Absorptive and refractive nonlinearity of carbon nanotubes grown on Si substrate

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The third-order susceptibility of multiwalled carbon nanotubes (MWCNTs) grown on Si substrate were measured using reflective Z-scan (RZ-scan) technique with femto-second laser pulses at 790 nm. The nonlinear absorption coefficient β and nonlinear refraction index γ were measured to be about 9×10^{2}cm/GW and 9.6×10^{-3}cm^2/GW, respectively. This is about one order of magnitude larger than the measurement of MWCNTs on transparent quartz substrate. The enhanced optical nonlinearities are contributed by the enhanced local field and the photoinduced off-resonant absorption of the π-plamon of MWCNTs on Si.

OCIS codes: 190.4400, 240.4350, 320.7110.

The active study on carbon nanotubes (CNTs) has last for more than a decade. Many excellent properties of CNTs on mechanical, electronic, magnetic and optical have been reported[1−5], showing a promising future of applications. About the optical nonlinearity of CNTs, most of the researches were focused on the nonlinear absorption[6−12]. Both the transient photobleaching and the saturable absorption were observed in single-walled CNTs[8,9]. CNTs dispersed in the solvents exhibit an optical limiting property[4,5]. But the nonlinear refraction of CNTs in this system is seldom reported, which is also very important in the application of optical switching.

The optical nonlinearities of multiwalled carbon nanotubes (MWCNTs) grown on the solid substrate are quite different from those of CNTs dispersed in liquid solvents. Recently, It is reported that MWCNTs grown on quartz have a negative nonlinear absorption coefficient ($\beta = -29$ cm/GW) and also a negative refractive index ($\gamma = -3 \times 10^{-4}$ cm^2/GW)[12]. This result implies that the optical nonlinearities of MWCNTs are strongly dependent on the microstructure. In this letter, we adopted a reflective Z-scan (RZ-scan) technique to directly investigate the absorptive and refractive nonlinearities of MWCNTs grown on Si substrate.

The CNTs were synthesized in chemical vapor deposition (CVD) method. One can find the details elsewhere[13]. Briefly, a silicon substrate was coated with Fe films (5-nm thickness) by electron beam evaporation. After annealed in air at 300 °C overnight, the substrate was inserted into a quartz tube furnace at about 700 °C in flowing Ar. Ethylene was flown for 5 to 10 min, after which the furnace was cooled to room temperature. Then MWCNTs were formed on the substrate.

The nonlinear absorption coefficient and the nonlinear refractive index of MWCNTs grown on Si were measured using the RZ-scan technique[14−16] at room temperature, since the Si substrate is not transparent and has a high reflection ratio. Femtosecond laser pulses generated by a mode-locked Ti:sapphire laser with a pulse width of 150 fs and a repetition rate of 76 MHz were employed in the measurements. The radius of the Gaussian beam spot at the focus (ω_0) is calculated to be about 9 μm with a converging lens of f= 150 mm.

Figure 1 is the scanning electron microscopy (SEM) image of MWCNTs on Si substrate. Highly ordered MWCNTs were not observed in the sample since the thickness is only ∼500 nm and the density of CNTs is relatively low. The RZ-scan setup is schematically shown in the inset.

The normalized open- and closed-aperture RZ-scans of MWCNTs are shown in Figs. 2(a) and (b) with Fig. 2(b) being the result of closed-aperture RZ-scan data divided to the open-aperture one. The RZ-scans were performed with a laser peak irradiance I_0 of 11 GW/cm^2. Theoretical calculations were carried out according to the basic transmission Z-scan theory[14] under an approach that the Si substrate of the sample be simply treated as a mirror. The theoretical calculations (solid lines) fit the experimental data well. It can be seen that in accordance with the reported results of MWCNTs on quartz, the sample of MWCNTs on Si has a negative nonlinear absorption coefficient and also a negative nonlinear refractive index. The RZ-scans of Si substrate are shown in Figs. 2(c) and (d), both nonlinear absorption and nonlinear refraction of Si substrate can be neglected comparing with MWCNTs sample.

The value of nonlinear absorption coefficient β is calculated from $\beta = q_0/I_0' L_{\rm eff}'$. $q_0 \approx$ -1, extracted from Fig. 2(a) according to

$$T = \sum_{m=0}^{\propto} \frac{(-q_0)^m}{(1+z^2/z_0^2)^m (1+m)^{3/2}}, \qquad (1)$$

where $I_0' = (1+R)I_0/2$, I_0 is the original laser peak irradiance at the beam waist and R is the reflection rate of the Si substrate at the wavelength of 790 nm. $L_{\rm eff}' = 2L_{\rm eff}/\cos\theta$ and $\theta \approx \pi/4$. We assume $L_{\rm eff} = [1-\exp(-\alpha_0 L)]/\alpha_0 \approx L$ with L the thickness of the MWCNTs layer, while in fact L is always larger than $L_{\rm eff}$. It is obtained $\beta \approx -9 \times 10^2$ cm/GW. The formula of γ is $\gamma = \Delta\Phi_0/kI_0' L_{\rm eff}' \approx -9.6\times10^{-3}$ cm^2/GW, with $\Delta\Phi_0 \approx -0.85$ extracted from Fig. 2(b) according to

$$T(z, s << 1) = 1 + \frac{4\Delta\Phi_0(z/z_0)}{[(z/z_0)^2+9][(z/z_0)^2+1]}. \qquad (2)$$

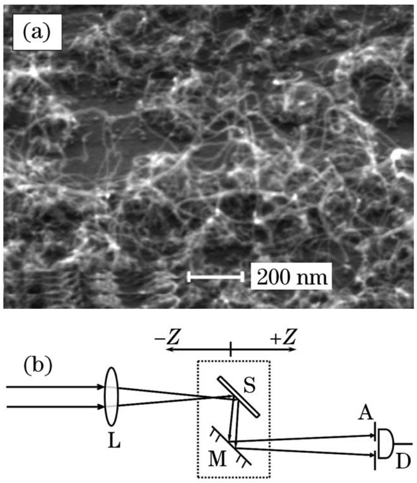

Fig. 1. SEM image of MWCNTs on Si. Inset is the schematic of reflective Z-scan setup. L: lens of f =150 mm; M: mirror; S: sample; A: aperture; D: detector.

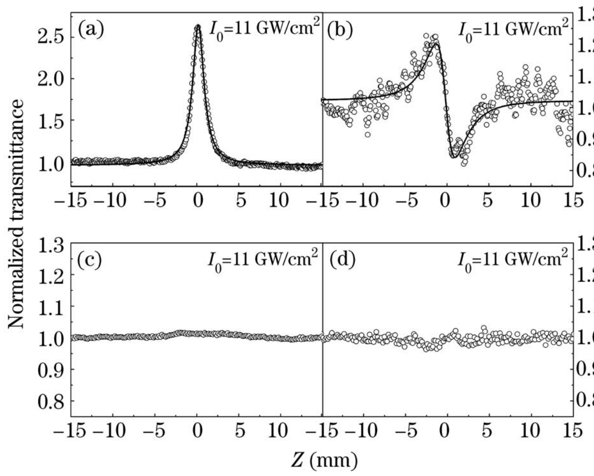

Fig. 2. RZ-scan results of MWCNTs on Si substrate. (a) Open-aperture RZ-scan of MWCNTs; (b) modified closed-aperture RZ-scan of MWCNTs; (c) open-aperture RZ-scan of Si substrate; (d) modified closed-aperture RZ-scan of Si substrate. The modified RZ-scans in (b) and (d) are the closed-aperture transmittance divided by the corresponding open-aperture ones.

Note that both nonlinear absorption coefficient and nonlinear refractive index of MWCNTs on Si substrate are about one order of magnitude larger than the measurements of MWCNTs on transparent quartz substrate reported in Ref. [12], while the density of MWCNTs of our sample is comparatively smaller. This enhancement of the third order nonlinearity is assumed due to the interaction between MWCNTs and Si substrate. Si substrate has a high refraction rate, resulting in a red-shift of the π-plamon resonance which enhanced the off-resonant absorption of metal-like MWCNTs.

It is reported that for high absorbing materials when the high repetition rate laser pulses with laser peak intensity larger than few GW/cm^2 were used, there is a high probability to induce a thermal effect which will mislead the Z-scan results analysis or even cause some irreversible changes to the sample structures[19,20]. In this letter, the measured refractive index γ is negative, opposite to the mainly thermal induced one reported in CNT and Cu:Al_2O_3 samples which is positive[21,22]. This implies that the thermal effects are insignificant in MWCNTs. Elim *et al.* reported a consistent (β,γ) of MWCNTs on quartz substrate measured with different I_0 up to 300 GW/cm^2, showing a good heat stability of the MWCNTs. The I_0 we used (11 GW/cm^2) is comparatively far smaller, and the RZ-scan curves repeated well in the same test point in our RZ-scans. These confirm us that there was no irreversible change of the sample, and the measured curves are reliable.

In summary, the absorptive and refractive nonlinearity of MWCNTs grown on Si substrate were investigated using reflective Z-scan technique. The nonlinear absorption coefficient and nonlinear refractive index (β,γ) of MWCNTs on Si substrate were measured to be (-9×10^2 cm/GW, -9.6×10^{-3} cm^2/GW), respectively. These large optical nonlinearities are contributed by the enhancement of local electrical field and the photoinduced off-resonant absorption of the π-plamon of MWCNTs.

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