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Large third-order optical nonlinearity in Au nanometre particle doped $BaTiO_3$ composite films near the resonant frequency*

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Nanometre-sized gold particles embedded in $BaTiO_3$ composite thin films (Au/$BaTiO_3$) were fabricated by the pulsed laser deposition technique. The films were grown on MgO (100) substrates at 700°C. The crystalline property of the films was studied with x-ray diffraction. X-ray photoelectron spectroscopy was used to check the Au composition and chemical nature for the deposited films. The absorption peak due to the surface plasmon resonance of Au particles was observed at the wavelength of about 570 nm, which increased as the metal particle size was increased. The nonlinear optical properties of the Au/$BaTiO_3$ films were determined using the z-scan method at the wavelength of 532 nm, which was close to the resonant frequency. The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ at an Au concentration of about 6.7 at.% were determined to be 6.62×10^{-7} esu and -6.24×10^{-8} esu, respectively. The films showed a very large absorption, masking the nonlinear refraction effect at high metal concentrations.

Keywords: Au/$BaTiO_3$, susceptibility, z-scan, pulsed laser deposition
PACC: 4270, 6146, 8115I

Many studies show that materials potentially interesting for nonlinear optical applications are those composites which consist of nanometre-size metal particles embedded in a dielectric matrix. The idea is that the cubic optical nonlinearity of a material with delocalized electrons can be enhanced by artificially confining the electrons in regions smaller than their natural delocalization length in the bulk.[1] Recently, many composite thin films with a large third-order optical susceptibility have been reported.[2–4] Several types of dielectrics, such as fused silica, Al_2O_3, and polymers have been used as the matrix of metal-doped composite materials.[5] However, the dielectric constant of these materials is usually not very large, which blocks the enhancement of the local field factor $f = 3\varepsilon_d/(\varepsilon_m + 2\varepsilon_d)$, where ε_m and ε_d are the dielectric constants of the metal clusters and the dielectric matrix. Oxides with high dielectric constant, large nonlinear optical effect, and ferroelectricity, such as $BaTiO_3$, $LiNbO_3$, can be proposed as a special type of matrix for metal nanocomposite thin films.[6] It can be predicted that this type of metal nanocomposite films should be interesting and significant for both fundamental and application aspects.

In this rapid communication, we report on the fabrication and properties of the Au/$BaTiO_3$ composite thin films deposited on MgO (100) substrates, using a pulsed laser deposition (PLD) technique. The combination of x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and the absorption spectroscopy techniques allows us to elucidate the crystal structure of the composite films, the core-level of the Au nanocluster, and the optical absorption of the films. The optical nonlinearity is investigated using the z-scan technique[7,8] in order to determine both the real and imaginary parts of the third-order susceptibility.

The films were deposited using a XeCl excimer laser beam. The processing parameters have been reported elsewhere.[9] In the PLD processing, the Au concentration in the films was easily controlled by changing the area of Au pieces. Four samples, called

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AU100, AU55, AU35 and AU20, were prepared with the area ratios of Au pieces to $BaTiO_3$ target of 1/10, 1/5.5, 1/3.5, and 1/2, respectively. The growth rate was measured using a film thickness monitor, and the thickness for the samples was about 110–120 nm.

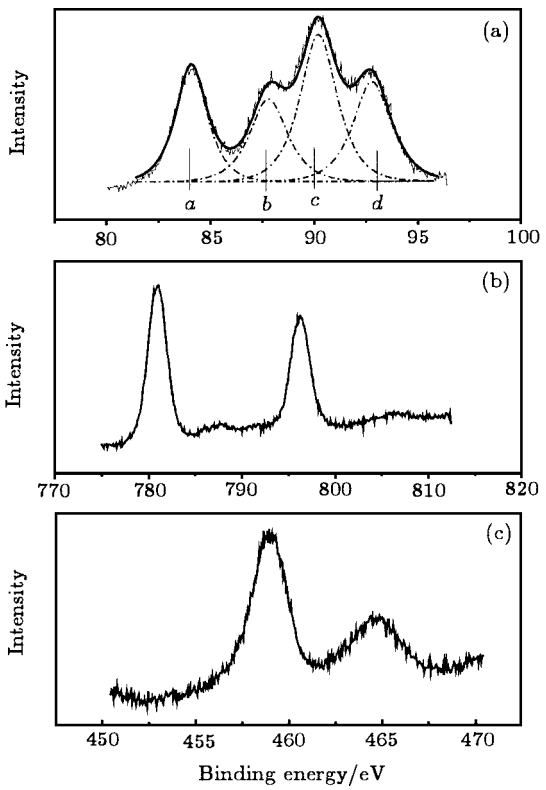


Fig.1. (a) Au 4f XPS spectrum of the sample AU55. (···) experimental data; (—) fitting curve; (–·–) four sub-peaks, *a*, *b*, *c*, and *d* corresponding to Au $4f_{7/2}$, Au $4f_{5/2}$, Ba $4d_{5/2}$ and Ba $4d_{3/2}$, respectively. (b) Ba 3d and (c) Ti 2p XPS spectra of the same sample.

XPS spectra were measured under a vacuum of 1.33×10^{-8} Pa using Mg $K\alpha$ x-radiation ($h\nu$= 1253.6 eV) for the films. The binding energies were corrected with reference to the assumed value of 284.6 eV for the resulting C 1s line from the adsorbed hydrocarbon contaminant. Figure 1(a) exhibits the x-ray photoelectron core-level spectra of Au 4f lines from the sample AU55. The broad peaks could be roughly deconvoluted into four unique peaks at 84.00, 87.67, 90.02 and 93.05 eV corresponding to Au $4f_{7/2}$, Au $4f_{5/2}$, Ba $4d_{5/2}$ and Ba $4d_{3/2}$, respectively. The binding energies of Au $4f_{7/2}$ and Au $4f_{5/2}$ proved that the films were composed of metal Au embedded in the dielectric matrix. The Ba 3d and Ti 2p XPS spectra of the same sample are also shown in Figs.1(b) and 1(c). The peak at 780.6 eV comes from Ba^{2+} $3d_{5/2}$ line (780.4 eV in $BaSO_4$), and the peak at 458.9 eV comes from Ti^{4+} $2p_{3/2}$ line (458.8 eV in TiO_2). The atomic ratio of Ba/Ti, which can be derived from the XPS data, was calculated to be 1:1.02. It can be concluded from the binding energies that the matrix of the films was successfully formed as $BaTiO_3$. The Au composition can also be calculated based on the data from Fig.1 that the concentration (Au/Au+Ba+Ti, at.%) of Au particles of sample AU55 was about 14 at.%. Table 1 shows the area ratio of Au to $BaTiO_3$ target, the Au composition of the films and the total thickness of the films for the four samples.

Table 1. The area ratio of Au piece to $BaTiO_3$ target, Au concentration in the films and thickness of the films for the four samples.

Sample	Area ratio of Au piece to $BaTiO_3$	Au/Au+Ba+Ti at.%	Thickness (nm)
AU100	1/10	6.7%	120
AU55	1/5.5	14%	120
AU35	1/3.5	19.2%	115
AU20	1/2	33.6%	110

The film crystallinity was characterized with an x-ray diffractometer using Cu $K\alpha$ radiation. Figure 2 shows the XRD patterns of our samples. It is evident from Fig.2 that the Au (220) peak becomes sharper with the increase of Au concentration in the films, indicating that larger Au particles are formed in the $BaTiO_3$ matrix.

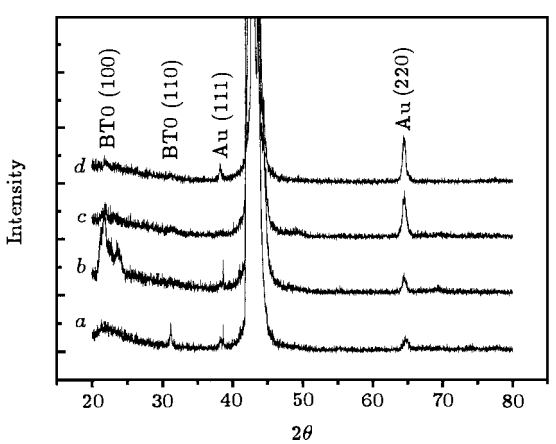


Fig.2. The XRD patterns for the Au/$BaTiO_3$ films grown at 700°C on MgO substrates with increasing Au concentration: *a*, AU100; *b*, AU55; *c* AU35; *d*, AU20.

The optical absorption of the samples was measured in the wavelength range of 330–800 nm, using a Spectrapro-500i spectrophotometer (Acton Research Corp.). The results are shown in Fig.3. The data have been automatically corrected by the spectrophotometer to account for the absorbance from the MgO substrates. As a reference, the optical absorption

spectrum of the undoped $BaTiO_3$ thin film was also recorded. Without Au in the $BaTiO_3$ films, no absorption peak was observed, as shown in Fig.3(e). When the $BaTiO_3$ films were doped with Au, the strong absorption peaks due to the surface plasmon resonance (SPR) of Au particles were found in the wavelength range of 564–618 nm. At 6.7 at.% Au, the wavelength of the absorption peak is close to 564 nm (Fig.3(a)). With increasing Au concentration, the resonance peak shifts to 578 nm at 14 at.% (Fig.3(b)), and 580 nm at 19.2 at.% (Fig.3(c)) accordingly. Accompanying this redshift phenomenon is the sharpening and increase of the intensity of the peak due to the size increase of the Au clusters. However, with a further increase of the Au concentration the resonance peak is broadened (Fig.3(d)). This can be explained by Mie theory[10] that the higher-order multipole expansions of the scattered electric and magnetic fields become increasingly important for larger metal particles.

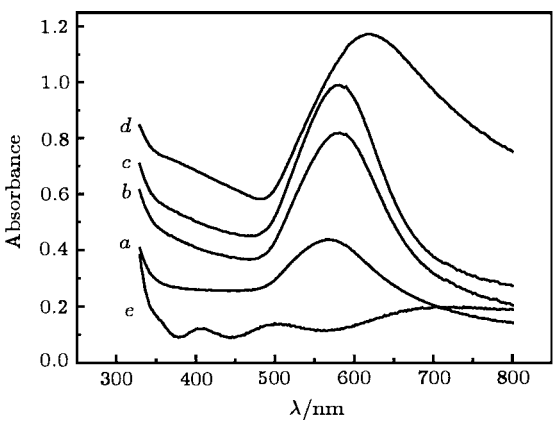


Fig.3. The optical absorption properties of the samples: *a*, AU100; *b*, AU55; *c*, AU35; *d*, AU20; *e*, undoped $BaTiO_3$.

The third-order nonlinear susceptibility of the films was characterized using the single-beam z-scan technique. A Nd:YAG Q-switched laser with a wavelength of 532 nm (near the SPR of the $Au/BaTiO_3$ film) and a pulse width of 10 ns was employed as the light source. The sample was moved in the direction of the incident beam close to the focus of the lens, which had a focal length of 120 mm. The radius of the beam waist (ω_0) was 30μm. The transmitted beam energy, the reference beam energy and their ratio were measured by an energy ratiometer (Rm6600, Laser Probe Corp.) simultaneously. The linear transmittance of the far-field aperture S, defined as the ratio of the pulse energy passing the aperture to the total energy, was measured to be 0.3.

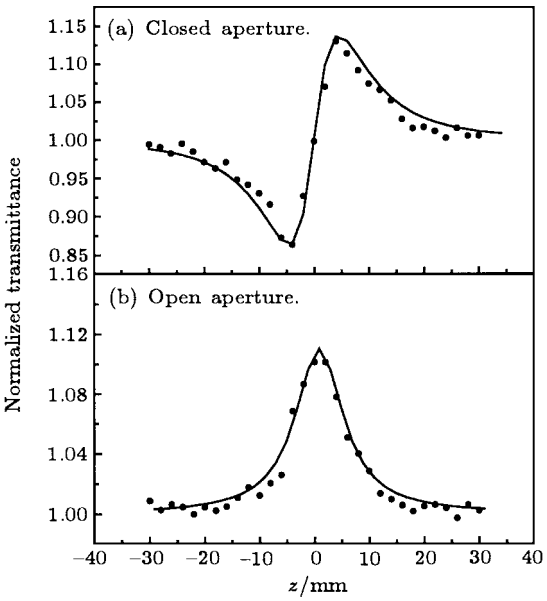


Fig.4. z-scan normalized transmittance with (a) closed aperture and (b) open aperture of the sample AU100 at a maximum laser intensity of 1.06×10^8 W.cm^{-2}. The solid curves are the theoretical fits to the data.

A typical result of the z-scan measurement is shown in Fig.4, which corresponds to the far-field transmission of the sample AU100 as a function of its distance (z) to the lens focus. The solid lines are the theoretical fits. The closed-aperture (CA) curve (Fig.4(a)) exhibits the valley-to-peak curve, indicating a positive value of the nonlinear refractive index n_2. The open-aperture (OA) curve (Fig.4(b)) comprises a normalized transmittance peak, showing the presence of the nonlinear saturation. In order to obtain nonlinear refraction information shown in Fig.4(a), a simple and approximate method[7] was used, in which the CA transmittance was divided by the corresponding OA data. Because the MgO substrate in our experiment has a very small nonlinear optical response at 532 nm, which has been measured by this method, the high nonlinear optical properties observed here result from the $Au/BaTiO_3$ films.

The data were analysed using the procedures described in Ref.[6]. The value of ΔT_{p-v}, which is the difference between the normalized peak and valley transmittances, can be obtained through the best theoretical fit from the results of the z-scan curve as shown in Fig.4(a). The calculated nonlinear refractive index n_2 of the sample AU100 is 2.71×10^{-6} esu, and the real part of the third-order nonlinear susceptibility, $\mathrm{Re}\chi^{(3)}$, is 6.62×10^{-7} esu, which is about one or two orders larger than some of those representative

nonlinear optical materials, such as Cu:Al_2O_3 composite films,[2] noble metals doped glasses,[4,11] and some transition-metal oxide thin films.[12] The large nonlinear optical effect shows that the Au/$BaTiO_3$ thin films have great potential applications for nonlinear optical devices. The absorption coefficients β(m/W) of the films can be calculated from the normalized transmittance for the open aperture in Fig.4(b). The obtained β value for the sample AU100 is -1.1×10^{-6} m/W, and the imaginary part of $\chi^{(3)}$ is -6.24×10^{-8} esu. Detailed expressions have been reported previously.[9]

With increasing Au concentration in the Au/$BaTiO_3$ films, the nonlinear absorption of the films increases greatly. Figure 5 shows the OA z-scan results of sample AU55. The calculated imaginary part of the $\chi^{(3)}$ is as large as -2.14×10^{-6} esu, which, to the best of our knowledge, has never been achieved at a metal concentration of 14 at.%. The strong saturation of the film dissatisfies the case of $\beta/2k\gamma \ll 1$ which represents the limits of the z-scan method for the measurement of the nonlinear refractive index n_2; n_2 and γ are related through the conversion formula γ (m^2/W)=$(40\pi/cn_0)$ n_2 (esu). Therefore, in CA z-scan measurements, the transmission curve does not reveal the typical peak-and-valley profile which is usually observed in the case of a weakly absorbing material. Consequently, we could not calculate the nonlinear refractive index in this case.

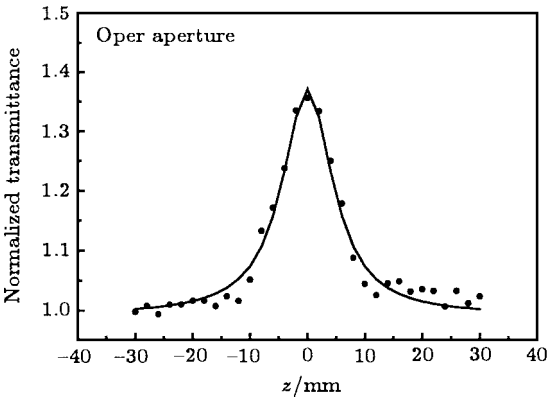


Fig.5. z-scan normalized transmittance with OA of the sample AU55 at a maximum laser intensity of 2.32×10^7 W.cm^{-2}. The solid curve is the theoretical fit to the data.

In summary, nanocomposite thin films Au/$BaTiO_3$ with different Au concentrations have been synthesized by PLD. The nonlinear optical properties of the films were determined using z-scan method at the wavelength of 532 nm near the SPR of Au particles. The results demonstrate that the nonlinear saturation is increased with increasing Au concentration. As a consequence, the large nonlinear saturation masks the nonlinear refraction, and the z-scan method cannot allow accurate determination of Re$\chi^{(3)}$ at high Au concentration.

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