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Large optical third-order nonlinearity of composite thin film of carbon nanotubes and $BaTiO_3$

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Abstract

Composite thin films of multiwalled carbon nanotubes and $BaTiO_3$ prepared by pulsed-laser deposition technique are investigated, which have large optical third-order nonlinearity. We characterized the films by using scanning electron microscopy, Raman spectroscopy, UV–vis absorption and X-ray diffraction. The observation reveals that the multiwalled carbon nanotubes are coated by the amorphous $BaTiO_3$. Nonlinear optical properties of the composite films are investigated by *z*-scan technique. The result shows that the value of third-order nonlinear susceptibility $\chi^{(3)}$ has achieved as high as 10^{-6} esu, which is more than three orders of magnitude larger than that of carbon nanotubes in suspension.

1. Introduction

The rapid progress of the optical communications require nonlinear optical material with large third-order nonlinear susceptibility $\chi^{(3)}$ and small relaxation time of photocarriers. In the last decade, carbon nanotubes (CNTs) have attracted widely interest because of their unique physical properties and many potential applications, such as, one dimension quantum wires, optical switches, nano-transistors and other essential electronic components. Regarding to nonlinear optical properties of CNTs, a great deal of experimental and theoretical studies have been reported [1–8]. Ultrafast nonlinear optical responses [9,10] and optical limiting properties [11–14] of CNTs in suspensions and in films have been investigated intensively. Moreover, theoretical calculations of the third-order nonlinear optical properties ($\chi^{(3)}$) of single-walled carbon nanotubes revealed a remarkable enhancement of $\chi^{(3)}$ as high as 10^{-6} esu at resonant excitation. Most of experimental works are focused on CNTs suspensions and CNTs/polymer composites, whose value of $\chi^{(3)}$ was about 10^{-10} esu [15–19]. At the same time, the films containing metal nanocluster (Au, Ag, Cu, e.g.) embedded in dielectric matrices have received much attention due to their specific optical absorption and large third-order nonlinear susceptibility. The composite films of noble metal (Ag and Au) and $BaTiO_3$, which has high dielectric constant and large nonlinear optical effect, have achieved high ($\chi^{(3)}$) as high as 10^{-6} esu [20,21]. Thus, We hope to combine the special optical properties of CNTs with the unique dielectric material such as $BaTiO_3$ in order to obtain composite material for a better nonlinear optical property. In this Letter, we report the fabrication of such CNTs/$BaTiO_3$ composite films using pulsed-laser deposition, and investigate nonlinear optical properties of the composite films with *z*-scan technique.

2. Experimental

The multiwalled carbon nanotubes (MWCNTs) were synthesized by conventional arc discharge. First, the

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pristine MWCNTs were treated by reflux in H_2O_2 and in a mixture of sulfuric and nitric acids (v/v 3:1) to remove the carbon nanoparticles and produce functional groups on them. The purified MWNTs are well dissolved in ethanol or in aqueous solutions [22,23]. The diameter of purified carbon nanotubes is 10–30 nm with length of 3–15 μm . All the films were deposited onto fused quartz substrates of 0.5 mm in thickness with both sides polished. The MWCNTs solution was purified and treated with ultrasonator, then the solution droplet was drop onto the clean substrate and dried under tungsten lamp. We can control the quantity of MWCNTs by adjusting the quantity of the droplet. Then, $BaTiO_3$ layer about 20–30 nm was deposited on the carbon nanotubes layer in vacuum (N2 $\sim 4.0 \times 10^{-3}$ Pa) using pulsed laser deposition (PLD) technique, and the substrate maintained at room temperature during the entire deposition process.

Five samples, namely, Samples 1–5, were prepared in our experiment. The composite films were layered structure. Samples (No. 1, 2, and 3) were prepared by depositing one layer MWCNTs firstly, then coating one layer $BaTiO_3$ using PLD technique. Thickness of $BaTiO_3$ layer is the same for all the three films. The quantity of MWCNTs of the films was different, increased steadily from Samples 1 to 3. We note such a double layers structure of Sample 1 as one period, Sample 4 has two double layers, which was elaborated by repeating twice the process of preparing Sample 1, and Sample 5 has three double layers.

Raman spectra of the pure MWCNTs and thin film samples were recorded at room temperature, using Micro-Raman system, model T-64000 (Jobin Yvon), with an excitation wavelength of 532 nm. Linear optical absorption measurements of the samples were made at room temperature in air from 330 to 800 nm using a SpectraPro-500i spectrophotometer (Acton Research Corporation). The third-order optical nonlinear susceptibility of the composite films was characterized using the single-beam it z-scan technique. In our experiment, a Q-switched Nd:YAG laser with frequency doubled at 532 nm and 10 ns duration as a light source, at a repetition rate of 1 Hz was employed to minimize average power and reduce accumulative thermal effects. The laser beam was focused onto the sample by a 120-mm focal length lens, leading to a measured beam waist of 30 μm and a pulsed energy of 12.5 μJ at the focus. A weak reference beam was used to monitor energy fluctuation. The transmitted beam energy, the reference beam energy, and their ratios were measured using an energy ratiometer simultaneously.

3. Results and discussion

A scanning electron microscopy picture of Sample 2 is shown in Fig. 1. As we know, carbon nanotubes has very high stability even in air at 600–700 °C. The MWCNTs in the film were mainly distributed randomly in the *X*–*Y* plane, and they maintained their features and structures in the composite films. In our experiment, because the MWCNTs have high chemical stability and smooth wall surface, the deposited $BaTiO_3$ did not damage or react with carbon nanotubes. The thickness of $BaTiO_3$ layer is about 20–30 nm, and mainly coated on the surface of the carbon tubes. And from the result of X-ray diffraction (XRD), not shown here, we know that $BaTiO_3$ is amorphous. After investigating the section of the composite films, the thickness of films was estimated from 150 to 540 nm as listed in Table 1.

Raman spectra of Sample 4 and pure MWCNTs are shown in Fig. 2. In the frequency range from 1200 to 1700 cm^{-1}, two peaks were observed at 1350 and 1578 cm^{-1}. The peak at 1350 cm^{-1} corresponds to disorder-induced phonon mode (D-band) of MWCNTs, and the strong peak at 1578 cm^{-1} can be assigned to E_{2g}-band of MWCNTs. It is obvious that Raman

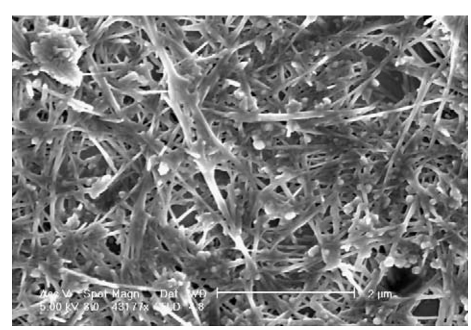

Fig. 1. SEM image of the MWCNT/$BaTiO_3$ composite films deposited on quartz substrate.

Table 1
The number, thickness, absorption coefficient, and nonlinear optical properties of the CNTs with $BaTiO_3$ samples at 532 nm

Sample no.	Film structure	Thickness (nm)	Linear $\alpha(10^4 cm^{-1})$	Re $\chi^{(3)}(10^{-6}$ esu)	Im $\chi^{(3)}(10^{-6}$ esu)	$\lvert\chi^{(3)}\rvert$ $(10^{-6}$ esu)	$\lvert\chi^{(3)}/\alpha\rvert$ (esu cm)
1	One period (One double Layers)	~150	0.83	−0.38	−0.26	0.46	5.54×10^{-11}
2		~160	0.90	−0.94	−0.35	1.01	1.12×10^{-10}
3		~180	1.21	−1.01	−0.43	1.10	0.91×10^{-10}
4	Two period	~280	3.08	−5.89	−2.96	6.61	2.15×10^{-10}
5	Three period	~540	2.18	−7.26	−3.45	8.06	3.70×10^{-10}

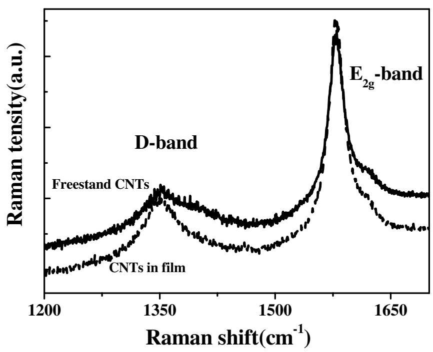

Fig. 2. Raman spectra of freestanding purity MWCNTs and the MWCNT/$BaTiO_3$ composite film.

spectroscopy of carbon nanotubes in the composite films is the same as those of freestanding carbon nanotubes. Such a kind of Raman results confirms further that the MWCNTs in the composite film maintain their characteristic structures and properties, which consist with the SEM observations, and have interacted with $BaTiO_3$ slightly. Moreover, we do not observe the Raman peak coming from $BaTiO_3$ crystal phase. That means $BaTiO_3$ should be amorphous, which is consistent with the result of X-ray diffraction.

The linear optical absorption spectra of the samples as a function of the photon energy are shown in Fig. 3. The linear absorption spectra of the composite films were similar to the results reported for carbon nanotubes, the light absorption property of the samples mainly come from the MWCNTs because of the transparence of $BaTiO_3$ in the range of about 330–800 nm. For one double layer structure, the inset figure in Fig. 3 clearly demonstrates that the absorption intensity at wavelength 532 nm increases gradually with increasing quantity of MWCNTs in the composite film. The absorption in multilayers structure increases greatly because of high quantity of MWCNTs. The results indicate a major characteristic feature of the MWCNTs/$BaTiO_3$ composite film.

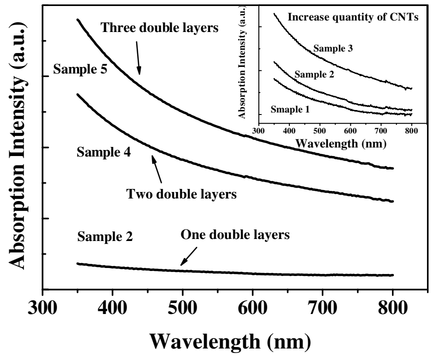

Fig. 3. UV–vis absorption spectrum of the MWCNT/$BaTiO_3$ composite films.

Typical open-aperture (OA) and closed-aperture (CA) z-scan profiles, normalized transmittance as a function of the sample position Z are shown in Figs. 4 and 5 for Sample 2 (one period, a double layered structure) and Sample 4 (two period, two double layered structure), respectively. The points are experimental data, and the solid lines are theoretical fitting results [24]. Because the fused quartz substrate in our experiment has a very small nonlinear optical response at wavelength of 532 nm, which has been measured by the same method, the high nonlinear optical properties observed here resulted from the MWCNTs/$BaTiO_3$ composite films. The reproducibility of the z-scan signals reveal that there has no detectable destruction of the composite films occurred during the measurements, which demonstrates a high stability of MWCNTs again.

The curve shown in Fig. 4 comprises a normalized transmittance peak for OA and a peak-valley for CA, indicating the presence of nonlinear saturation and negative nonlinear refractive. Note that most of the investigation of CNTs solid films focus on the imaginary part of $\chi^{(3)}$, its picosecond relaxation, and its light limiting effects. In our study, we observed obviously the real part of the third-order nonlinear susceptibility of the composite films. With increasing of the quantity of CNTs

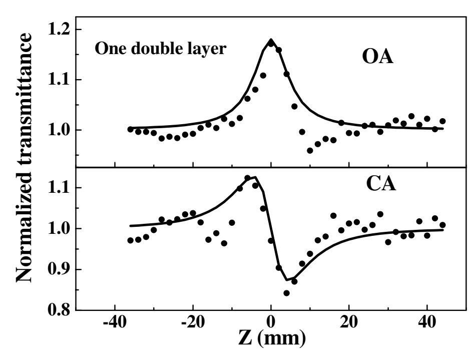

Fig. 4. z-scan normalized transmittance of Sample 2 (one period layered structure) with an open and closed aperture. The solid lines indicate the theoretical fit.

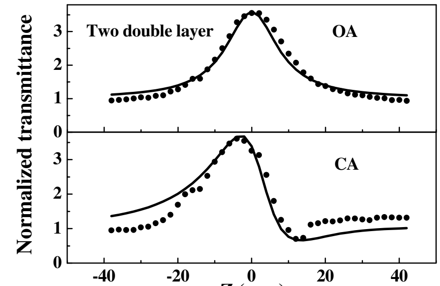

Fig. 5. z-scan normalized transmittance of Sample 4 (two period layered structure) with an open and closed aperture. The solid lines indicate the theoretical fit.

in the composite films, even the value of $\chi^{(3)}$ increases, but the valley in the CA transmittance is relatively reduced, as shown in Fig. 5, which indicates a large nonlinear saturation. The relative uncertainty in the values is estimated to 10–20%, which is typical of z-scan measurements. We also performed z-scan experiments on Samples 1, 3 and 5, and the real and imaginary parts of the third-order nonlinear susceptibility are calculated and summarized in Table 1. The $|\chi^{(3)}/\alpha|$ value increases steadily from Sample 1 to 5, except for Sample 3, because the value of $\chi^{(3)}$ and α did not increase at the same ratio. There could be an optimal ratio of CNTs/$BaTiO_3$ for better $|\chi^{(3)}/\alpha|$ value. And we can obtain higher $|\chi^{(3)}/\alpha|$ value from the multi-layer structured film than mono-layer structured film.

Theoretical calculations of the third-order nonlinearity are mostly focus on single walled carbon nanotubes (SWCNTs). The $\chi^{(3)}$ value of SWCNTs was calculated theoretically based on the third-harmonic generation theory in [7], which revealed a remarkable enhancement of a $\chi^{(3)}$ as high as 10^{-6} esu under a resonant excitation. While, in the present report, MWCNTs are used in the composite films, and the laser wavelength is off-resonant excitation. It is clear from Table 1 that the composite films have very large nonlinear optical susceptibility, the valve of $|\chi^{(3)}|$ of the films is three orders of magnitude larger than that of the previously reported MWCNTs in suspension [15,16]. The large value of $|\chi^{(3)}|$ was commonly ascribed to the high concentration of CNTs in the film under the off-resonant excitation as reported in [25–27]. However, it is more important to consider that MWCNTs behave like metals, generally accepted, because the π-electrons play an important role in the electronic structure and optical properties of MWCNTs. And the composite thin films of noble metal (Ag and Au) and $BaTiO_3$ have achieved high third-order nonlinear optical properties ($\chi^{(3)}$), which partly ascribed to high dielectric constant and large nonlinear optical effect of $BaTiO_3$ matrix [20,21]. Moreover, Sheng and his co-workers proposed the use of electrorheological method to realize anisotropic grains to enhance the optical nonlinearity [28]. The effects of geometric anisotropy has a pronounced effect on the nonlinearity, which separates the absorption peak from the nonlinearity enhancement peak, so that merit may be increased by orders of magnitude. Therefore, we consider that the metallic behaviour and anisotropic geometry of MWCNTs play an important role for the large third-order nonlinear susceptibility.

4. Conclusion

In summary, we have prepared the composite solid films of MWCNTs and $BaTiO_3$ by physical deposition method. The composite films were characterized using SEM, Raman spectroscopy, and UV–vis absorption. Nonlinear optical properties of the composite films were investigated with z-scan technique. This measurements show the composite films have very large three-order nonlinear optical absorption and refraction, the valve of $|\chi^{(3)}|$ of the films exhibits magnitude of $\sim 10^{-6}$ esu, which is three orders of magnitude larger than those of CNTs suspension. Such composite films could be used to take advantage of the unique properties of CNTs in optic–electronic applications.

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