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Optical nonlinearities of $BaTiO_3$ matrix-embedded Au nanoparticles

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Abstract

Composite thin films Au/$BaTiO_3$ comprising nanometer-sized gold particles embedded in $BaTiO_3$ matrices were synthesized on MgO(1 0 0) substrates by co-depositing Au and $BaTiO_3$ targets using pulsed laser deposition technique. The nanostructure of the films and the size distributions of the Au particles were analyzed by high-resolution transmission electron microscopy. Crystal lattice fringes from the Au nanocrystals and $BaTiO_3$ matrices were observed. The nonlinear optical properties of the Au/$BaTiO_3$ films were measured using *z*-scan method at the wavelength of 532 nm with a laser duration of 10 ns. The nonlinear refractive index n_2 and the nonlinear absorption coefficient β were determined to be 2.72×10^{-6} esu and -1.1×10^{-6} m/W, respectively.

Keywords: A. Composites; A. Nanostructure; A. Optical materials; B. Laser deposition

1. Introduction

Nanocomposites comprising metallic nanoparticles embedded in dielectric matrices exhibit attractive nonlinear optical properties, which have opened many possibilities for their use in various technological applications. The greatly enhanced third-order nonlinearities in these materials were known to stem from the giant amplification of the local electric field near and inside the metal particles at the surface plasmon resonance [1]. Recently, many composite thin films with a large third-order optical susceptibility have been reported [2–5]. Several kinds of dielectrics, such as Al_2O_3 and SiO_2 have been used as the matrices of metal-doped composite materials. However, in these films the embedding dielectric matrices were amorphous, and the metal particles were approximately spherical-shaped. The nonlinear optical properties of well-crystallized ferroelectric matrices doped with metal nanocrystals in ellipsoidal shape have not been reported to our knowledge. Barium titanate ($BaTiO_3$), which has a very high dielectric constant, significant ferroelectricity, and large nonlinear optical effect [6], can be proposed as a special kind of matrix for composite films. It can be predicted that nanometer-sized metal particles doped $BaTiO_3$ films should be interesting and significant for both fundamental and application aspects.

In this paper, we report the fabrication and properties of Au/$BaTiO_3$ composite thin films deposited on MgO(1 0 0) substrates using pulsed laser deposition (PLD) technique. The combination of using high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and the absorption spectroscopy allowed us to elucidate the morphology and nanostructure, the crystal property, and the optical absorption of the composite films. X-ray photoelectron spectroscopy (XPS) was used to determine the core-level of the embedded Au particles and the chemical

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composition of the films. The optical nonlinearity was investigated with z-scan technique [7,8] in order to determine both the real and imaginary parts of the third-order susceptibility.

2. Experimental procedure

The films were deposited using a XeCl excimer laser [308 nm, 17 ns full width at half maximum (FWHM), 5 Hz repetition rate] focused onto a high-purity target of $BaTiO_3$ ceramic, on which some small Au pieces were uniformly placed, at a typical energy density of about 5 J/cm^2. The target was mounted on a rotating holder, 35 mm from the MgO(1 0 0) substrates. During the deposition process, the different target materials (Au and $BaTiO_3$) were alternately ablated by the pulsed laser beam and deposited onto the substrates. The MgO(1 0 0) substrates polished on both sides (0.5 mm in thickness) were maintained at 700 °C. The experiments were carried out under vacuum at a pressure of 2×10^{-3} Pa. The growth rate was measured using a film thickness monitor. The sample thickness was determined as about 120 nm.

The morphology and nanostructure of the films were analyzed with in-plane view by HRTEM. The HRTEM studies were carried out in a Philips CM200-FEG (field emission gun) transmission electron microscope equipped with a Gatan image filtering (GIF) system, operated at 200 kV. The samples observed were prepared using the standard techniques, such as mechanical polishing and argon ion milling. The crystallinity of the films was characterized by XRD using the Cu Kα radiation. XPS spectra were measured under a vacuum of 1.33×10^{-8} Pa using Mg Kα X-radiation ($h\nu$ = 1253.6 eV) for the films. The binding energies were corrected with reference to the assuming value of 284.6 eV for the resulting C1s line from the adsorbed hydrocarbon contaminant. The optical absorption of the films was measured in the wavelength range of 330–800 nm, using a Spectrapro-500i spectrophotometer (Acton Research Corporation).

The third-order nonlinear susceptibility of the films was characterized using the single beam z-scan technique. The z-scan technique is simple and sensitive, and relies on the fact that the intensity of a focused laser beam, which passes through a sample, varies along the axis of a lens. When the transmittance measurement was performed through a finite aperture placed in the far field of the sample, the z-scan curve was affected by the beam distortion induced by the nonlinear refraction n_2 in addition to the nonlinear absorption β. The normalized transmittance $T(z)$, defined as the mean power transmitted through the aperture normalized by the linear mean power, is given by [9]:

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

where I_0 is the laser peak intensity on the sample, $L_{\text{eff}} = 1 - \exp(-\alpha L)/\alpha$ is the effective thickness of the films (L is the sample thickness, α is the linear absorption coefficient), the coupling factor:

$$\xi = \frac{cn_0\beta}{80\pi k n_2} = \frac{Im\,\chi^{(3)}}{Re\,\chi^{(3)}} \quad (2)$$

c (m/s) is the speed of light in vacuum, n_0 the linear refractive index of the sample, $k = 2\pi/\lambda$ the wave vector), and $x = z/z_0$ (z_0 is the diffraction length of the beam). When the measurements were performed without the aperture, the z-scan profile revealed the nonlinear absorption β alone. The normalized transmittance by the sample without aperture could be written as [7]:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}}, \quad (3)$$

where $q_0(z) = \beta I_0 L_{\text{eff}}/(1 + z^2/z_0^2)$.

The z-scan measurements were performed using a Nd:YAG Q-switched laser at the wavelength of 532 nm (near the SPR of the Au/$BaTiO_3$ film) and with the pulse width of 10 ns. 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 30 μm. The diffraction length of the beam z_0 was calculated to be 5.3 mm, which was much longer than the films plus substrate thickness. The transmitted beam energy, the reference beam energy and their ratio were measured by an energy ratiometer (Rm6600, Laser Probe Corp.) simultaneously.