and SiO_2. Post heat treatment was performed at 900 °C in air for 1 h. The microstructure of the annealed thin film was observed by an transmission electron microscope (TEM) (JEOL, JEM-2000EXII). The composition was determined by an energy-dispersion x-ray (EDX) spectroscope (JEOL, TN-5500) attached to the TEM. The absorption spectra were measured by a UV-visible spectrophotometer (UNIC UV-2800).

3. Results and discussion

Figure 1 shows the XRD patterns of Au/SiO_2 nano-films with 5–65 vol% Au which were annealed in air at 900 °C for 1 h. Except for a typical halo pattern of silica (SiO_2) glass at about 22°, four diffraction peaks are observed at 38.1°, 44.4°, 64.6° and 77.6°, which correspond to (111), (200), (220) and (311) reflections of Au phase, respectively. The face-centred cube (fcc) structure of the Au phase remains there clearly, and peaks intensified by increasing Au content are also seen obviously. The corresponding selective area electron diffraction pattern (SAEDP) of the Au/SiO_2 thin films with 37 vol% Au in Fig.2(a) also shows that the diffraction rings from inner to outer correspond to Au crystal faces (111), (200), (220), (311), respectively. The mean diameters of Au particles calculated by Scherrer's equation are 10–30 nm and increase as Au content increases as shown in Fig.2(b). The bright-field TEM micrograph indicates that Au particles are shaped into perfect spheres and dispersed uniformly in the SiO_2 matrix. The size distribution counted from more than 200 grains is concentrated in a range of 10–30 nm (Fig.2(c)) and the average diameter of the particles is about 20 nm. The narrow distribution also suggests that the Au/SiO_2 thin films are quite uniform.

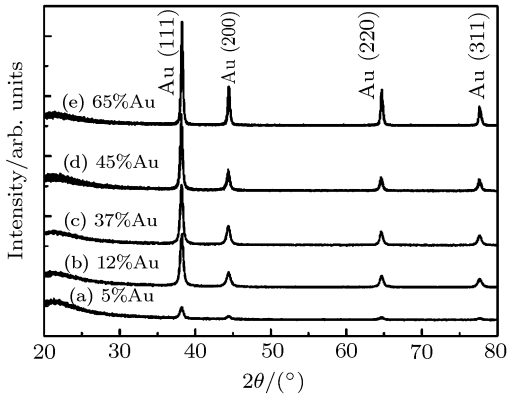


Fig.1. XRD patterns of the Au/SiO_2 thin films.

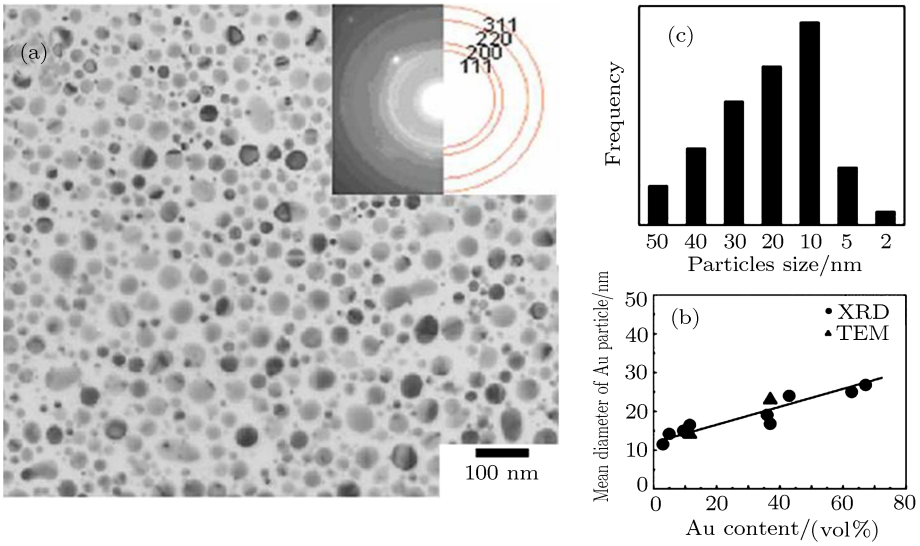


Fig.2. Bright-field TEM micrograph and corresponding selected area (a), the size distributions of Au particles (b) for the Au/SiO_2 thin film with 37 vol% Au, and the relationship between Au content and mean diameter of Au particles for all films (c).

Figure 3 shows the optical absorption spectra of the Au/SiO_2 thin films with different values of Au content. All samples exhibit an absorption peak around 2.3 eV due to the SPR effect. The absorption peak intensifies by increasing Au content up to 37 vol% but decreases as the Au content goes over 37 vol%. The weakened peak at high Au content may be due to highly dispersed Au as reported elsewhere.[17] Liao *et al*[2] reported that the maximum intensity of the optical absorption peak appeared in the 45 vol% Au/SiO_2 films after annealing at 850 °C for 1 min and that when Au content further increased over 59% a downward trend in the peak intensity was produced and a transmission window in the resonant region came into being as the Au content of the sample was higher than a threshold value. In the present work the maximum intensity of the SPR absorption peak even for a film containing 37% Au is comparable to that reported. The maximum absorption taking place in the film with a low Au content in the present study may be attributed to the high dispensing degree and the homogeneous size distribution of Au particles, which is caused by a high annealing temperature and a long treatment time. An enhanced SPR property without the transmission window is even achieved in the sample containing 65% Au. No obvious change in peak position is observed between 3–12 vol% Au, while the resonance peak shows a redshift as the Au content is 12–37 vol% and then turns to a blueshift by further increasing the Au content from 37 vol% to 65 vol%. Kreibig *et al*[19] reported that the size of Ag particles would also induce the shift of the SPR peak, but the position of the SPR peak was independent of particle sizes as the particle diameters were between 4 nm and 15 nm. The independence of particle sizes on optical absorption of the colloid gold in photosensitive glasses was also reported as the particles were smaller than several hundred atoms.[20−22] This was interpreted as collisions of the conduction electrons with the particle surface, which reduced their effective mean free path, that is, the free path effect. The unaltered SPR peak position for the samples with 3–12 vol% Au may be due to similar behaviours in which the particle diameters are smaller than 15 nm as shown in Fig.2(b). The redshift of the SPR peak in the samples with 12–37 vol% Au may be due to the quantum size effect. Likewise, accompanying the SPR shift is the sharpening of the peak when the Au content increases from 3 vol% to 37 vol%, which is attributed to the enhanced intrinsic free electron oscillation inside metal particles. The broadening of the relevant SPR band may be due to the mean free path effect as well as the influence of conduction electron collisions with particle surfaces.[19] The blueshift accompanied with a broadening of the peak in the samples above 37 vol% Au is related to the partial connection of Au. The theoretical optical absorption coefficient (α) in the left inset of Fig.3 of the Au/SiO_2 composite was calculated by using Mie theory which is expressed as

$$\alpha = \frac{18V_0\pi n_s^3}{\lambda}\frac{\varepsilon_{m2}}{[\varepsilon_{m1}+2n_s^2]^2+\varepsilon_{m2}^2}, \tag{1}$$

where V_0, n_s, λ, ε_{m1} and ε_{m2} are the volume fraction of metal, the refraction rate of SiO_2, the wavelength, the real part and the imaginary part for the dielectric constant of metal, respectively. The dielectric constant of metal particles is

$$\varepsilon_m = \varepsilon_{m1} + \mathrm{i}\,\varepsilon_{m2}, \tag{2}$$

and $\varepsilon_{m1} = n_m^2 - k_m^2$, $\varepsilon_{m2} = 2n_m k_m$, where n_m and k_m are the refraction rate and the extinction coefficient of metal. The n_m and k_m of Au are cited from Ref.[23] The calculated SPR peaks for all samples in Fig.3 are constantly located at 2.2 eV along with a monotonic increase in intensity with increasing Au volume fraction, for Mie theory considers only a case of perfectly spherical metal particles and does not take into account the effect of particle size. The uniform dispersion and the perfect spheres in Fig.2(a) contribute to a good agreement between the experimental optical absorption and the theoretical one for the films with low Au content, while there exist some small differences among the films containing more than 37 vol% Au. The spectral intensities of the latter ones decrease and their peaks shift firstly toward higher energies and then toward lower energies as the Au content increases from 45 vol% to 65 vol%. This may be due to the growth of the particle by increasing Au content (Fig.2(b)). Moreover, Au particles would be partially connective if the Au content was increased to a high level, whereby the intensity of the absorption peak would be down and close ultimately to the optical absorption of the bulk. The SPR peak broader than the calculated one is attributed to the broader distribution of the particles (Fig.2(c)).

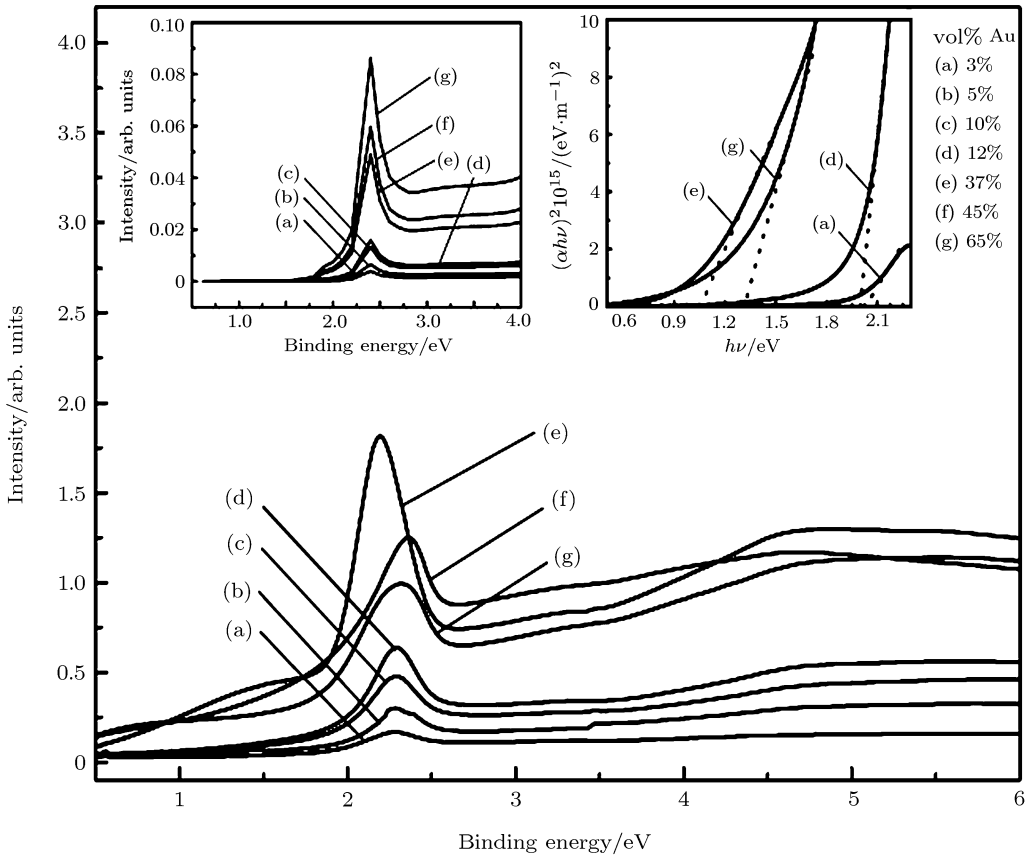


Fig.3. Optical absorption spectra and relation between $(\alpha h\nu)^2$ and photon energy of Au/SiO_2 thin films.

To further understand the behaviour of the optical absorption, the energy band gap (E_g) is estimated from the following formula[24]

$$\alpha(\nu) = A\frac{(h\nu - E_g)^m}{h\nu}, \tag{3}$$

where m is an index which determines the type of optical transition ($m = 2$, 3, 1/2 and 1/3 corresponding to indirectly allowed, indirect forbidden, directly allowed and direct forbidden transitions, respectively), A, E_g and $h\nu$ are a constant, the optical band gap energy and the incident photon energy, respectively. The dependence of $(\alpha h\nu)^2$ in the right inset of Fig.3 on photon energy $h\nu$ indicates that all samples are the directly allowed nature of band-to-band transitions. The values of E_g in the plot of $(\alpha h\nu)^2$ versus $h\nu$ are determined by extrapolating the linear region of the curve to the $h\nu$ axis where $(\alpha h\nu)^2 = 0$, and they are 2.03, 2.0, 1.06 and 1.3 eV for the Au/SiO_2 nano-composite films with 3, 12, 37 and 65 vol % Au respectively. The E_g peak is initially narrowed with Au content increasing up to 37 vol% and then widened as the Au content is over 37 vol%. This evolution is consistent with the absorbance results. Cai *et al*[25] reported that redshift of the absorption edge took place with Ag loading increasing from 0.75 wt% to 1.72 wt% in Ag/SiO_2 films, which was caused by simple scattering. There is a scattering dipole term as well as an absorption dipole term, which both contribute to the extinction. The redshift of the absorption edge with increasing Au content could also be attributed to an increase in scattering centres. Even if the particles grew with Au content, the scattering term in extinction would again increase giving rise to a redshift in the absorption edge. For the heavily dispersed SiO_2 thin films (> 37 vol% Au), the optical gap increases which can be ascribed to the Burstein–Moss effect,[26] in which the donor electrons occupy states at the bottom of the conduction band. Since the Pauli principle prevents states from being doubly occupied, the optical gap is given by the energy difference between states with Fermi momentum in the conduction and the valence bands. Increasing Au content induces the

shift of the Fermi level into the conduction band of the Au/SiO_2 films. So the blocking of the low-energy transitions results in the widening of the optical gap.

4. Conclusions

Au/SiO_2 nano-composite thin films with 3 vol% to 65 vol% Au are prepared by inductively coupled plasma sputtering and subsequently annealed at 900 °C for 1 h. Au particles as perfect spheres with diameters between 10 nm and 30 nm are uniformly dispersed in the SiO_2 matrix. Nonlinear optical absorption peaks due to the surface plasmon resonance are observed for all films. The absorption properties enhanced by increasing Au content from 3 vol% to 37 vol% are consistent with the theoretical spectra calculated from the Mie resonance equation. However, Au particles would become connective with Au contents increasing over 37 vol%, thereby resulting in a decrease in absorption intensity and ultimately leading the optical absorption of Au particles to be replaced by the optical absorption of the bulk. The E_g decreases by increasing Au content from 3 vol% to 37 vol % but increases with further increasing Au content. The redshift of the edge induced by increasing Au content is mainly attributable to the scattering of Au particles, while the blueshift is ascribed to the Burstein–Moss effect.

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