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Enhanced optical nonlinear absorption of graded Au–TiO_2 composite films*

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This paper reports that single-layer and graded Au–TiO_2 granular composite films with Au atom content 15%–66% were prepared by using reactive co-sputtering technique. The third-order optical nonlinearity of single-layer and graded composite films was investigated by using s- and p-polarized Z-scans in femtosecond time scale. The nonlinear absorption coefficient $\beta_{\rm eff}$ of single-layer Au–TiO_2 films is measured to be $-2.3\times10^3-0.76\times10^3$ cm/GW with Au atom content 15%–66%. The $\beta_{\rm eff}$ value of the 10-layer Au–TiO_2 graded film is enhanced to be -2.1×10^4cm/GW calculated from p-polarized Z-scans, which is about ten times the maximum $\beta_{\rm eff}$ of single-layer films. Broadened response in the wavelength region 730–860 nm of the enhanced optical nonlinearity of graded Au–TiO_2 composite films was also investigated.

Keywords: Au–TiO_2 granular composites, graded composite films, Z-scan, optical nonlinear absorption

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1. Introduction

Owing to large third-order nonlinear susceptibility and ultrafast response properties, nano-sized noble metal particles and dielectric matrix composite materials have wide potential applications in optical devices, such as all-optical switches and optical correlators.[1,2] The local electric field inside and near the nano-sized metal particle is greatly enhanced due to the resonant absorption of surface plasmons, and it leads to a strong abnormal optical absorption and large third-order susceptibility in nano-sized metal/dielectric composites.[3–7] Numerous papers reported the effective dielectric function and the enhancement effect of metallic dielectric granular composite materials.[8–11] Highly efficient avalanche multi-photon luminescence from coupled Au nanowires in the visible region were reported.[12] The appropriate one- and two-photon figures of merit (FOM) of Ag nanowire polarizing glass which satisfies the demand, $W > 1$ and $T < 1$, for applications in all-optical switching have been obtained.[13]

The linear and nonlinear optical properties of metal dielectric granular composites strongly depend on the microstructure, the shape, the concentration and the distribution of the nano-sized metallic particles.[5,14–18] The third-order optical nonlinearity of Au–TiO_2 composite films reached the maximum at percolation threshold, which increased with sputtering pressure.[19] It's reported that the capped Au nano-particle films with high concentration and the rod like metal nanoparticles exhibited a large nonlinearity.[20–23] The dielectric with large refractive index such as TiO_2 and nano-sized metal particles was employed as the host matrix and the alternating layers to improve the enhancement factor.[24,25] The (Au, Ag)–TiO_2 composite films annealed at 600°C exhibits strong resonant absorption at wavelengths of 400 and 670 nm and the ultrafast third-order nonlinear optical susceptibility at 820 nm is about 70% larger than that of Au–TiO_2 composite film.[3] Recently, a large enhancement of third-order nonlinearity was theoretically predicted in the graded metallic films.[26] But the enhancement properties of the graded metallic dielectric granular composite materials are unexplored. In this paper, we investigated the giant enhancement of third-order nonlinearity in graded Au–TiO_2 composite films by using femtosecond p- and s-polarized pulses.

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2. Experiment

A series of single-layer Au–TiO_2 composite films with different Au atom content (q_{Au}) and a graded Au–TiO_2 composite film were prepared by a reactive co-sputtering method.[17] The q_{Au} in the composite films was adjusted by controlling the relative area of Au and Ti on the composite target (ϕ: 100 mm, thickness: 3 mm). The sputtering pressure and power were 3.99 Pa and 240 W, respectively. The graded sample consists of ten layers with the same thickness and different q_{Au} (illustrated in Fig.1(a)). The total thickness of the 10-layer film is about 150 nm. The Au atom content in the composite is expressed by the parameter $q_{Au} = N_{Au}/(N_{Au}+N_{Ti})$, where N_{Au} and N_{Ti} represent the atom number of Au and Ti in the composite films. The values of q_{Au} for 10 layers are about 15%, 24%, 32%, 39%, 45%, 50%, 55%, 59%, 62%, 64–66%, respectively, which are estimated from the relative area of the Au and Ti on the composite target.

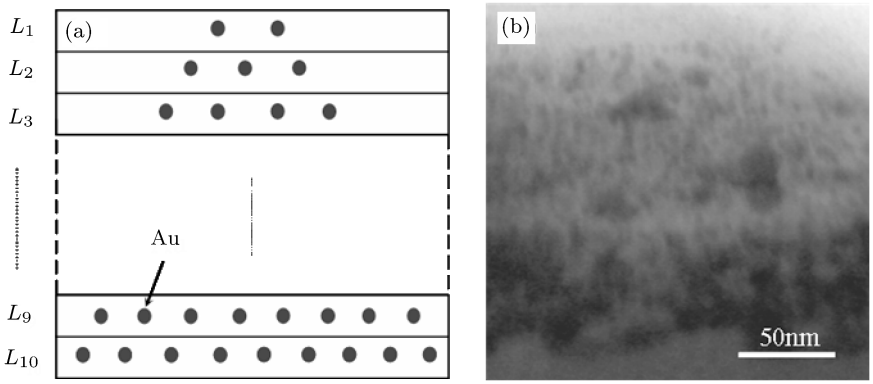


Fig.1. The structure and TEM image of the 10-layer graded film. (a) The structure that each layer has the same thickness and q_{Au} is in the region 15%–66%. (b) TEM image.

3. Results and discussion

Figure 1(b) shows transmission electron microscope (TEM) image of a 10-layer Au–TiO_2 composite film, which indicates a graded distribution of Au content in layers. The absorption spectra of a 10-layer graded sample and single-layer composite films with different q_{Au} are shown in Fig.2. Note that the linear absorption of the graded sample is the sum of ten layers, which is much smaller than that of Au–TiO_2 composite with high q_{Au} of 62%.

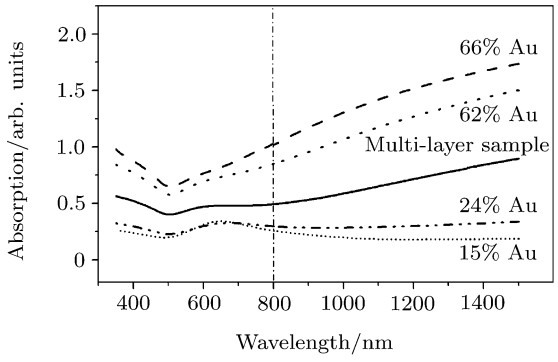


Fig.2. The absorption spectra of the 10-layer graded sample and single-layer films with different q_{Au}.

The nonlinear absorption of composite films was measured by an open-aperture Z-scan method using a mode-locked Ti:sapphire (Mira 900-F) laser at a wavelength of 790 nm. The pulse duration is 130 fs and the repetition rate is 76 MHz. The normalized transmittance and nonlinear absorption coefficient β_{eff} of single-layer Au–TiO_2 samples with different q_{Au} are shown in Fig.3. The value of β_{eff} is calculated from the theoretical expression (given by Refs.[27–29]) between the transmittance T and the position z of a sample. It is clearly shown that the β_{eff} changes dramatically when the q_{Au} increases from 63% to 66%, reaching the maximum -2.3×10^3 cm/GW when q_{Au}=55% and decreasing rapidly to 0.76×10^3 cm/GW when q_{Au} increases to 66%. The Au–TiO_2 composite films exhibit saturable nonlinear absorption in the q_{Au} region of 15%–64%. This saturable absorption (SA) behaviour is mainly attributed to the resonant plasmon absorption of coated Au particles, as it is reported in other articles. When the q_{Au} increases to 66%, the nonlinear absorption changes from SA to reverse saturable absorption (RSA) and the composite film becomes conductive, which is very similar to the observations in conductive pure Au thin films since the resonant wave-

length of the TiO_2 coated Au particle is far away from 790 nm and the resonant absorption is very weak at this high q_{Au}. Therefore, the maximum q_{Au} in the graded sample should be controlled in the range of 0–65% to obtain a large enhanced nonlinearity in the graded films. Figure 4 shows the difference of open-aperture Z-scans between two 10-layer graded films with q_{Au} in the range of 15%–64% and 15%–66%. The former exhibits a pure peak of SA and the latter has a small dip in the peak due to the conversion from SA to RSA.

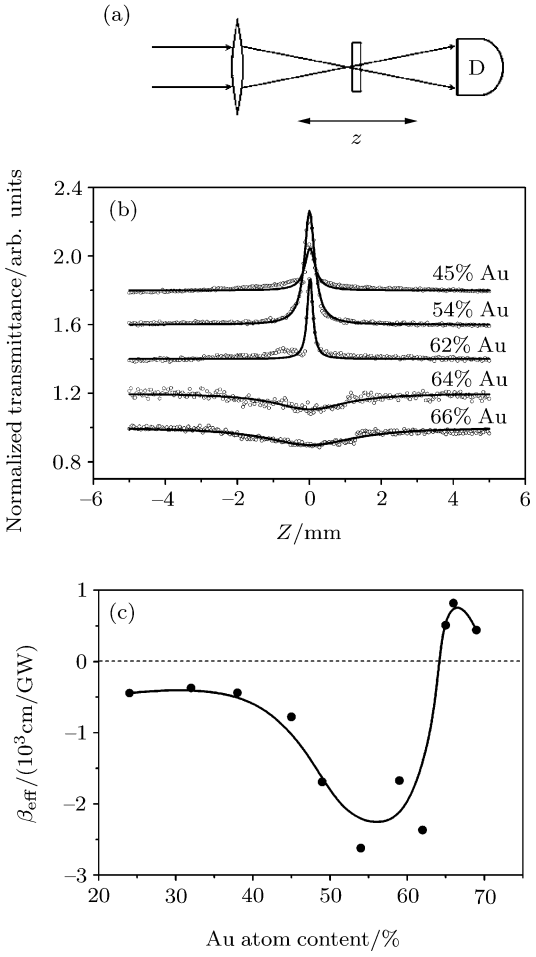


Fig.3. Open-aperture Z-scan results of single-layer Au–TiO_2 samples. (a) Illustration of optical path in Z-scans. (b) Normalized transmittance for different z-position, the dots are experimental data, the solid lines are fitting curves. (c) The effective nonlinear absorption coefficient β_{eff} of the single-layer samples with different q_{Au}, which has positive value (SA) for q_{Au} <65% and negative value (RSA) for q_{Au} >65%.

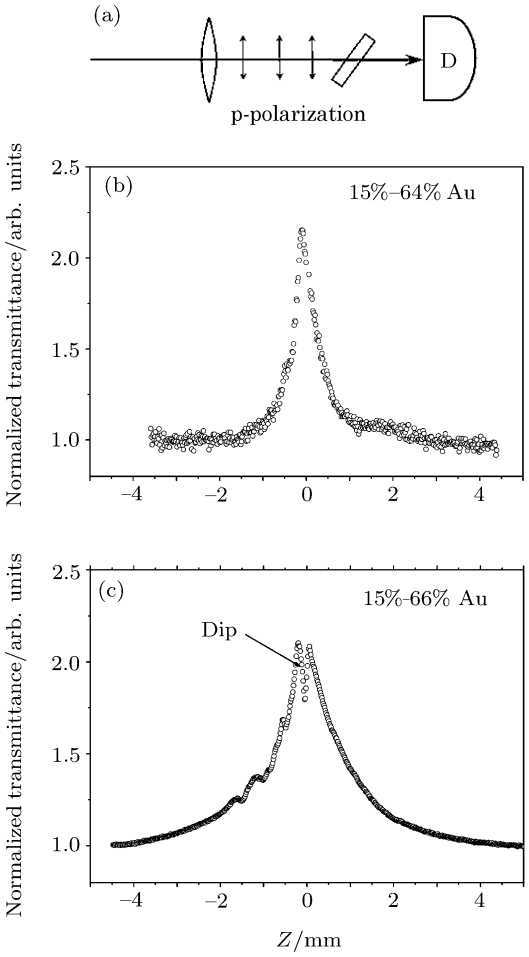


Fig.4. Open-aperture Z-scan results of graded Au–TiO_2 sample. (a) Illustration of optical path p-polarized open-aperture Z-scans. (b) Normalized transmittance versus z-position with q_{Au} of 15%–64%. (c) Normalized transmittance versus z-position with q_{Au} of 15%–66%. A conversion of SA to RSA is occurred in the graded multilayer sample.

To compare the enhancement factor of the parallel local field with perpendicular local field to the plane of the graded film, s-polarization and p-polarization laser pulses were employed in the Z-scan experiments. The incident angle of the laser beam to the film is 45°, which decreases to about 18° inside the TiO_2 films due to refraction. The electric field of s-polarization is parallel to the plane of the film ($E_s(//) = E$, $E_s(\perp)=0$), and that of p-polarization is parallel to the incident plane, which has two components, parallel and perpendicular to the plane of the film ($E_p(//) \approx E\cos 18°$, $E_p(\perp) \approx E\sin 18°$). The change of the normalized transmittance of s-polarization and p-polarization are expressed as ΔT(s) and ΔT(p)

($\Delta T = [T(z=0) - T(z \gg z_R)]/T(z \gg z_R)$, z_R is the diffraction distance of the laser beam), respectively. The open-aperture Z-scans give the results of $\Delta T(p)$=1.2 and $\Delta T(s)$=0.4, which means that the enhancement factor of local field of the p-polarization is much larger than that of s-polarization in the graded sample. The measured value of $\beta_{\rm eff}$ in this experiment is about -2.1×10^4 cm/GW for the graded films when the peak irradiance at the beam waist reaches 12 GW/cm^2. Comparing with the maximum -2.3×10^3 cm/GW of single-layer composite film obtained at $q_{\rm Au}$ of 55%, we find that the enhancement of nonlinear absorption is as large as a factor of 10.

Figure 5 shows the dependence of nonlinear absorption of graded films with the $q_{\rm Au}$ of 15%–64% on the wavelength. A large nonlinear absorption near 730 nm is mainly attributed to the resonant absorption of TiO_2 coated Au particles with small $q_{\rm Au}$. The $\beta_{\rm eff}$ value decreases from -2.4×10^4 cm/GW to -1.6×10^4 cm/GW slowly in the wavelength region of 760–840 nm. The resonant wavelength of each layer is different since the atom content is graded, and the average of 10 layers leads to broadened response in both linear absorption (see Fig.2) and nonlinear absorption (see Fig.5).

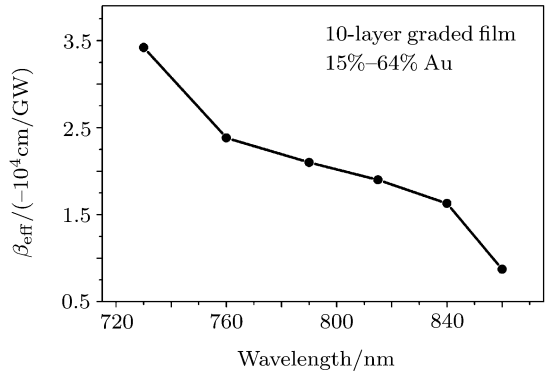


Fig.5. Nonlinear absorption coefficient of the graded Au–TiO_2 film in the wavelength range of 730–860 nm. The $\beta_{\rm eff}$ value decreases slowly from -2.4×10^4 cm/GW to -1.6×10^4 cm/GW in the wavelength region 760–840 nm.

The enhancement of the optical nonlinearity in graded metallic films is reported in the previous works. Several theoretical models have been developed to calculate the local field enhancement factor and effective dielectric constant in metallic graded films[26] and metallic granular composite materials.[8] The dielectric function for the ith (i=1, 2,..., 10) layer composite films is predicted by Sheng's model,[8]

$$g_{\rm A}\frac{\varepsilon_{\rm A}-\varepsilon}{\varepsilon+L_{\rm A}(\varepsilon_{\rm A}-\varepsilon)}+g_{\rm B}\frac{\varepsilon_{\rm B}-\varepsilon}{\varepsilon+L_{\rm B}(\varepsilon_{\rm B}-\varepsilon)}=0,$$

$$g_{\rm A}=(1-q_{\rm Au}^{1/3})^3/((1-q_{\rm Au}^{1/3})^3+(1-q_{\rm TiO_2}^{1/3})^3),$$

$$\begin{aligned}&\frac{\varepsilon_{\rm A}-\varepsilon_{\rm TiO_2}}{\varepsilon_{\rm TiO_2}+L_{\rm A}(\varepsilon_{\rm A}-\varepsilon_{\rm TiO_2})}\\ =&q_{\rm Au}\frac{\varepsilon_{\rm Au}-\varepsilon_{\rm TiO_2}}{\varepsilon_{\rm TiO_2}+L_{\rm A}(\varepsilon_{\rm Au}-\varepsilon_{\rm TiO_2})},\\ &\frac{\varepsilon_{\rm B}-\varepsilon_{\rm Au}}{\varepsilon_{\rm Au}+L_{\rm B}(\varepsilon_{\rm B}-\varepsilon_{\rm Au})}\\ =&q_{\rm TiO_2}\frac{\varepsilon_{\rm TiO_2}-\varepsilon_{\rm Au}}{\varepsilon_{\rm Au}+L_A(\varepsilon_{\rm TiO_2}-\varepsilon_{\rm Au})},\end{aligned}\quad(1)$$

where $g_{\rm B}=1-g_{\rm A}$, $L_{\rm A}$ and $L_{\rm B}$ are the depolarized factors of unit-A (TiO_2 coated Au particle unit) and unit-B (Au coated TiO_2 unit) respectively, $q_{\rm Au}$ and $q_{\rm TiO_2}$ are the volume fractions of Au and TiO_2 in the composite films respectively. The third-order susceptibility of the ith layer is,[30]

$$\chi_i^{(3)}=|f|^2f^2q_i\chi_{\rm Au}^{(3)}\quad(2)$$

where f=3$\varepsilon_{\rm d}$/((1-q_i)$\varepsilon_{\rm Au}$+(2+q_i)$\varepsilon_{\rm d}$) is the local field enhancement factor caused by the coated Au particles, $\varepsilon_{\rm d}$ is the dielectric constant of the coating layer titanium oxide, q_i is the volume fraction of Au particle in the ith layer. For light polarization parallel to the planes of the layers (s-polarization field), the effective dielectric function and third-order susceptibility of the ten layers are given by simple volume averages, $\varepsilon_{\rm eff}(//)=\frac{1}{10}\sum_{i=1}^{10}\varepsilon_i$ and

$$\chi_{\rm eff}^{(3)}(//)=\frac{1}{10}\sum_{i=1}^{10}\chi_i^{(3)}.\quad(3)$$

For light polarization perpendicular to the planes of the layers, the effective dielectric function is $\varepsilon_{\rm eff}(\perp)=10\left(\sum_{i=1}^{10}1/\varepsilon_i\right)^{-1}$ and the effective third-order susceptibility is given by

$$\chi_{\rm eff}^{(3)}(\perp)=\frac{1}{10}\sum_{i=1}^{10}\left|\frac{\varepsilon_{\rm eff}(\perp)}{\varepsilon_i}\right|^2\left(\frac{\varepsilon_{\rm eff}(\perp)}{\varepsilon_i}\right)^2\chi_i^{(3)}.\quad(4)$$

The value of $\chi_{\rm eff}^{(3)}(\perp)/\chi_{\rm eff}^{(3)}(//)$ for the graded sample used in this work is estimated to be about 3 from Eqs.(3) and (4). There is a perpendicular component for the p-polarization pulse field ($E_{\rm p}(\perp)\approx E\sin18°$), which leads to a larger enhancement of optical nonlinearity of graded films with the p-polarization irradiance.

The nonlinear absorption coefficient of the single layer Au–TiO_2 composite film reaches the maximum -2.3×10^3 cm/GW with a relatively high $q_{\rm Au}$ of 55at%.

Contrasting with this single layer Au–TiO_2 film, the graded sample has a larger nonlinear absorption and a smaller linear absorption, which leads to an improvement of FOM.

4. Conclusion

The single-layer Au–TiO_2 granular composite films exhibit SA with the Au atom content of 15%–64% and RSA with the Au atom content over 66%. The graded Au–TiO_2 composite film has less linear absorption and an enhancement of optical nonlinearity by p-polarized femtosecond pulses. The nonlinear absorption coefficient β_{eff} of the graded 10-layer Au–TiO_2 composite film with the Au atom content of 15%–64% is measured to be about -2.1×10^4 cm/GW, which exceeds largely the maximum β_{eff} of single-layer Au–TiO_2 films.

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