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Nonlinear optical properties of Cu nanocluster composite fabricated by 180 keV ion implantation

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ABSTRACT

Metal nanocluster composite glass prepared by 180 keV Cu ions into silica with dose of 5×10^{16} ions/cm^2 has been studied. The microstructural properties of the nanoclusters has been verified by optical absorption spectra and transmission electron microscopy (TEM). Third-order nonlinear optical properties of the nanoclusters were measured at 1064 and 532 nm excitations using Z-scan technique. The nonlinear refraction index, nonlinear absorption coefficient, and the real and imaginary parts of the third-order nonlinear susceptibility were deduced. Results of the investigation of nonlinear refraction by the off-axis Z-scan configuration were presented and the mechanisms responsible for the nonlinear response were discussed. Third-order nonlinear susceptibility $\chi^{(3)}$ of this kind of sample was determined to be 8.7×10^{-8} esu at 532 nm and 6.0×10^{-8} esu at 1064 nm, respectively.

1. Introduction

Metal nanoclusters possess linear and nonlinear optical properties. Increasingly attention has focused on the third-order nonlinear susceptibility and the photorefractive effect of noble-metal clusters embedded in dielectric matrices [1–3]. Third-order nonlinearities of metal/dielectric composite materials are influenced not only by the type and size of the embedded metal clusters, but also by the dielectric constant, thermal conductivity and heat capacity of the dielectric matrices [1–6]. The most conspicuous manifestation of confinement in optical properties of metal nanocluster composite glasses (MNCGs) is the appearance of the surface plasmon resonance (SPR) that strongly enhances their linear and nonlinear responses around SPR wavelength [7–9]. Amongst the nanoclusters studied by earlier papers, high nonlinear absorption and nonlinear refraction coefficients are found in copper and copper containing nanomaterials [10–12].

Ion implantation has been utilized to produce high-density metal colloids in glasses. The high precipitate volume fraction and the small size of nanoclusters in glasses lead to the generation of third-order susceptibility much greater than those for metal doped solid. The third-order nonlinear optical responses of the metal nanocluster-glass composites can be understood in the framework of dielectric and quantum confinement effects. Application aspects of the material are the most relevant to the change of optical properties versus the nanocluster structure.

In this paper, MNCGs were prepared by Cu$^+$ implantation into silica. We focused our interest on studying the nonlinear optical properties of this kind of metal nanoclusters. Nonlinear optical properties were measured by Z-scan method under the wavelength of 532 and 1064 nm.

2. Experiment

Silica slides were implanted at room temperature with copper ions at 180 keV. The current density of ion implantation was 1.5 μA/cm^2. Optical absorption spectra was recorded at room temperature using a UV–vis dual-beam spectrophotometer with wavelengths from 1200 to 300 nm. Transmission electron microscopy (TEM) observations were carried out with a JEOL JEM 2010 (HT) microscope operated at 200 kV. TEM bright field images were used to determine the size distribution, and the shape of nanoclusters.

The measurements of third-order nonlinear optical of the sample were carried out by using the standard Z-scan method.

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The excitation source was a mode-locked Nd:YAG laser (PY61-10, Continnum), with a pulse duration of 38 ps and a repetition frequency of 10 Hz. 1064 nm wavelength and doubled frequency (532 nm) were used for excitation in the experiment. The detector was a dual-channels energy meter (EPM2000). With a converging lens of $f = 260$ mm, the radiuses of the Gaussian beam spot at focal waist ϖ_0 were about 45 and 26 μm for 1064 and 532 nm, respectively. In the Z-scan test, the sample was moved step by step along the propagation direction of the Gaussian beam under the control of a PC. Meanwhile, a detector monitored the transmitted laser power and the signals were sent back to the computer and recorded. Nonlinear refraction and nonlinear absorption were performed by both open- and closed-aperture Z-scans of a series of the samples at room temperature.

3. Result and discussion

The TEM micrograph for the sample implanted by 5×10^{16} Cu$^+$ ions/cm^2 is shown in Fig. 1. As can be seen from the image, spherical copper clusters are formed during the implantation process; the particle size distribution is not uniform. The size of nanoclusters varies from 1 to 5 nm. Then the comparative size distribution of Cu nanoclusters is shown in Fig. 2. The average size of nanoclusters in this sample is 3.2 nm.

The linear optical absorption spectra of the sample investigated is shown in Fig. 3. The spectra ranges between 200 and 1200 nm. Only increasing shoulders of the sample was observed in the range of 500–650 nm. The dependence of this absorption band on the mean cluster diameter has been reported, and it has been shown that the band becomes noticeable and sharpens only when the diameter is about larger than 5 nm [13,14]. The Cu cluster sizes estimated from the absorption spectra are thus consistent with the values obtained from Fig. 2. This selective absorption band is due to the surface plasmon resonance (SPR) that extra evidence of Cu nanoclusters formation. The various multipoles excitations may compensate each other and lead to large apparent widths of the resonances.

The nonlinear absorption in the sample can be described as β, which includes saturated absorption (SA) and reversed saturated absorption (RSA) [15]. The nonlinear absorption is expressed as $\alpha = \alpha_0 + \beta I$, where α_0 is the linear absorption coefficient of the sample and I is the intensity of the laser. The third-order nonlinear absorption and refraction are investigated by Z-scan techniques [16]; and the techniques are simple and sensitive experimental techniques for studying nonlinear optical properties and determining the sign of the nonlinear refractive and absorption indices.

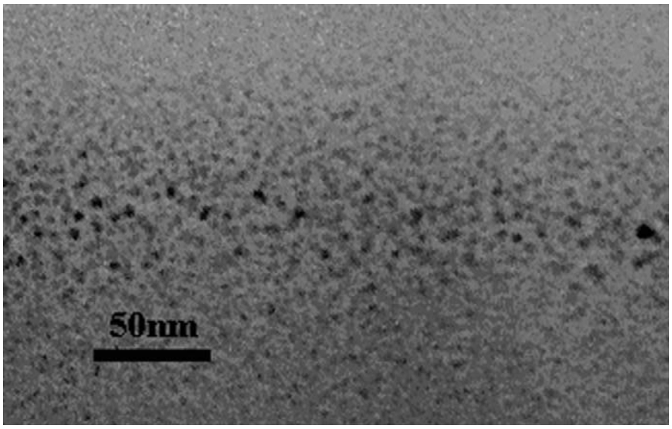

Fig. 1. Cross-sectional TEM image for the sample implanted by 180 keV, 5×10^{16} Cu$^+$ ions/cm^2.

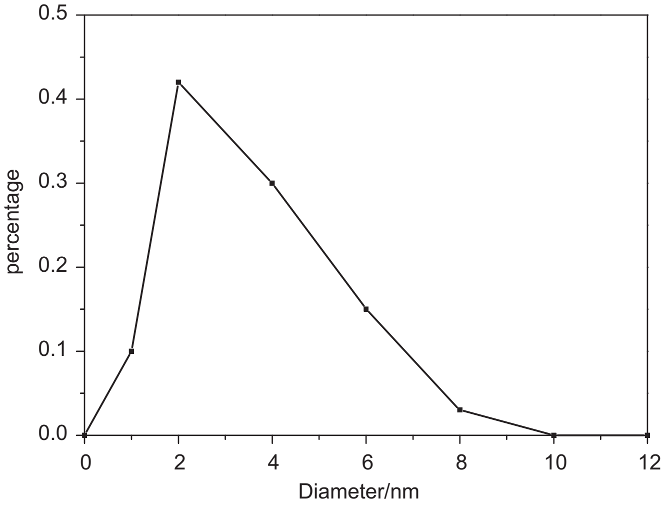

Fig. 2. Comparatively size distribution profiles of 5×10^{16} Cu$^+$ ions/cm^2 nanoclusters in silica sample.

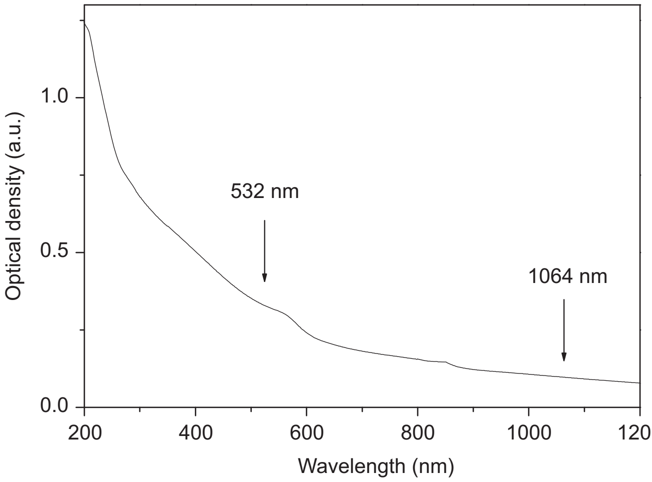

Fig. 3. Optical absorption spectra of the Cu implanted sample to dose of 5×10^{16} ions/cm^2.

The open- and closed-aperture Z-scan curves are theoretically fitted by [16]:

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

$$T(z) = 1 + \frac{4\Delta\Phi_0 x}{(x^2+9)(x^2+1)} \tag{2}$$

where $x = z/z_0$, T is the normalized transmittance and z is the distance along the lens axis in the far field. The nonlinear absorption coefficient β can be obtained by $q_0 = \beta I_0 L_{eff}$, where I_0 is the intensity of the laser beam at the focus ($z = 0$), L_{eff} is the effective thickness of the sample, which can be calculated from the real thickness L and the linear absorption coefficient α_0, in the form of $L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0$. The nonlinear refractive index is calculated by $\Delta\Phi_0 = (2\pi/\lambda)\gamma I_0 L_{eff}$, where $2\pi/\lambda$ is the wave vector of the incident laser.

Normalized open-aperture Z-scan of sample is displayed in Fig. 4(a). The open-aperture measurement shows an obvious enhanced transmittance near the focus, occurring due to the saturation of absorption. This reveals negative nonlinear