Enhancement of optical nonlinearity in $Ag:BaTiO_3$ composite films by applying an electric field during growth

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We prepared the $Ag:BaTiO_3$ composite films by pulsed-laser deposition technique. The films were grown on MgO (100) substrates under a nitrogen pressure of 10.0 Pa at 600°C, and a parallel electric field was applied on the substrate during growth. The chemical natures of Ag in the films were measured by x-ray photoelectron spectroscopy. The linear optical properties of the films were studied in the wavelength range of 330 to 700 nm. The third-order nonlinear optical susceptibilities of the films were determined by *z*-scan method at the wavelength of 532 nm with a laser duration of 10 ns. The figure of merit (FOM) was ~1 order of magnitude larger than that of the films that were grown without an electric field and reached 1.62×10^{-10} esu cm. Our experimental results have demonstrated that an external electrical field can induce the metal-particle orientation in order and therefore enhances the FOM of the metal-dielectric composite films. © 2005 Optical Society of America

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In recent years, considerable work has been devoted to the large optical nonlinearity of metal-dielectric composite materials.[1–3] Among these materials, noble metal particles embedded in dielectric hosts have drawn great interest, owing to the large values of third-order nonlinear susceptibility, $\chi^{(3)}$. The great enhancement of $\chi^{(3)}$ in such a composite system derives from the enhancement of the local-field factor near the surface-plasmon resonance (SPR). However, the absorption coefficient α also enhances near the SPR, limiting the application of the material. In practical application, the figure of merit (FOM), defined as $\chi^{(3)}/\alpha$, is more useful.[4] The theoretical calculations of Yuen *et al.*[5] and of Huang and Yu.[6] indicate that the geometric anisotropy in nonlinear thin films will greatly enhance the optical nonlinearity. The electrorheological or the magnetorheological effect was suggested to induce the geometric anisotropy.[7,8] This study demonstrates that applying an electric field can enhance the FOM of Ag-dielectric composites.

The films were prepared by a pulsed-laser deposition method similar to the one used in Ref. 9. A Xe–Cl excimer laser (308 nm, 17 ns, 4 Hz) was used as the laser source. Several fan-shaped chips of 99.99% pure Ag were uniformly placed on the surface of the $BaTiO_3$ target, and the ratio between the Ag area and the target area was 1:8. The target was mounted on a rotating holder, 40 mm from the MgO substrate. The films were deposited in an N_2 atmosphere with pressure of 10.0 Pa. The substrate was maintained at 600°C during the entire deposition process. An electric field was parallel to the surface of the substrate, and the distance between two electrodes was 2 cm. The samples were grown with external voltages of 0 (Sample A) and 2000 V (Sample B). All the samples were deposited under the same conditions with the same thickness of 150 nm. The distribution and shape of the Ag particles were analyzed by a transmission electron microscope (TEM), shown in Fig. 1. The dark regions in the images are Ag particles, and the light regions are $BaTiO_3$. It is observed that the Ag particles in sample A are in a disordered orientation, and some of the Ag particles in sample B are stretched through the same direction, indicating that Ag particles have some ordering orientation in sample B induced by an electric field but that the geometric anisotropy was not obvious. The possible cause is the lower applied electrical field.

To investigate the structure and crystallinity of the $Ag:BaTiO_3$ films deposited on MgO substrates at 600°C,

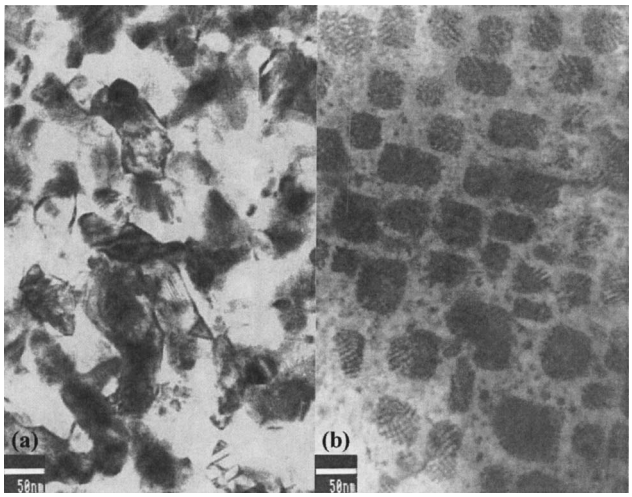

Fig. 1. TEM images of the $Ag:BaTiO_3$ composite films: (a), sample A (without an applied electric field); (b), sample B with an applied electric field of 1000 V/cm.

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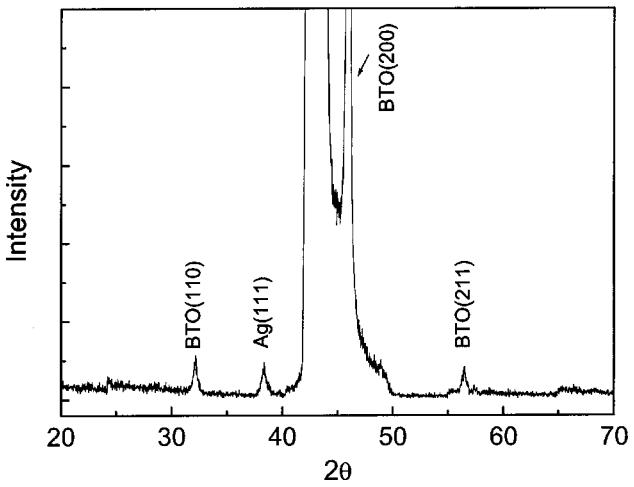

Fig. 2. X-ray diffraction patterns of Ag:$BaTiO_3$ composite films grown at 600°C on MgO substrates.

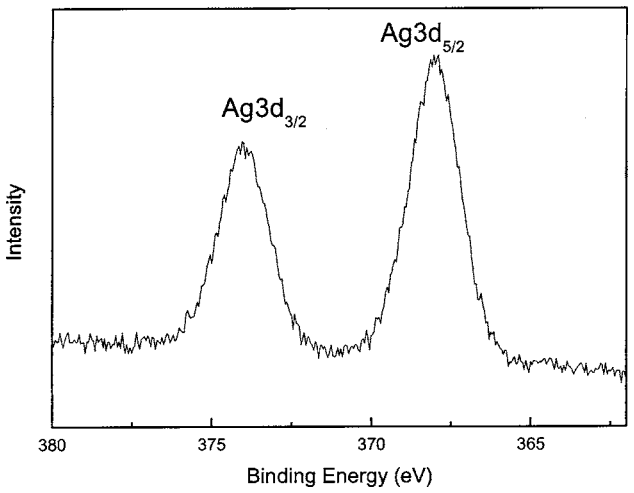

Fig. 3. X-ray photoelectron core-level-spectra of Ag 3*d* for the Ag:$BaTiO_3$ composite films.

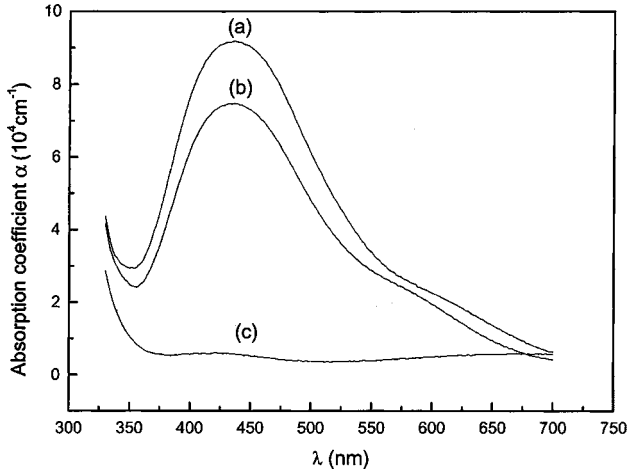

Fig. 4. Absorption spectra for sample A (without an applied electric field) and sample B (with an applied electric field of 1000 V/cm). Curve (c) is the absorption spectrum for the pure $BaTiO_3$ film.

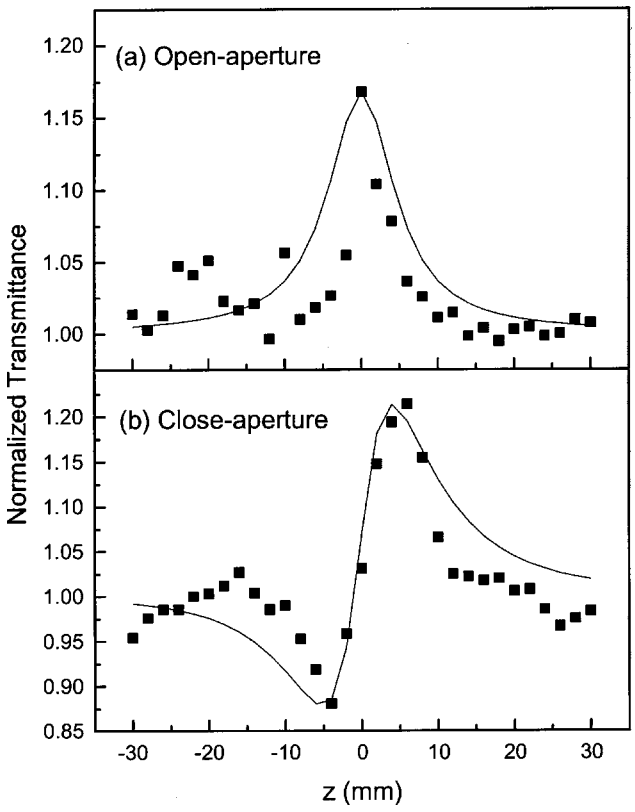

Fig. 5. The *z*-scan data of sample A (without an applied electric field) with (a) an open and (b) a closed aperture. The solid curves indicate the theoretical fit.

we measured the x-ray diffraction (XRD) patterns. Figure 2 shows the typical XRD spectra of the composite films. The diffraction peaks corresponding to $BaTiO_3$ (100), (200), and (211) could be observed. The peak at 38.27 corresponds to Ag (111). The XRD results indicate that the Ag:$BaTiO_3$ composite films are well crystallized.

To determine the chemical nature of Ag in the films, we made the x-ray photoelectron spectroscopy (XPS) measurement. XPS spectra of the films were measured under vacuum of 1.33×10^{-8} Pa using Al$K\alpha$ x radiation (hv = 1486.6 eV). The binding energies were corrected using the assumed value of 284.6 eV for the resulting C1*s* line from the adsorbed hydrocarbon contaminant as a reference. The XPS results of the Ag 3*d* photoelectron core levels and the valence-band regions acquired from the surface of the samples are shown in Fig. 3. The peaks of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ are located at 368.1 and 374.0 eV, respectively, which correspond to the normal XPS spectra of Ag metal. These results prove that the films are composed of metal Ag embedded in the $BaTiO_3$.

The linear optical measurements were made at room temperature in air from 330 to 700 nm using a SpectraPro500i spectrophotometer. The data were automatically corrected by the spectrophotometer to account for the absorbance from the MgO substrates. Figure 4 shows the optical absorption spectra of the samples A and B as a function of the wavelength, where the curve (c) is the absorption spectrum of the undoped $BaTiO_3$ films for contrast. Without Ag in the $BaTiO_3$ films, no absorption peak is observed in curve (c). When the $BaTiO_3$ films are

doped with Ag, absorption peaks due to the SPR of Ag particles are found around 436 nm. With the electric field applied, the peak of the SPR does not shift as prospecting, but is reduced. Possible reason for this may be the orientation order in sample B.

The nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β) were measured with the z-scan technique.[10] In our measurements, a Q-switched Nd:YAG laser frequency doubled at 532 nm and characterized by a pulse duration of 10 ns was employed as the light source. The repetition rate of the laser was 1 Hz in order to reduce the possible thermal accumulative effect. The laser beam was focused on the sample by a 120 mm focus length lens, leading to a measured beam waist of 30 μm and a pulse energy of 9.9 μJ at the focus. A weak reference beam was used to monitor energy fluctuation. The z-scan experimental details were reported previously.[11]

Typical open-aperture (OA) and closed-aperture (CA) z-scan profiles for samples A and B are shown in Figs. 5 and 6, respectively. The solid curves are theoretical fits. Because the MgO substrate in our experiment has a very small nonlinear optical response at 532 nm that has been measured by the same method; the high nonlinear optical properties observed here result from the films. It is shown in Figs. 5(a) and 6(a) that the OA curves for samples A and B both comprise normalized transmittance peaks. This phenomenon indicates the presence of nonlinear saturation in Ag:$BaTiO_3$ films. Figures 5(b) and 6(b) show the CA curves for samples A and B. Both exhibit positive values for the nonlinear refractive indexes. We

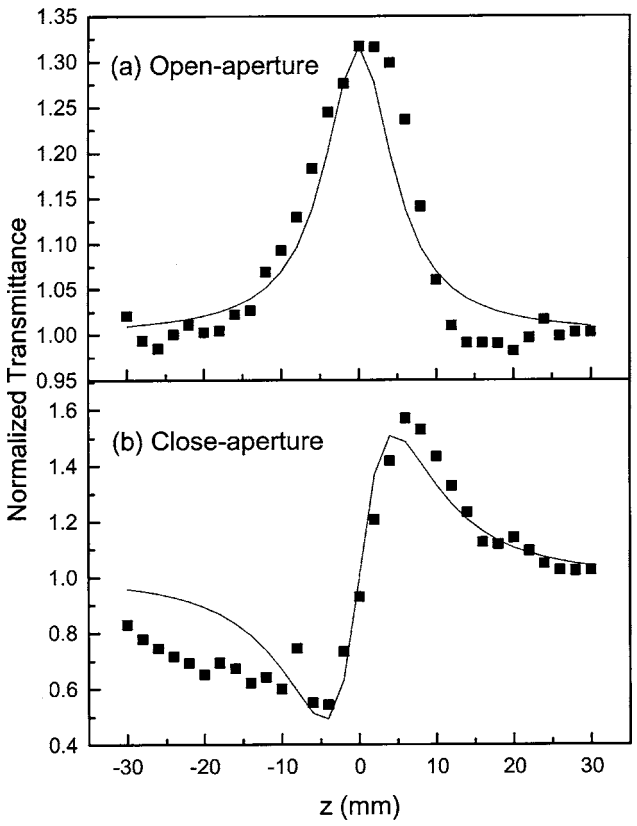

Fig. 6. The z-scan data of sample B (with an applied electric field of 1000 V/cm) with (a) an open and (b) a closed aperture. The solid curves indicate the theoretical fit.

Table 1. Linear and Nonlinear Optical Properties of the Samples at 532 nm

Sample Label	Applied Electric Field (V/cm)	α (10^4 cm^{-1})	Re $\chi^{(3)}$ (10^{-6} esu)	Im $\chi^{(3)}$ (10^{-7} esu)	$\chi^{(3)}/\alpha$ (esu cm)
a	0	4.18	1.77	5.12	4.41×10^{-11}
b	1000	3.38	5.47	9.67	1.62×10^{-10}

can calculate n_2 and β from the CA and OA curves, respectively. And the values of $|\mathrm{Re}\,\chi^{(3)}|$ and $|\mathrm{Im}\,\chi^{(3)}|$ can be derived from n_2 and β. It is clear from Table 1 that the values of $|\mathrm{Re}\,\chi^{(3)}|$ and $|\mathrm{Im}\,\chi^{(3)}|$ of sample B are larger than those of sample A. This increase could be also related to the orientation in order of Ag particles in sample B prepared under an applied electrical field. It is worth noting that the FOM of sample B is about 1 order of magnitude larger than that of sample A prepared without an applied electrical field and reaches 1.62×10^{-10} esu cm. This result has demonstrated that we can improve the nonlinearity by ordering the orientation of metal particles in the films.

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