A Sign Alternation of Nonlinear Absorption in Gold Composite Films in Z-Scan

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Au–TiO_2 composite films with Au atom content varying from about 15% to 82% are prepared by co-sputtering technique. Both open- and closed-aperture Z-scan of the samples are performed in the femtosecond time region. A conversion of the nonlinear absorption from negative to positive is observed as the Au atom content increases due to the saturation of reverse saturable absorption. The nonlinear refractive index γ and effective nonlinear absorption coefficient $\beta_{\rm eff}$ at the Au atom content of 54% are measured to be 1.6×10^{-2} cm^2/GW and -2.6×10^3 cm/GW, respectively. The corresponding third-order optical nonlinearity $\chi^{(3)}$ is about 6.3×10^{-8} esu.

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Nanometre-sized metallic particles and their dielectric composite films have been studied for years because they possess large optical nonlinearity,[1−3] which is essential for the applications in optical switching[4] and optical limiting.[5] There are various methods to prepare these composite materials, such as melt quenching,[6] sol-gel,[7] ion implantation,[8] laser deposition,[9,10] and sputtering.[1] To increase the metal concentration in the composite film which is believed to enhance the optical nonlinearity effectively, we employ a sputtering technique similar to the one used in Ref. [11]. According to the local electric field enhancement theory under the resonance condition, it has been found that the larger the refractive index n is, the larger the local field enhancement factor f of the composite becomes.[3] Since pure TiO_2 films deposited by the sputtering method have a refractive index of 2.4–2.7, they are a kind of good matrices for the Au–dielectric composite. Large third-order susceptibility in Au–TiO_2 composite films has been reported by means of degenerated four-wave mixing (DFWM).[2] However, the features about the nonlinear absorption and nonlinear refraction with different Au contents in these composites are seldom reported. Z-scan[12,13] is a simple and sensitive technique that can measure the nonlinear refractive index and nonlinear absorption coefficient simultaneously. Noticing the recent progress in Z-scan theory,[14,15] in this Letter, we report open- and closed-aperture Z-scans performed to measure the effective nonlinear absorption coefficient $\beta_{\rm eff}$ and nonlinear refractive index γ. Both nonlinear saturable absorption (SA) and reverse saturable absorption (RSA) are investigated.

The Au–TiO_2 composite films were prepared by the co-sputtering technique, using a Ti target (Φ100 mm) with several pieces of pure Au attached to it. The atomic proportion of Au and Ti in the composite films was controlled by adjusting their relative area ratio on the composite target. The deposition was carried out in the argon atmosphere at a pressure of about 3.4×10^{-2} Torr. Au content in the samples was controlled in the range of 15 wt.%–82 wt.%.

We adopted the Z-scan method to determine the third-order optical nonlinearities of these films. There were 150-fs-laser pulses at 76 MHz repetition rate employed. The 790 nm femtosecond laser was generated by a mode-locked Ti:sapphire laser (Coherent, Mira 900). With a converging lens of $f = 50$ mm, the radius of the Gaussian beam spot at focal waist w_0 is calculated to be about 3 μm. In the Z-scan test, the sample was moved step by step along the propagation direction of the Gaussian beam under the control of a PC. Meanwhile, the transmitted laser power was monitored by a detector and the signals were sent back to the computer and recorded. To determine γ and $\beta_{\rm eff}$, both open- and closed-aperture Z-scans of a series of the samples were performed, all of which were performed under the same laser power at room temperature.

The scanning electron microscopy (SEM) images are shown in Fig. 1, indicating that the average particle size is about 30 nm, 20 nm and 45 nm for the sample of (a) 15%, (b) 54% and (c) 69% Au, respectively. The thickness of the films was measured to be about 120 nm. The optical transmittance spectra of the films were recorded using an UV-VIS-NIR spectrophotometer (Varian, Cary 5000) and are displayed in Fig. 2. The strong plasmon resonant absorption peak near 650 nm is observed for the low Au concentration samples.

Normalized open-aperture Z-scans are displayed in Fig. 3(a). It shows clearly that for the samples whose Au contents are equal to or less than 62%, the curves are typical peaks, thus the corresponding nonlinear

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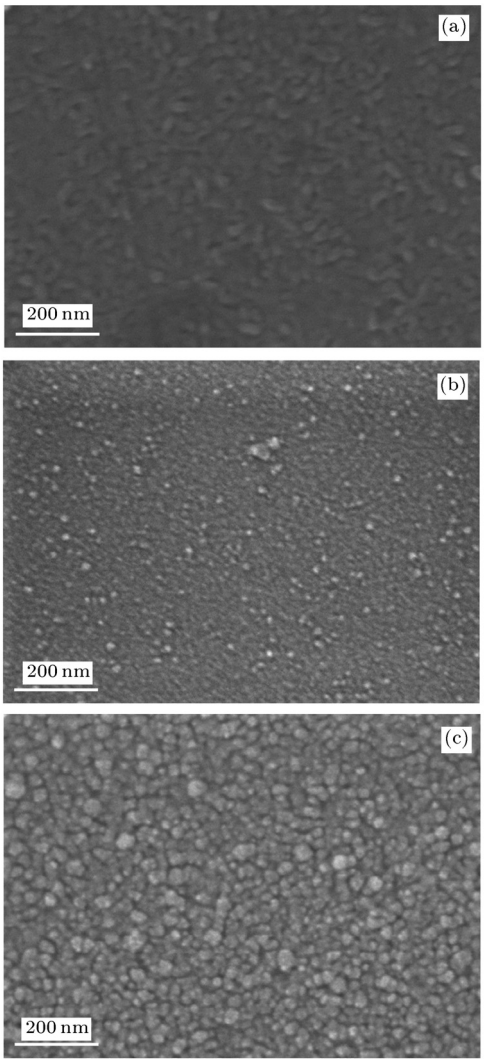

Fig. 1. Morphologies of the samples at 15% Au (a), 54% Au (b) and 69% Au (c) scanned by SEM.

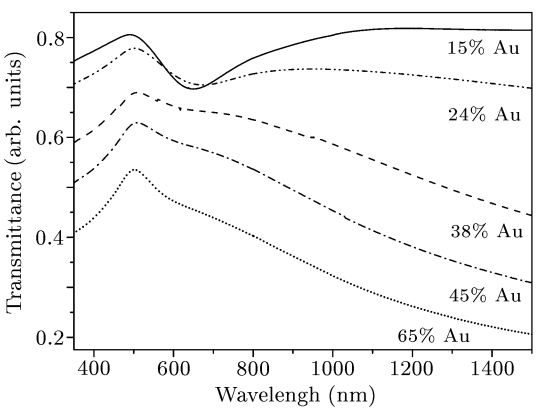

Fig. 2. Transmittance spectra of the samples at 5 different Au contents.

absorption is negative. As the Au content reaches 64%, the peak turns into a valley, which means that the nonlinear absorption changes to positive. According to the open-aperture Z-scan theory,[13] the effective nonlinear absorption coefficient β_{eff} was calculated and plotted as a function of Au content in Fig. 3(b). One can see that β_{eff} is negative when the Au content is less than 64%, and it becomes positive as Au content is above 64%. The maximum value of β_{eff} is measured to be -2.6×10^3 cm/GW at 54% Au.

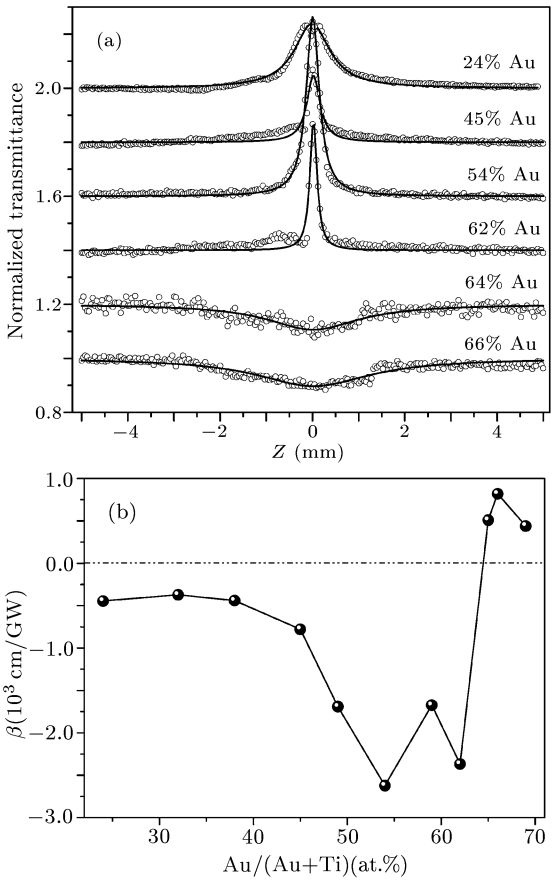

Fig. 3. Open-aperture Z-scans of samples at six different Au contents (a). Curves are shifted vertically for clear presentation. The radius of the Gaussian beam spot on the lens ($w(l)$) is about 6 mm. The radius of the Gaussian beam spot at focal waist w_0 is calculated to be about 3 μm with a focus lens of $f = 50$ mm. The effective nonlinear absorption coefficient β_{eff} against Au contents (b).

A typical result of the closed-aperture Z-scan divided to the open-aperture one is displayed in Fig. 4(a), which reveals a self-focusing effect. $|\Delta\Phi_0|$ is calculated from Eq. (1) with $|\Delta\Phi_0| < 1$ indicating a small phase change:

$$\Delta T_{p-v} \approx 0.406|\Delta\Phi_0|. \quad (1)$$

The nonlinear refractive index γ is calculated and plotted as a function of Au content in Fig. 4(b), which implies a sudden increase of γ around 38% Au. The largest γ is determined to be 1.6×10^{-2} cm^2/GW at 54% Au, which also has the largest β_{eff}. The corresponding third-order optical nonlinear susceptibility $\chi^{(3)}$ is calculated to be about 6.3×10^{-8} esu, with $\alpha_0 \approx 6.3\,\mu\text{m}^{-1}$ and $n_0 = 2.4$.

The change from peak to valley of open-aperture

Z-scans (shown in Fig. 3) with the increasing Au content can be explained by the theory of saturation of RSA. Since the composite film with high Au content is conductive, this change is coincident with the measurement reported in Ref. [18] for a positive nonlinear absorption in a continuous thin Au film.

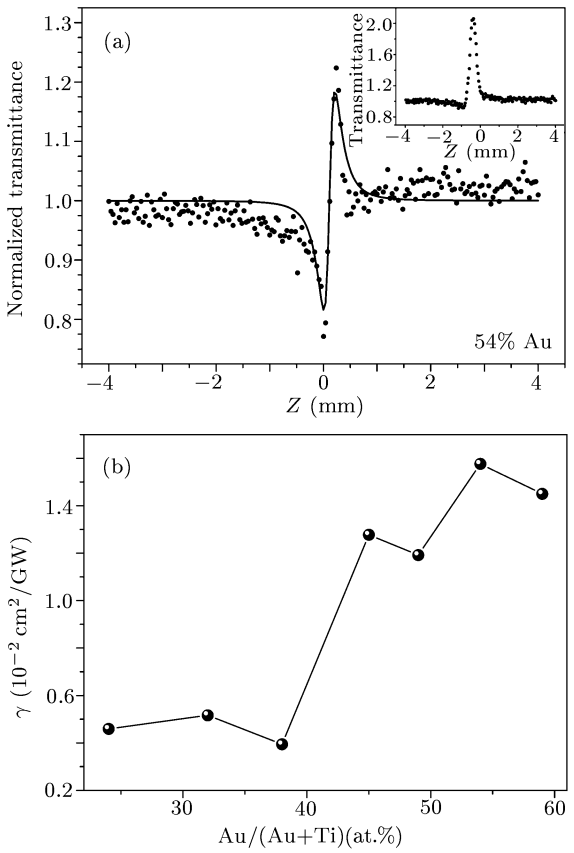

Fig. 4. The closed-aperture Z-scan curve and its fitting line of the sample at 54% Au (a), the inset in graph (a) is a typical closed-aperture Z-scan which has not been divided to the open-aperture one. The nonlinear refractive index γ against Au contents (b).

A sign alternation of nonlinear absorption has been studied in silver nanosol before.[16] Similarly, we attribute it to the saturation of RSA. It is reported that there is an intensity threshold I_c in the four-energy level model. Once the intensity is over I_c, the RSA-to-SA conversion occurs.[17] Here I_c is supposed to be appropriately the same for the samples of different Au contents. The real incident intensity $I'(z)$ in the sample depends on two conditions: (1) the sample position z in Z-scan. Since the beam is a focused one, the closer the sample is to the focal point, the larger the value of $I'(z)$ is. $I'(z)$ comes to a climax I'_0 while $z = 0$. (2) The different surface reflection rates for different samples. I'_0 is calculated ranging from 23 to 170 GW/cm^2 for these samples. Returning to the Z-scans of Fig. 3(a), in the case of the high Au content samples, due to the stronger reflection on the surface of the film, I'_0 is relatively weaker as compared with the low content sample and may be weaker than I_c (considering the same laser power and a lower reflection on the surface of a low Au content sample), so the RSA-to-SA conversion never occur and RSA is dominant, which results in a pure valley in the open-aperture Z-scan. For the low content sample, I'_0 may be much stronger than I_c, which means $I'(z) > I_c$ with the sample moved close enough to the focal point, so the RSA-to-SA conversion occurs and SA becomes dominant, resulting in a peak in the open-aperture Z-scan.

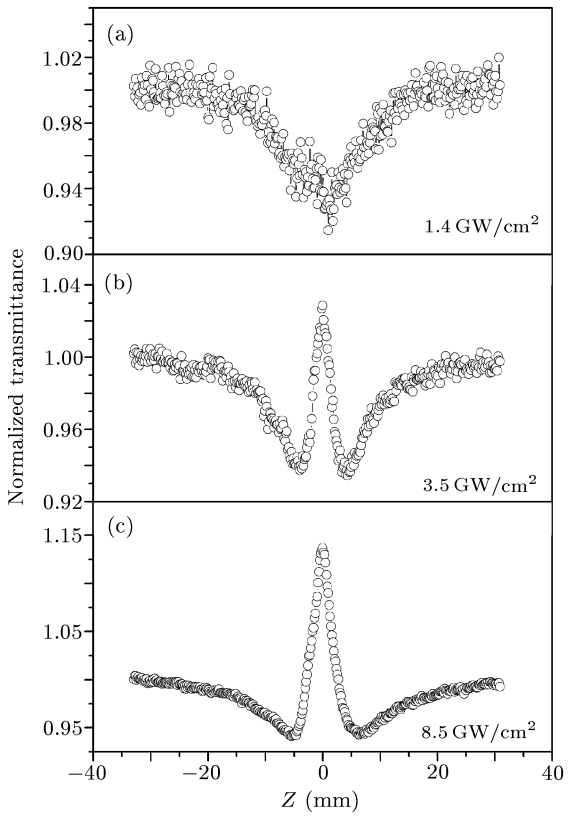

Fig. 5. Open-aperture Z-scans of the 82% Au sample at three different incident intensities (a), (b) and (c).

To further support this explanation, a special sample was prepared at 82% Au using the same co-sputtering technique but with a higher pressure of about 9.5×10^{-2} Torr. The deposition time (30 s) was much shorter than that series of samples (e.g. 20 min). The open-aperture Z-scan tests of this sample were performed under different laser power with a converging lens of $f = 150$ mm, the results are shown in Fig. 5. In Fig. 5(a), $I'_0 > I_c$, the conversion from RSA to SA never occurs, so the open-aperture Z-scan is a valley. In Figs. 5(b) and 5(c), $I'_0 > I_c$, so RSA changes into SA and the peak arises from the valley. This is consistent with the change observed in the open-aperture Z-scan tests of the series of samples under a single laser power.

We notice that with a high repetition-rate laser

and especially when the laser peak intensity is larger than few GW/cm^2, there is a very high probability for the high absorbing materials to be damaged at the tested point due to cumulative heating, which will produce an ablation hole. The closed-aperture Z-scan curve of the ablation hole is symmetric and has a peak-valley pattern similar to the one of some materials with negative nonlinear refraction.[19] The inset in Fig. 4(a) is a typical closed-aperture Z-scan of the Au–TiO_2 composite films. It is not symmetric and the curve has a valley-peak pattern, which is different from the calculation result of the ablation hole. Furthermore, the asymmetric curve changes little when repeated at the same point. Thus we assume there was no formation of the ablation hole in these samples during the Z-scan, i.e. the Z-scans are true signals representing optical nonlinearities of the samples. Considering the error in evaluation of $w0$ and I'_0, the uncertainty in γ, $\beta_{\rm eff}$ and $\chi^{(3)}$ values is still under discussion.

In summary, we report on the preparation and third-order nonlinear optical properties of the Au–TiO_2 films evaluated by the Z-scan technique in the femtosecond time region. A change from peak to valley was observed in the open-aperture Z-scan curves as the Au content increasing, which means the nonlinear absorption change from negative to positive. This phenomenon is seldom reported and has been explained with the theory of saturation of RSA. The largest third-order optical nonlinearity $\chi^{(3)}$ is calculated to be 6.3×10^{-8} esu at 54% Au.

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