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Optical nonlinearity in nanostructured carbon thin films fabricated by pulsed laser deposition technique

Indrajeet Kumar, Alika Khare *

Laser and Photonics Lab, Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

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ABSTRACT

In the present paper, the measurement of nonlinear refractive index coefficient in nanostructured carbon thin films deposited via pulsed laser deposition (PLD) technique is reported. The PLD carbon thin films were characterized by micro-Raman spectroscopy and ellipsometry. Raman spectra showed characteristic D and G band around ~1350 cm^{-1} and ~1580 cm^{-1} respectively. The nonlinear refractive index of the carbon films was measured by closed aperture Z-scan technique using He-Ne laser. The nonlinear refractive index coefficient of carbon thin films was found to increase from $(6.08 \pm 0.75) \times 10^{-4}$ cm^2/W to $(1.69 \pm 0.13) \times 10^{-3}$ cm^2/W with the deposition temperature from room temperature to 750 °C, respectively.

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1. Introduction

Nanostructured carbon thin films possess a wide range of electrical resistivity, wear resistance, friction coefficient, chemical inertness, biocompatibility, optical transparency, etc. Such a high degree of flexibility in its properties is due to the bonding of carbon atoms having different degrees of hybridization [1–4]. Nanostructured carbon thin film is a combination of sp^2 and sp^3 bonded carbon atoms in a random network. In the sp^3 configuration, the adjacent carbon atoms are bonded strongly via σ bonds which give rise to a large band gap and hardness to the film. In the sp^2 configuration of carbon network, three of the valence electrons form trigonally σ bond and the remaining fourth electron forms a π bond. The π bond lies normal to the plane of σ bonds, weaker in strength and is closer to the Fermi level. Thus the presence of a π bond provides the small band gap and hence contributes towards the optical absorption and nonlinear optical response [5,6]. Carbon nanostructures in the form of carbon nanotubes, graphene, carbon black, onion like carbon and fullerenes are sp^2 enriched and have been investigated for nonlinear optical response. The nonlinear absorption coefficient (β) and nonlinear refractive index coefficient (n_2) of single wall carbon nanotube via Z-scan technique using nanosecond laser at a wavelength of 532 nm are reported to be ~7.1×10^{-5} cm/W and ~-1.2×10^{-9} cm^2/W, respectively [7]. Multiwall carbon nanotubes in ethylene glycol (0.4 mg/ml) has been reported to exhibit reverse saturation effect under picosecond laser (532 nm) illumination and the corresponding value of β from Z-scan is observed to be 7.6×10^{-10} cm/W [8]. Its third order nonlinear susceptibility '$\chi^{(3)}$' via four wave mixing (nano as well as pico second laser) has also been documented by the same group [8]. The saturation absorption behaviour in few layer graphene fabricated by chemical vapor deposition under the irradiance of picosecond laser of wavelength 1550 nm is demonstrated and the measured value of n_2 is reported to be ~10^{-7} cm^2/W [9]. The reverse saturation absorption is reported in linear carbon chains at a wavelength of 532 nm from nanosecond laser. Its experimentally measured value for β and n_2 are reported to be 2.1×10^{-10} cm/W and -3.0×10^{-15} cm^2/W, respectively [10]. The optical limiting in carbon black suspension, onion-like carbon, fullerenes and diamond nanoparticles has been reported in the literature [6, 11,12]. The various forms of nanostructured carbon enriched with sp^2 bond are being envisaged as a good candidate for nonlinear optical photonic device application. For the photonic applications, normally thin film geometry is preferred. The nonlinear optical properties of nanostructured carbon, particularly in the form of thin film can be assessed experimentally by various techniques. Among them, Z-scan technique has emerged as a very handy tool for these measurements [13]. In this technique, the sample is translated along the optic axis on either side of the focal plane of a lens. The transmitted beam through the sample is recorded as a function of its position 'z' with respect to the focal plane. The nonlinear absorption (NLA) coefficient and nonlinear refractive index (NLR) coefficient can be obtained by open aperture (OA) and closed aperture (CA) Z-scan, respectively.

In the present paper, the measurement of the third order nonlinear refractive index of pulsed laser deposited (PLD) carbon thin films using modified Z-scan setup is reported [14]. In the modified Z-scan setup, the photodiode of the conventional Z-scan is replaced by a

* Corresponding author.
E-mail address: alika@iitg.ernet.in (A. Khare).

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charged coupled device (CCD) camera as a detector, thereby improving the sensitivity of the technique [15]. The effect of deposition temperature on the NLR coefficient of the PLD carbon thin film is presented.

2. Experimental details

The carbon thin films were deposited by PLD technique. The schematic of the experimental setup is shown in Fig. 1. The deposition was carried out by loosely focusing the second harmonic of a Q-switched Nd:YAG laser (QUANTA SYSTEM HYL-101, 532 nm, 10 Hz) onto the graphite target under a base pressure of the order of ~10^{-3} Pa. The films were deposited onto the fused silica substrate at room temperature (RT), 300 °C, 500 °C and 750 °C for a deposition time of 5 min. The target to substrate distance and the laser fluence were kept at ~3 cm and ~5 J/cm^2, respectively for all the samples. During the deposition, the target was continuously rastered so as to provide the fresh surface for each and every shot of the laser pulse. The PLD thin films of carbon were subjected to micro-Raman Spectrometer (HORIBA Jobin Yvon LabRAM HR800) for the structural characterization using Argon ion laser at 514 nm as the excitation source. The thickness of the films was measured using stylus profilometer (Veeco Dektak 150). The rotating polarizer ellipsometer (Semilab GES5-E) was used to obtain the linear absorption coefficients of these films. Fig. 2 shows the schematic of the modified Z-scan setup used for the measurement of third order NLR coefficient. A He-Ne laser (MELLES GRIOT 05-LHP-927, wavelength 632.8 nm) was focused on the carbon thin film using a convex lens of focal length 50 mm. The film was mounted on an translation stage and scanned along optical axis on either side of the focal plane. The transmitted beam was imaged on a CCD camera (PCO PixelFly) interfaced with computer. The images of the transmitted laser beam through the film were recorded as a function of film position (z) w.r.t. the focal plane. A neutral density (ND) filter was placed in front of CCD to avoid its saturation. An iris diaphragm was placed before ND filter to block the scattered light from entering into CCD. The transmitted intensity through the film was obtained by integrating the gray values of recorded images using MATLAB program. For the CA Z-scan, the images were obtained from complete recorded images (open aperture) by implementing a suitable synthetic aperture via software using the MATLAB program. The synthetic aperture size was selected so as to obtain the ratio of integrated intensity of the image with aperture to that of without it (S) ~ 0.4. Thus the modified Z-scan setup enables the recording of open as well as closed Z-scan data in a single scan.

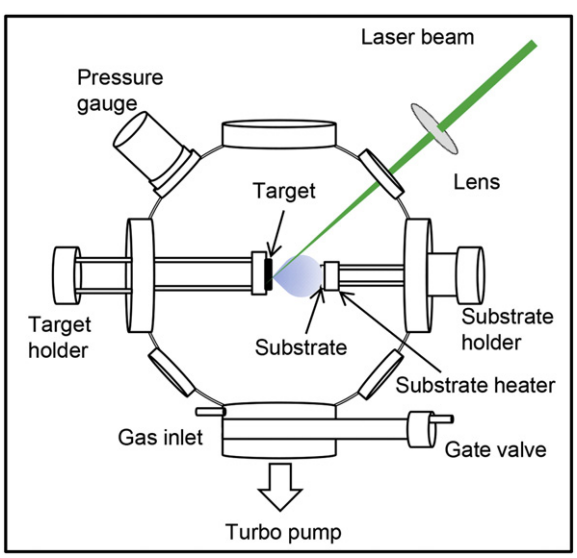

Fig. 1. Schematic of PLD setup for thin film deposition of carbon thin films.

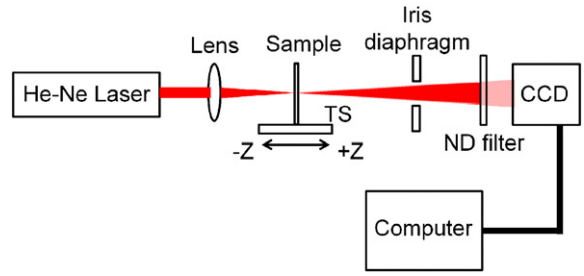

Fig. 2. Schematic of Z-scan setup.

3. Results and discussions

The Raman spectra of the PLD carbon thin films deposited at RT, 300 °C, 500 °C and 750 °C are shown in Fig. 3. The spectrum for the sample deposited at RT, Fig. 3(a), shows a broad band centered at ~1540 cm^{-1}, indicating that the film is rich in the sp^3 bonded carbon atoms [16]. The films deposited at substrate temperatures of 300 °C, 500 °C and 750 °C, exhibit the evolution of D (~1350 cm^{-1}) and G (~1580 cm^{-1}) distinct bands, Fig. 3(b), (c) and (d), the characteristic of the disordered sp^2 and sp^3 network of carbon atoms [5,17]. The D band corresponds to the breathing vibrations of aromatic rings and activated from the structural disorder in the film. The G band is assigned to the stretching modes of C—C sp^2 bonds in aromatic rings or in chains containing C═C sp^2 bonds [17]. The position of G band lies at ~1575 cm^{-1} in the case of single crystal graphite whereas for disordered graphite it is in the range of 1580–1600 cm^{-1} [17,18]. The G band shifts towards lower wavenumber when it originates from the sp^2 clusters embedded in the amorphous matrix of diamond-like structures [16]. The deconvoluted spectra using multiple peak fitting with Gaussian function are also shown in Fig. 3. The deconvoluted Raman spectra of all the samples display the dominating G band. The peak position of the G band for film deposited at RT is at 1552 cm^{-1}. This shift of G band towards the lower wavenumber from its graphitic position and the smaller value of the integrated intensity ratio of D band to G band (I_D/I_G), ~0.34, are due to the presence of higher concentration of sp^3 bonds [16,19]. The higher fraction of sp^3 bonds of carbon atoms was also confirmed by the dispersion of G band using Eq. (1) [20].

$$sp^3\ content = -0.07 + 2.50 \times Dispersion(G) \pm 0.06 \quad (1)$$

The dispersion of G band was measured by recording Raman spectra at three distinct excitation laser wavelengths; 488, 514 and 633 nm, Fig. 4(a). The dispersion rate of the films are plotted in Fig. 4(b). The dispersion of G band was observed to be decreased with the increase in deposition temperature and vanished for the film deposited at the temperature of 750 °C, Fig. 4(b). The corresponding sp^3 contents of the film deposited at RT was ~68% which decreases to ~25% and ~10% at substrate temperature of 300 °C and 500 °C, respectively and the film becomes nearly free from sp^3 bonded carbon atoms at the deposition temperature of 750 °C.

As the deposition temperature increased, D and G bands appeared resolved and the I_D/I_G value was found to be increased from ~0.34 to ~1.59 for the deposition temperature from RT to 750 °C, respectively, as shown in Fig. 5. The evolution of D and G band along with the increase in I_D/I_G with increase in substrate temperature suggests that diamond-like amorphous matrix is shrinking while sp^2 clusters are growing with the deposition temperature. The increase in concentration of sp^2 clusters with the deposition temperature is also confirmed by the shift of G band position towards higher wavenumber from 1552 cm^{-1} to 1586 cm^{-1}, Fig. 5, and decrease in corresponding full width at half maximum (FWHM) from 208 cm^{-1} at RT to 135 cm^{-1} at 750 °C. This is due to the conversion of sp^3 sites into sp^2 aromatic rings as a result of enhanced surface diffusion at elevated substrate temperature during

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