Vacuum 82 (2008) 1220–1223

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Optical nonlinearities of Au nanocluster composite fabricated by 250 keV ion implantation

Y.H. Wang [a,*], J.D. Lu [a], R.W. Wang [a], Y.L. Mao [b], Y.G. Cheng [b]

[a] Department of Applied Physics, Wuhan University of Science and Technology, Wuhan 430081, China
[b] Department of Physics, Henan University, Kaifeng 475001, China

ARTICLE INFO

Article history:
Received 5 September 2007
Received in revised form 24 January 2008
Accepted 24 January 2008

Keywords:
Ion implantation
Gold nanoclusters
Optical nonlinearity
Z-scan

PACS:
61.46.+W
61.72.Ww
42.65.−K

ABSTRACT

Metal nanocluster composite glass prepared by 250 keV Au ions into silica with dose of 1×10^{17} ions/cm^2 has been studied. The microstructural properties of the nanoclusters are characterized by optical absorption spectra and transmission electron microscopy (TEM). Third-order optical properties of the nanoclusters are studied by the Z-scan technique under 1064 nm and 532 nm excitations. The nonlinear refraction index, nonlinear absorption coefficient, and the real and imaginary parts of the third-order nonlinear susceptibility are deduced. The results of the investigation of nonlinear refraction using the off-axis Z-scan configuration are presented and the mechanisms responsible for the nonlinear response are discussed. The third-order nonlinear susceptibility $\chi^{(3)}$ of this kind of sample was determined to be 1.6×10^{-7} esu at 532 nm and 1.3×10^{-7} esu at 1064 nm.

1. Introduction

Metal nanoclusters possess interesting linear and nonlinear optical properties. Recently, there has been an increasing interest in the third-order nonlinear susceptibility and the photorefractive effect of noble-metal clusters embedded in dielectric matrices [1–4]. Third-order nonlinearities of metal/dielectric composite materials were influenced by the type and size of the embedded metal clusters, by the dielectric constant, thermal conductivity and heat capacity of the dielectric matrices [1–7]. 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 [8–10]. Amongst the nanoclusters studied by recent researchers, nonlinear absorption and nonlinear refraction were found to be potential used for nonlinear optical devices in Au and Au containing nanomaterials [11–13].

Ion implantation has been shown to produce high-density metal colloids in glasses [14]. 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 optical nonlinear responses of the metal nanocluster–glass composites can be understood in the framework of dielectric and quantum confinement effects [15]. Application aspects of the material are most relevant to the optical properties change versus the nanocluster structure.

In this paper, MNCGs were prepared by Au^+ implantation into silica. We focused our interest on study the nonlinear optical properties of this gold nanoclusters. Nonlinear optical properties were measured by Z-scan method under the wavelengths of 532 and 1064 nm.

2. Experiment

Silica slides were implanted at room temperature by gold ions at 250 keV. The current density of ion implantation was 2.5 μA/cm^2. Optical absorption spectra were recorded at room temperature using an UV–VIS dual-beam spectrophotometer with wavelengths from 1200 to 200 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 shape of nanoclusters.

* Corresponding author.
E-mail address: wyh61@163.com (Y.H. Wang).

0042-207X/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2008.01.045

The measurements of third-order optical nonlinearities of the sample were carried out using the standard Z-scan method. The excitation source is a mode-locked Nd:YAG laser (PY61-10, Continuum), with a pulse duration of 38 ps and a repetition frequency of 10 Hz. Wavelength (1064 nm) and doubled frequency (532 nm) are used for excitation in the experiment. The detector is a dual-channels energy meter (EPM2000). With a converging lens of $f = 260$ mm, the radius 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 1×10^{17} Au^+ ions/cm^2 is shown in Fig. 1. As can be seen from the image, spherical gold clusters are formed during the implantation process; the particle size distribution is not uniform. The size of nanoclusters varies from 5 to 20 nm. Interestingly, the comparative size distributions of Au nanoclusters are shown in Fig. 2. The average size of nanoclusters in this sample is 8 nm.

The linear optical absorption spectra of the sample investigated are shown in Fig. 3. The spectra range from 200 to 1500 nm. The surface plasmon resonance (SPR) absorption peaks of Au nanoclusters around 540 nm are observed, superimposed on the monotonous absorption stemming from interband transitions in gold nanoclusters. This selective absorption band is due to the surface plasmon resonance (SPR), which is extra evidence of Au nanoclusters formation.

The nonlinear absorption in the sample can be described by β, which includes saturated absorption (SA) and reversed saturated absorption (RSA) [16]. The nonlinear absorption is expressed by $\alpha = \alpha_0 + \beta I$, 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 [17], which are simple and sensitive experimental technique for the study of nonlinear optical properties and allow determining the sign of the nonlinear refractive and absorption indices. The open- and closed-aperture Z-scan curves are theoretically fitted by [17]:

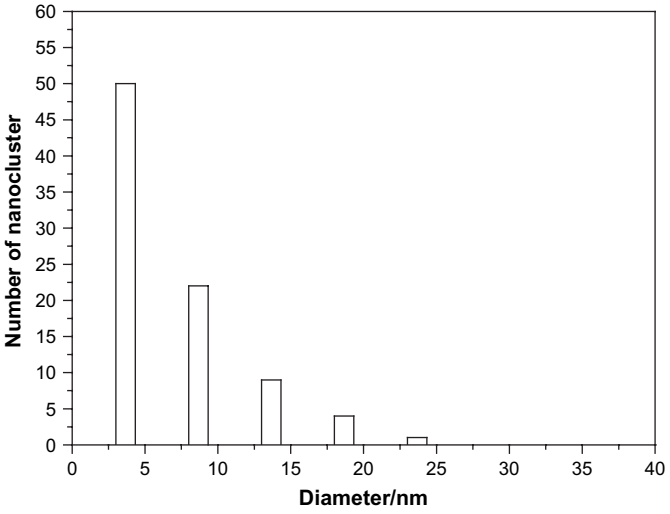

Fig. 2. Comparatively size distribution profiles of 1×10^{17} Au^+ ions/cm^2 nanoclusters in silica sample.

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

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

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 $q_0 = \beta I_0 L_{\text{eff}}$, 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 $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$. The nonlinear refractive index is calculated by $\Delta\Phi_0 = (2\pi/\lambda)\gamma I_0 L_{\text{eff}}$, 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 absorption coefficient. For visible light and for particle diameters $d \leq \lambda$, λ is the vacuum wavelength of the optical wave, only the electric-dipole

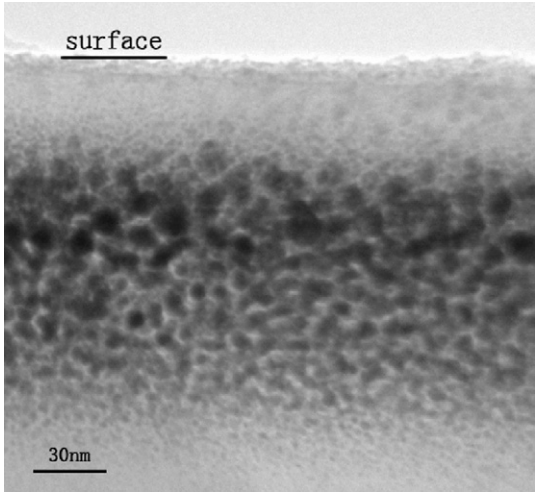

Fig. 1. Cross-sectional TEM image for the sample implanted by 250 keV, 1×10^{17} Au^+ ions/cm^2.

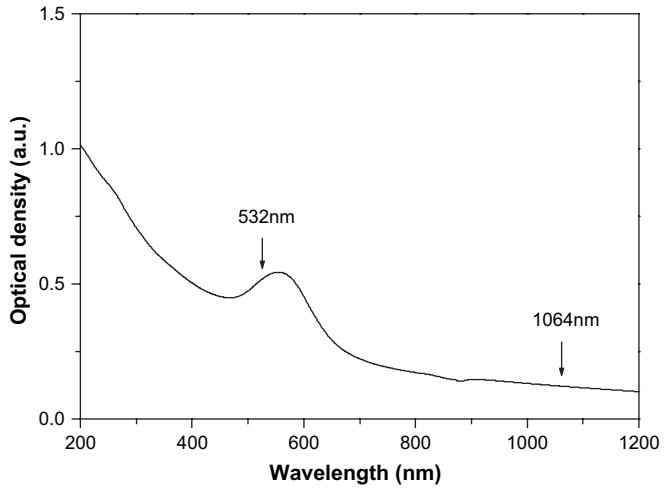

Fig. 3. Optical absorption spectra of the Au implanted sample to dose of 1×10^{17} ions/cm^2.