Ultrafast nonlinear optical response of Ag:$BaTiO_3$ composite films at the near-ultraviolet wavelengths

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The ultrafast nonlinear optical response of Ag:$BaTiO_3$ composite films synthesized by pulse laser deposition (PLD) is studied at the near-ultraviolet (400 nm) wavelength. The pulse duration of the laser used in the measurement is 200 fs. The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ of the composite materials are measured. The composite films indicate self-focusing effect and nonlinear saturation, the values of $\mathrm{Re}\chi^{(3)}$ and $\mathrm{Im}\chi^{(3)}$ are measured to be 3.42×10^{-10} and -1.37×10^{-10} esu respectively, which are much lower than those reported before. It is mainly because that the duration of the laser used in the measurements is too short to induce the hot electron excitation and the thermal effect. The ultrafast nonlinear saturated absorption response of the Ag:$BaTiO_3$ composite films may have potential applications for femtosecond laser mode locking.

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Dielectric materials containing metal nanoparticles are of interest because of their potential for applications such as optical switches with an ultrashort time response[1] and optical limiters of laser radiation intensity[2,3]. Moreover, such composite structures can exhibit nonlinear saturated absorption, which can be used for laser mode locking[4].

Most of the previous studies to obtain the nonlinear optical characteristics of nanoparticle metals in various dielectric matrices were carried out using lasers with pulse duration of nanosecond or picosecond duration[5−7]. It is of interest to determine nonlinear optical characteristics of materials with metal nanoparticles exposed to the ultrashort pulse laser. In this work, we use the laser with a pulse duration of 200 fs to measure the nonlinear susceptibilities of Ag:$BaTiO_3$ thin films at the wavelength of 400 nm by z-scan technique.

The films were fabricated on quartz substrates by pulse laser deposition (PLD). A XeCl excimer laser (308 nm, 17 ns, 4 Hz) was focused on a rotating $BaTiO_3$ target. Several fan-shaped Ag chips were placed uniformly on the surface of the target so that the Ag particles can be embedded uniformly in $BaTiO_3$ dielectric matrix. The pulse energy at the target was about 1.5 J/cm^2. The films were deposited on MgO substrates, which were polished on both sides and 0.5 mm in thickness, at 600 °C under 7-Pa nitrogen pressure.

To investigate the distribution of Ag particles in $BaTiO_3$ matrix, transmission electron microscopy (TEM) was performed. Optical absorption spectra for the samples were measured in the wavelength range from 330 to 800 nm. The thickness of the films was measured to be 140—150 nm with the Dektak 8 surface stylus profiler (Veeco company). The optical nonlinearities were determined by a single beam z-scan method, using a pulsed Ti:sapphire laser with a pulse duration of 200 fs and a pulse repetition rate of 10 Hz. The wavelength of the laser was 400 nm and the pulse energy was about 8.0 μJ. The laser beam was focused on the sample with a 120-mm focal length lens, leading to a measured beam waist of 40 μm. The Rayleigh length z_{R} was calculated to be much longer than the thickness of films plus substrate. The transmitted beam energy, the reference beam energy, and the ratio between them were measured using an energy ratiometer simultaneously.

Figure 1 shows the TEM image of the composite film. The dark regions in the image are Ag particles and the light regions are $BaTiO_3$. The image exhibits homogeneous distribution of Ag clusters that are approximately spherical with diameters of about 10 nm.

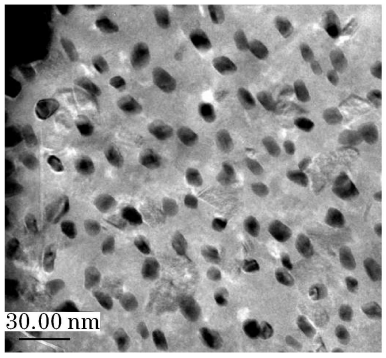

Fig. 1. TEM image of Ag:$BaTiO_3$ composite films, the dark regions are Ag nanoparticles.

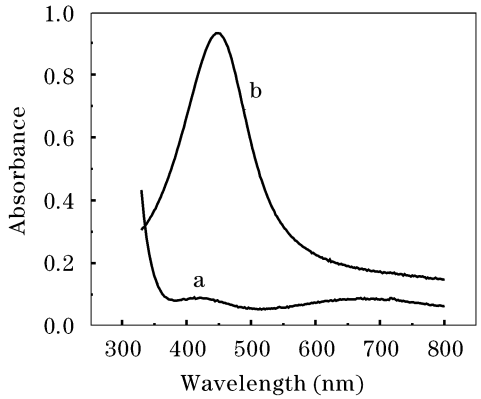

Fig. 2. Absorption spectra of the undoped $BaTiO_3$ (a) and Ag:$BaTiO_3$ films (b).

Figure 2 displays the linear absorption spectra of the Ag:$BaTiO_3$ films in the range of 330—800 nm. The data are automatically corrected by the spectrophotometer to account for the absorbance of the MgO substrates. As a reference, the linear absorption spectrum of undoped $BaTiO_3$ thin film is also recorded (curve a). Without Ag in the $BaTiO_3$ films, no absorption peak is observed. When the $BaTiO_3$ films are doped with Ag, the strong linear absorption peak is found at the wavelength of about 450 nm. The peak is due to the surface plasmon resonance of Ag particles.

The normalized open-aperture (OA) and closed-aperture (CA) z-scan curves of the Ag:$BaTiO_3$ films measured at 400 nm are shown in Fig. 3. Because the MgO substrate has weak nonlinear optical property, the high nonlinear optical properties result from the Ag:$BaTiO_3$ films. The OA curve in Fig. 3(a) comprises a strong transmittance peak, and the solid curve is the theoretic fitting according to[8]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \approx 1 - \frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}(1+z^2/z_{\text{R}}^2)}, \quad (1)$$

where $q_0(z) = \beta I_0 L_{\text{eff}}/(1+z^2/z_{\text{R}}^2)$, I_0 is the intensity at the focus, L_{eff} is the thickness of the film. The nonlinear absorption β is obtained from the fitting parameter as -3.22×10^{-9} m/W, and $\text{Im}\chi^{(3)}$ is derived to be -1.37×10^{-10} esu. The nonlinear absorption is negative, indicating the presence of nonlinear saturation in the films. It is well known that the intraband transition, the interband transition, the hot electron excitation, and the thermal effect all contribute to nonlinear susceptibility of the material[9]. Because the Ag particles are relatively large and the wavelength for the measurement is near the linear absorption resonance wavelength, the contribution of the interband transition is much larger than that of the intraband transition[10]. Therefore, in our case the nonlinear absorption is mainly contributed by the interband transition and the hot electron excitation. The interband transition mainly behaves as a nonlinear saturation with a response time of about 10^{-13} s, while the hot electron excitation with a response time of about 10^{-12} s[11,12]. Since the pulse duration is 200 fs, the interband transition can occur but the hot electron excitation cannot, so it is reasonable that the films represent the nonlinear saturation effect. In the CA measurement (Fig. 3(b)), the nonlinear saturation enhances the peak and reduces the valley, giving an asymmetric curve and exhibiting a positive value for the nonlinear refractive index. We usually divide the CA data by the OA data to remove the influence of the nonlinear absorption from the CA data. However, in our measurement, the value of $q_0(z)$ is very large due to the high intensity of the laser and cannot satisfy the condition $q_0(z) \le 1$[13], so we cannot use this method. In Fig. 3(b), we use the following formula[14] to fit the experimental data:

$$T(z) = 1 - \frac{\beta I_0 L_{\text{eff}}\left(\xi x^2 + 2x + 3\xi\right)}{\xi\left(x^2+9\right)\left(x^2+1\right)}, \quad (2)$$

where $\xi = \frac{\text{Im}\chi^{(3)}}{\text{Re}\chi^{(3)}}$, $x = z/z_{\text{R}}$. The factor ξ is obtained from the fitting parameter as -0.4 and $\text{Re}\chi^{(3)}$ can be derived as 3.42×10^{-10} esu. With the value of $\text{Im}\chi^{(3)}$ of -1.37×10^{-10} esu above, the values are much less than those reported previously, which are 8.567×10^{-6} and 4.151×10^{-7} esu[15]. In our measurements, the pulse duration of the laser is very short and the repetition rate is only 10 Hz, so the thermal effect cannot be detected. Moreover, as mentioned above, only the interband transition contributes to the nonlinear effect but the hot electron excitation does not. We consider that the above reasons reduce the value of the nonlinear susceptibility of the composite film.

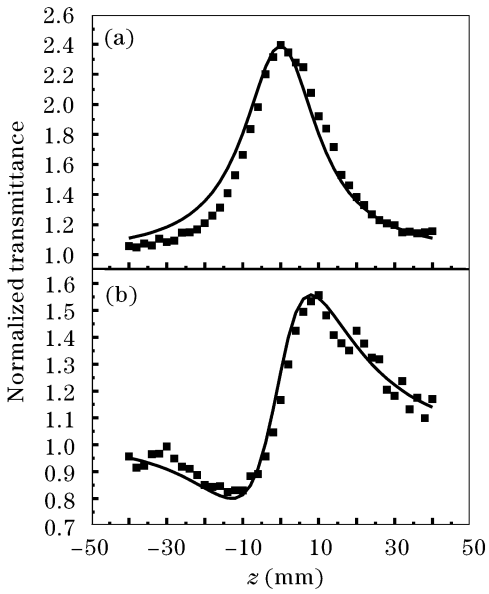

Fig. 3. z-scan data for Ag:$BaTiO_3$ films with an OA (a) and a CA (b) at the wavelength of 400 nm. The solid curves indicate the theoretical fitting. The laser intensity in measurement is 8.0 μJ.

We have studied the nonlinear optical properties of the Ag:$BaTiO_3$ composite films at the wavelength of 400 nm using a femtosecond laser. The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ of the composite materials are measured. The pulse duration of the laser is 200 fs and it is shown that $\chi^{(3)}$ is much less than that reported before in the ultrafast process. More importantly, our Ag:$BaTiO_3$ composite films exhibit ultrafast nonlinear saturated absorption, which may have potential applications for femtosecond laser mode locking.

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