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Nonlinear optical properties of pulsed laser deposited Cu and Zn single and double layer nanostructure thin films

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ABSTRACT

In this study single and double layer of Cu and Zn nanostructure thin films are prepared by pulse laser deposition technique. The samples are characterized by field emission scanning electron microscopy and optical absorption spectroscopy. The nonlinear refractive index and absorption coefficient of Cu, Zn, Zn/Cu, and Cu/Zn nanostructure thin films are studied by Z-scan method. Zn, Cu/Zn and Zn/Cu nanostructure thin films exhibit positive and Cu nanostructure thin films exhibit negative thermal nonlinear refractive indices, all of the order of 10^{-4} cm^2/W. Nonlinear absorption coefficient signs of Cu/Zn and Zn nanostructure thin films were positive and those of Zn/Cu and Cu were negative. It is shown that the nonlinear phase shift and the nonlinear refractive index have increased in double layer thin films in comparison with single layer thin films, and also the nonlinear absorption behaviour of double layer thin films is similar to that of the upper layer thin films. Contrary to normal trend, nonlinear absorption coefficient of Cu/Zn double layer thin film has increased in comparison with Zn single layer thin film in spite of increasing thickness. Thus tuneable nonlinear absorption coefficient maybe attainable.

1. Introduction

Nanostructures have got lots of attractive and useful applications due to the basic differences with their bulk counterparts in some determinant characteristics. The unique characteristics of metal nanostructures including heat capacity, plasmon phenomena, magnetic, electronic, peculiar optical and nonlinear optical properties are dependent to size, shape and surface morphology of the nanostructure [1–8]. Metal nanostructures have been produced as colloids or thin films of composite glasses, organometallic compounds and deposited nanoparticles on solid substrates. Deposition of metal nanoparticles on solid substrates has been done by different methods such as sputtering, thermal evaporation and pulsed laser deposition (PLD). PLD is one of the well-known methods for growing nanostructure thin films of various materials [9–11]. The merit of PLD is the ease of controlling important parameters like substrate temperature, gaseous ambience, target to substrate distance and laser fluence, each of which has an effective role in the morphology and quality of the prepared thin film [12]. Furthermore congruent ablation and preserving the stoichiometry of the target is of unique aspects of PLD.

The surface structure has a strong influence on the optical properties of nanostructures and also the surface plasmon resonance (SPR) peak in metallic nanostructures is dependent on the dielectric environment of the materials. Nonlinear optical properties of nanostructures have been studied in many researches [13–15]. Various nonlinear optical processes may occur in nanostructure materials [16]. Third-order contribution to nonlinear polarization and thermal nonlinear optical effects which leads to intensity dependant refractive index, and also nonlinear absorption have attracted more attention. Among different approaches for obtaining the nonlinear refraction and absorption coefficients, Z-scan is one of the most simple and sensitive methods which gives both magnitude and sign of the nonlinear refraction index and absorption coefficient and is sensitive to both electronic and thermal effects [17,18].

Nonlinear optical properties of colloids, composite glasses and organometallic compounds of Cu and Zn nanoparticles have been researched [19–21] and about Cu nanoparticles deposited on solid substrates, some other specifications such as morphology and optical responses [22], catalytic performance [23], electrical conductivity [24,25] and so on have been studied.

In this paper Cu and Zn single layer nanostructure thin films (SNTF) and Cu/Zn and Zn/Cu double layer nanostructure thin films (DNTF) were deposited on the lamella glass by PLD technique. Morphology of the nanostructure thin film samples were characterized by scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM). The thickness of nanostructure thin films is measured by interference microscopy. Linear optical absorptions of the samples were obtained by UV–Visible absorption spectroscopy. The X-

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ray diffraction (XRD) patterns were prepared to study the crystalline structure of the samples. The nonlinear refractive index and absorption coefficient of Cu, Zn, Zn/Cu, and Cu/Zn nanostructure thin films were studied by Z-scan method. The effect of the first layer on the linear and nonlinear optical properties of the second layer is also discussed.

2. Experimental details

Cu and Zn SNTFs and DNTFs were deposited on glass substrate by pulsed laser deposition technique. The fundamental wavelength (1064 nm) of Nd:YAG pulsed laser with 10 Hz repetition rate, 3 mm spot size and 20 ns pulse duration was used for Zn thin films while for Cu thin films the second harmonic wavelength (532 nm) of Nd:YAG was used. Duration time of deposition for Zn and Cu thin films are 15 and 45 min, respectively. In all cases of deposition, the vacuum pressure was approximately 2.7×10^{-3} Pa and the target to substrate distance was 2.5 cm. The laser beam was focused by a 40 cm focal length lens on the surface of the copper or zinc targets placed in the vacuum chamber. In the deposition process of Cu/Zn DNTF, first Cu nanoparticles were deposited on the glass substrate and then, by changing the target, Zn nanoparticles were deposited on the Cu thin film. Each deposition process was performed at the same circumstances mentioned earlier. For Zn/Cu DNTF the process was vice versa.

The thickness of the samples was estimated by LEITZ D-6330 interference microscopy. To study the morphology of the thin films, SEM and FESEM images were obtained using KYKY-EM3200 scanning electron microscope at 25 kV and Hitachi S-4160 field emission electron microscope at 20 kV, respectively. The crystalline structure of the samples were characterized by using an XRD patterns. The XRD measurements were carried out using a Rigaku X-ray diffraction with CuKα radiation in θ–2θ Bragg Brentano configuration. Optical absorption spectra of the samples were collected in the region of 200–900 nm by a Carry500 UV–Visible spectrometer. Nonlinear absorption coefficient and refractive index of the thin films were measured by the well-known Z-scan method. Z-scan method is based on transforming phase distortions of the laser beam passing through a nonlinear medium to variation of power transmittance. The sample mounted on a moving stage is translated along the focused laser beam direction (z axis) a few centimetre before and after the focal plane of the lens. According to the open aperture Z-scan experiment, the transmitted laser power through the sample is measured as a function of the sample position. Using the normalized transmitted power as a function of position the value and sign of the nonlinear absorption coefficient can be determined. In the closed aperture experiment used to measure nonlinear refractive index, an aperture is placed before the detector in a distance from the focus much longer than $z_{0,}$ the diffraction length of the focused beam. Then the transmitted laser power through the aperture is recorded as a function of the sample position with respect to the focal plane.

In our experiment, a continues wave (CW) diode laser with the power of 130 mW and spot size of 1.3 mm operating at the wavelength of 532 nm was employed as a source for Z-scan. Beam waist and diffraction length of the focused beam in front of a 20 cm lens was estimated to be 39 μm and 0.9 cm respectively. A photodiode power sensor was used as a detector.

3. Results and discussion

Linear optical properties of SNTFs and DNTFs prepared samples were investigated by UV–Visible absorption spectra. Linear absorption spectra of Cu and Zn SNTFs three days after deposition are shown in Fig. 1. Cu and Zn SNTFs show surface plasmon resonance (SPR) at the wavelength of 596 nm and 318 nm, respectively.

Fig. 2 shows the linear absorption spectra of Cu/Zn and Zn/Cu DNTFs. In order to see whether the SPR of the first layer has been changed or not after deposition of the second layer, linear absorption spectrum of the first layer before deposition of the second one is also shown in Fig. 2. The SPR peaks in the absorption spectra of Cu and Zn thin films after two weeks and before deposition of second layer were around 583 and 320 nm, respectively. It has been shown that the wavelength of SPR absorption peak depends on the shape and the size of the nanoparticles as well as the dielectric constant of the surrounding medium [24–32]. The SPR wavelength will red shift with an increase in the dielectric constant of the nanoparticles environment, compared to the vacuum SPR wavelength. Also increase or decrease in size of the nanoparticles, should cause a red or blue shift in the SPR position. Moreover, the changes of the SPR peak position and amplitude of a metallic nanoparticle can be assigned to the formation and growth of an oxide layer (or corrosion) and the change of the dielectric constant of the nanoparticles' surrounding environment. Since the oxidation rate (or corrosion) of zinc is faster than copper one can conclude that the oxide layer of Zn nanoparticles is formed faster than Cu oxide layer. According to some reports the SPR peak of Zn nanoparticles is around 250 nm, and the excitonic peak of ZnO is about 350 nm [26]. The SPR peak position of metallic Cu nanoparticles and absorption peak of copper oxide have also been reported at around 600 nm, and 500 nm, respectively [19]. As shown in Fig. 1 the absorption peak of Zn SNTF three days after deposition is placed at 318 nm, which is due to oxidation and can lead to the formation of ZnO nanoparticles. Comparing the results of Figs. 1 and 2, one could find that the SPR peak of Cu SNTF is blue shifted about 13 nm and absorption edge is red shifted which indicates that the copper oxide layer is also formed on the surface of copper nanoparticles after two weeks in room conditions [27], while the SPR peak of Zn

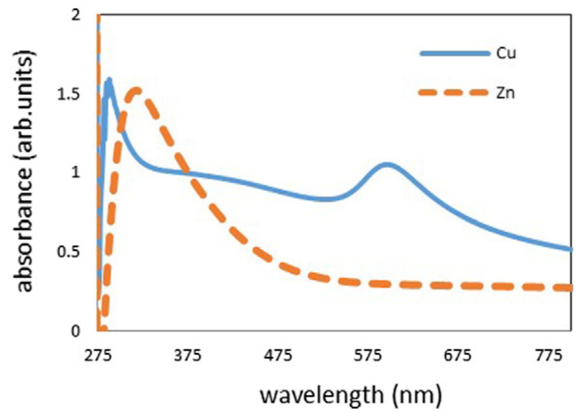

Fig. 1. Linear absorption spectra of Cu and Zn SNTFs three days after deposition.

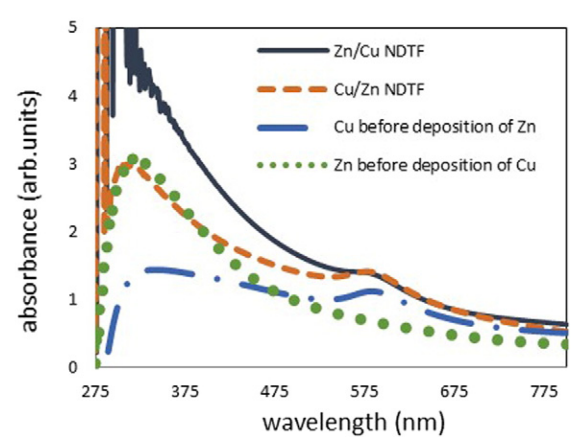

Fig. 2. Linear absorption spectra of Zn and Cu thin films before deposition of the second layer and Zn/Cu and Cu/Zn DNTFs.