Optical nonlinear characteristics of MgF_2 films containing Cu nanoparticles

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An investigation is made on the optical nonlinear characteristics of MgF_2 films containing Cu nanoparticles. When the Cu volume fraction is 0.1, at approximately $\varepsilon_m + 2\varepsilon_d = 0$, the film exhibits a strong third-order optical nonlinear refractive coefficient of 1.0×10^{-9} cm^2/W, a nonlinear refractive index of about -4.0×10^{-7} esu, a third-order optical nonlinear response of about 6.8×10^{-8} esu, and a figure of merit of about 1.0×10^{-11}. The result shows that the film may have potential applications in optoelectronic technology.

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According to the Mie[1] and Maxwell-Garnett[2,3] theories, the maximum third-order optical nonlinear response for a metal/dielectric particle system occurs very close to the surface plasmon resonance (SPR) absorption peak. Therefore, by coordinating material parameters and wave frequency, optical bistability can be achieved in metal/ceramic composite particle films. Such cermet particle films are generally formed by randomly embedding metal nanoparticles in a ceramic matrix. As the embedded metal nanoparticles are influenced by the strong three-dimensional (3D) domain confinement of the dielectric barrier, they exhibit an enhanced third-order optical nonlinear response.

Some researches have shown that a number of cermet particle films with Au, Ag, Cu, Sn, and Ni nanoparticles embedded in a glass, SiO_2, or Al_2O_3 matrix have a strong third-order nonlinear optical response[4−11]. It is reported that MgF_2 films containing Au, Ag, and Cu nanoparticles have a prospective application in 3D CD-ROM[12], while Ag-BaO films show ultrafast transient optical response[13] and optical bistability has been achieved in Au-SiO_2 films and Ag-CdS films[5,14]. We used a z-scan apparatus and an ultraviolet-visible (UV-vis) spectrophotometer to characterize the optical absorption properties of the films[15]. The result shows that the films also possess strong third-order optical nonlinear response and SPR absorption. Similarly, they may have promising applications in optical information storage and high-speed switching devices for optical communication.

The films were prepared by radio frequency (RF) magnetron co-sputtering. The composite target was made by sticking Cu strips (99.99% purity) onto a MgF_2 target (99.99% purity). The Cu volume fraction of the film can be calculated by

$$q_M = \frac{x m_M \rho_D S_{MD}}{x m_M \rho_D S_{MD} + m_D \rho_M}, \quad (1)$$

where q_M is the Cu volume fraction; m_M and m_D are the molar masses of Cu and MgF_2, respectively; ρ_M and ρ_D are the densities of Cu and MgF_2, respectively; S_{MD} is the ratio of Cu sputtering yield to that of MgF_2, with an experimental value of 7.9; and x is the ratio of exposed Cu area to that of MgF_2. The composition of the films prepared in this manner is very close to the design values[16].

In our experiment, the films were prepared onto pure carbon film, Si(111), and quartz substrates, respectively, at room temperature. The film thickness, monitored by a quartz oscillator, was 600 nm. After deposition, all the

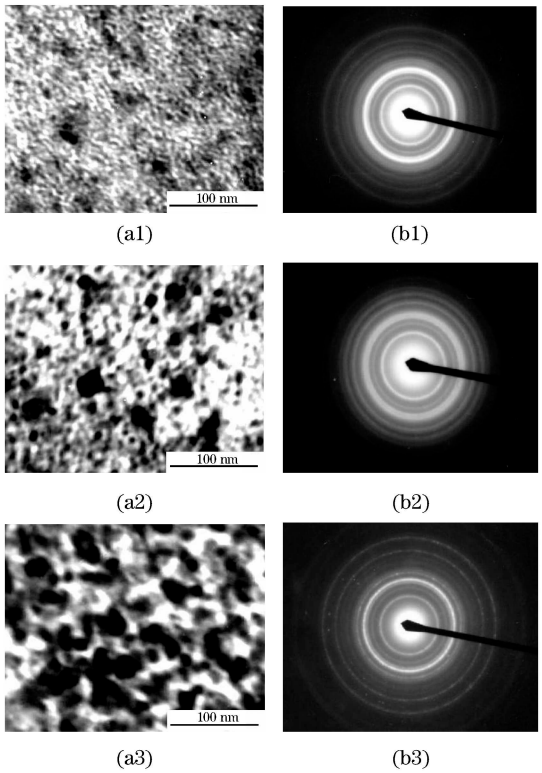

Fig. 1. (a) TEM bright-field micrographs and (b) electron diffraction patterns of MgF_2 films containing different Cu fractions. (a1), (b1): 10 vol.%; (a2), (b2): 20 vol.%; (a3), (b3): 30 vol.%.

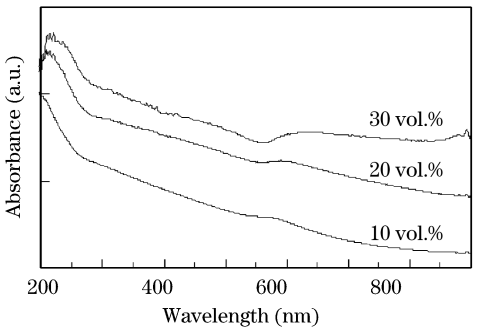

Fig. 2. Optical absorption spectra of MgF_2 films containing Cu nanoparticles.

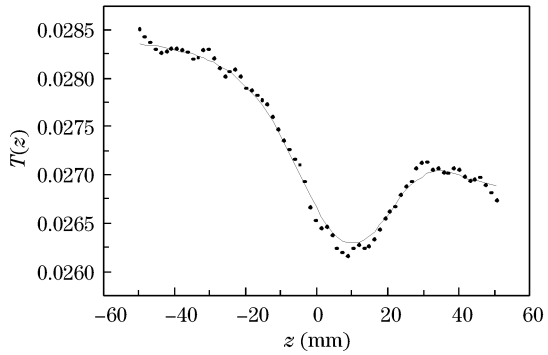

Fig. 3. $T(z)$-z curve of MgF_2 film containing 10 vol.% Cu.

films were annealed in a high vacuum ($< 8\times10^{-3}$ Pa) at 200 °C for four hours.

A JEM-100SX transmission electron microscope (TEM) was employed to examine the microstructure of the films. The TEM bright-field micrographs of MgF_2 films containing 10, 20, and 30 vol.% Cu are shown in Figs. 1(a1)−(a3), and the corresponding electron diffraction patterns for the films are shown in Figs. 1(b1)−(b3). As shown in Figs. 1(a1)−(a3), the size of Cu particles increases with the increase in Cu fraction. Size analysis shows that the mean sizes of Cu particles for MgF_2 films containing 10, 20, and 30 vol.% Cu are 12, 20, and 24 nm, respectively. No self-aggregating effect can be observed for the Cu nanoparticles. For Figs. 1(b1)−(b3), indices of the Debye-Scherrer rings from inside to outside are arranged as follows: MgF_2(110), MgF_2(111), Cu(111), MgF_2(210), Cu(200), Cu(220), MgF_2(211), and MgF_2(220). This suggests that the films are composed of a polycrystalline MgF_2 matrix with embedded face-centered cubic (fcc) Cu nanoparticles.

A Shimadzu UV-240 UV-vis spectrophotometer was used to analyze the optical absorption of the films over 200−900 nm. Figure 2 shows the optical absorption spectra of the films. From the spectra, it can be seen that the SPR absorption peaks of Cu nanoparticles occur at λ_1=578 nm, λ_2=588 nm, and λ_3=606 nm for MgF_2 films containing 10, 20, and 30 vol.% Cu, respectively. Based on the Mie theory, the SPR peak for the film should occur around 540 nm[15]. Obviously, the experimental SPR absorption peak red-shifts as Cu fraction increases.

In Fig. 2, the absorption edge (λ <300 nm) is caused by the Cu free electron absorption and electron interband transition in the films. We have analyzed the effect of Cu particle in the films on interband transition[17]. When the Cu volume fraction q_M is 0.1, 0.2, and 0.3, the energy gap E_g is 4.38, 4.18, and 4.00 eV, respectively. It is obvious that the energy gap decreases with the increasing Cu volume fraction.

A z-scan apparatus was employed to characterize the optical nonlinearity of the films. For the experiments, we used ∼15 ns, ∼0.2 mJ pulses at 532 nm multiplication wavelength from a Q-switched YAG laser. Using a 200 mm focal length lens, the laser beam was focused to the spot size of approximately 26 μm in diameter. The beam diameter on the receiving plane was 5 mm, and the aperture diaphragm diameter was 3 mm.

The relation between the sample transmittance $T(z)$ and the position z for the film containing 10 vol.% Cu is illustrated in Fig. 3. From the figure, it can be seen that with the movement of the film along the z direction, a transmittance peak occurs about 35 mm away from the focal point in the positive z direction. This indicates that a strong nonlinear absorption exists for the film. The difference in transmittance between the peak and the valley $\Delta T_{\mathrm{P-V}} = 0.002$ can be obtained from the curve. Through the location of the peak and the valley, it can be deduced that the film has a negative nonlinear refractive index. This indicates that such films have self-defocusing properties, which means the light intensity in the optical axis of the distant field strengthens with the movement of the sample along the negative z direction.

The nonlinear refractive coefficient γ, the third-order nonlinear refractive index n_2, and the third-order nonlinear optical response $X_R^{(3)}$ for the nanoparticle film can be calculated by putting the z-scan experimental data into the following equations[18]:

$$\gamma = \frac{\Delta T_{\mathrm{P-V}}}{0.406(1-s)^{0.25} K I_0 L_{\mathrm{eff}}}, \tag{2}$$

$$X_R^{(3)} = \frac{n_0^2}{0.0395}\gamma, \tag{3}$$

$$n_2 = \frac{cn_0}{40\pi}\gamma, \tag{4}$$

where $s = 1 - \exp(-2r_a^2/\omega_a^2)$ denotes the linear transmissivity of the aperture diaphragm, r_a is the radius of the aperture diaphragm, and ω_a is the beam radius of the receiving plane; $L_{\mathrm{eff}} = (1 - \mathrm{e}^{-\alpha L})/\alpha$ is the effective thickness of the film sample, α is the linear absorption coefficient of the sample (6.5×10^3 cm^{-1}), and L is the actual film thickness (600 nm); c is the speed of light in vacuum; $K = 2\pi/\lambda$ is the wave vector, λ is the laser wavelength; I_0 is the peak power (2.3×10^6 W/cm^2) of the laser pulse; and n_0 is the linear refractive index of the film sample. In Eqs. (2)−(4), γ is in the unit of cm^2/W, and n_2 is in the unit of esu. By putting the experimental data into Eq. (2), we obtain $\gamma \approx 1.0\times10^{-9}$ cm^2/W. Next by putting $\gamma \approx 1.0\times10^{-9}$ cm^2/W and n_0=1.65, as given by the literature[19] into Eqs. (3) and (4), we get $X_R{}^{(3)}\approx 6.8\times10^{-8}$ esu, $n_2\approx -4.0\times10^{-7}$ esu, and the figure of merit $X_R{}^{(3)}/\alpha\approx1.0\times10^{-11}$. These results are slightly smaller than the results for Cu/glass films [4] ($X_R{}^{(3)} = 3.5\times10^{-6}$ esu) and Cu/Al_2O_3 films[8] ($X_R{}^{(3)}=2.4\times10^{-7}$ esu). The investigation for the optical nonlinear characteristics of the films containing a Cu fraction other than 10 vol.% is still underway.

In summary, the optical nonlinear characteristics of the

films with different Cu fractions are studied using the z-scan method. When the Cu volume fraction q_M=0.1, at approximately $\varepsilon_m + 2\varepsilon_d = 0$, the film exhibits a strong third-order optical nonlinear refractive coefficient $\gamma \approx 1.0\times10^{-9}$ cm^2/W, a nonlinear refractive index $n_2 \approx -4.0\times10^{-7}$ esu, a third-order optical nonlinear response $\chi_R{}^{(3)} \approx 6.8\times10^{-8}$ esu, and a figure of merit $\chi_R{}^{(3)}/\alpha \approx 1.0\times10^{-11}$. This indicates that such films may have promising applications in optical information storage and high-speed switching devices for optical communication. The fact that the maximum third-order optical nonlinear response for the films occurs very close to the SPR absorption peak of Cu nanoparticles reveals that the interband transition of Cu nanoparticles plays a major role in the third-order optical nonlinear response.

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References

1. G. Mie, Ann. Phys. (Leipzig) **25,** 377 (1908).
2. J. C. M. Garnett, Phil. Trans. R. Soc. Lond. **203,** 385 (1904).
3. J. C. M. Garnett, Phil. Trans. R. Soc. Lond. **205,** 237 (1906).
4. K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A. J. Ikushima, T. Tokizaki, and A. Nakamura, J. Opt. Soc. Am. B **11,** 1236 (1994).
5. R. Neuendorf, M. Quinten, and U. Kreibig, J. Chem. Phys. **104,** 6348 (1996).
6. T. Tsuchiya, T. Sei, Y. Watanabe, M. Mori, and T. Kineri, J. Sol-Gel Sci. Technol. **8,** 685 (1997).
7. J. M. Ballesteros, J. Solis, R. Serna, and C. N. Afonso, Appl. Phys. Lett. **74,** 2791 (1999).
8. R. de Nalda, R. del Coso, J. Requejo-Isidro, J. Olivares, A. Suarez-Garcia, J. Solis, and C. N. Afonso, J. Opt. Soc. Am. B **19,** 289 (2002).
9. S. Qu, C. Zhao, Y. Gao, Y. Song, S. Liu, J. Qiu, and C. Zhu, Acta Phys. Sin. (in Chinese) **54,** 139 (2005).
10. Z. Sun, C. Cao, X. Song, and Q. Cai, Acta Opt. Sin. (in Chinese) **28,** 403 (2008).
11. P. Wang, H. Dai, X. Zhao, X. Song, and Z. Sun, Acta Opt. Sin. (in Chinese) **26,** 1871 (2006).
12. K. Baba, R. Yamada, S. Nakao, and M. Miyagi, Appl. Opt. **32,** 3137 (1993).
13. J. Wu and Q. Wu, *Several Novel Thin Film Materials* (in Chinese) (Peking University Press, Beijing, 1999).
14. H. Ma, R. Xiao, and P. Sheng, J. Opt. Soc. Am. B **15,** 1022 (1998).
15. Z.-Q. Sun, D.-M. Sun, and T.-N. Ruan, Chin. Phys. Lett. **19,** 1365 (2002).
16. Z. Sun, Y. He, X. Song, and D. Sun, Acta Phys. Sin. (in Chinese) **52,** 1455 (2003).
17. D. Sun and Z. Sun, *Cermet Films and Application in Optoelectronic Technology* (in Chinese) (Science Press, Beijing, 2004).
18. M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. van Stryland, IEEE J. Quantum Electron. **26,** 760 (1990).
19. Y. He, "Preparation, microstructure and properties of Cu-MgF_2 nanoparticle cermet films" (in Chinese) Master Thesis (Anhui University, Hefei, 2002).