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Optical properties of carbon nanotubes and $BaTiO_3$ composite thin films*

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Multiwalled carbon nanotubes and $BaTiO_3$ composite films have been prepared by pulsed-laser deposition technique at room temperature and high temperature of 600°C, separately. The structures of the composite films are investigated by using scanning electron microscopy and x-ray diffraction. The optical behaviours of the samples produced at different temperatures are compared with Raman spectroscopy, and UV-visible absorption. And the observation by Z-scan technique reveals that the composite films have a larger optical nonlinearity, and the samples prepared at high temperatures have better transmittance and opposite sign imaginary part of optical third-order nonlinearity.

Keywords: carbon nanotubes, $BaTiO_3$, composite, optical properties
PACC: 4270, 6148, 4265

1. Introduction

Carbon nanotubes (CNTs) have attracted extensive interest because of their unique physical properties and many potential applications. In regard to their optical properties, most of the experimental studies have concentrated on the nonlinear optical properties, the optical limiting properties and the ultrafast optical switching properties.[1−3] Moreover, the use of composite materials could be considered as a route to obtain better performances. For example, the polymer and CNTs composite materials have attracted much interest for their electric and optical properties.[4,5] On the other hand, the thin films containing metal nanoclusters (Au, Ag, etc.) 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 $BaTiO_3$ or TiO_2 have high dielectric constant and large nonlinear optical effect.[6−9] However, studies on composite materials of CNTs and $BaTiO_3$ have been few. The composite CNTs/$BaTiO_3$ materials have been fabricated via the spark plasma sintering technique or blending and hot-moulding technique, and the electrical, rectificative and dielectric properties have been investigated.[10,11] In our previous work, we reported the fabrication of CNTs/$BaTiO_3$ composite films with different quantities of CNTs using pulsed-laser deposition, and the large optical nonlinear properties of composite films prepared at room temperature.[12] Here, we will show the optical properties of CNTs/$BaTiO_3$ composite films prepared at high a temperature of 600°C.

2. Experiment

The composite films were of layered structures, and produced by depositing one layer of CNTs first, then coating one layer of $BaTiO_3$ using the pulsed-laser deposition (PLD) technique. A typical multilayered structure of our samples is shown in the inset of Fig.1 schematically. The raw soot of CNTs was produced by conventional arc discharge. Then, the pristine CNTs were purified by a chemical-wet method and the well-dissolved solutions were attained. The diameter of the purified carbon nanotubes obtained was 10–30 nm with a length of 3–15 μm. The CNTs solution was purified and treated with ultrasonator, then the solution droplet was dropped onto the clean substrate and dried under a tungsten lamp. All the films

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were deposited onto fused quartz substrates of 0.5 mm in thickness with both sides polished. Then, $BaTiO_3$ layer about 30 nm was deposited on the CNTs layer in vacuum (N_2 $\sim 4.0\times10^{-3}$Pa) using PLD technique, and the temperature of substrate was kept at 600°C for Sample A, and room temperature for Sample B during the entire deposition process.

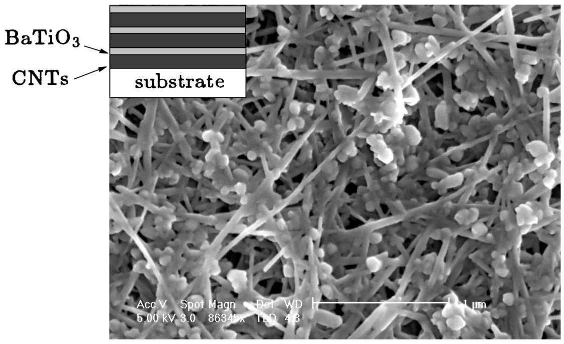

Fig.1. SEM image of CNTs/$BaTiO_3$ composite film.

The surface morphology and thickness of the composite film were investigated by scanning electron microscope (SEM). X-ray diffraction was also used to characterize the composite film. Raman spectra of the samples were recorded at room temperature using Micro-Raman system model T-64000 (Jobin Yvon), with an excitation wavelength of 532 nm. Linear optical extinction measurements of the samples were carried out 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 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 was focused onto the sample by a 120 mm focal length lens.

3. Results and discussion

A typical scanning electron microscopy picture of the composite film is shown in Fig.1. The CNTs mainly overlap randomly on the substrate surface, and maintain their features and structures in the composite films. The $BaTiO_3$ layer is about 30 nm thick, and has a bi-model microstructure: one is coated onto the surface of the CNTs, another is nanoparticles with a diameter of 30–60 nm. The x-ray diffraction (XRD), not shown here, implies that $BaTiO_3$ is amorphous for the composite film prepared at room temperature, but $BaTiO_3$ of the composite film prepared at high temperatures has a crystalline phase.

Figure 2 shows the Raman spectra of the composite films prepared at 600°C (curve a) and room temperature (curve b). The inset shows the Raman spectra ranging from 1300 to 1650 cm^{-1}, two peaks were observed at 1350 and 1578 cm^{-1}, which correspond to disorder-induced phonon mode (D-band) of multiwalled CNTs, and E_{2g}-band of multiwalled CNTs, respectively. Raman spectroscopy of carbon nanotubes in the composite films is similar to those of freestanding carbon nanotubes. The CNTs in composite film, despite the annealing temperature during elaboration of composite, maintain their characteristic structures and properties, which is consistent with the SEM observations. Since CNTs have high chemical stability and smooth wall surface, and have interacted with $BaTiO_3$ slightly, the deposited $BaTiO_3$ did not damage or react with carbon nanotubes. The Raman scattering band at about 311 and 523 cm^{-1} for the sample prepared at 600°C corresponds to the vibration modes of $BaTiO_3$ crystalline phase. The Raman scattering spectrum indicates the $BaTiO_3$ in Sample A has a crystalline phase obviously. But we do not observe the Raman peak of $BaTiO_3$ for Sample B, the Raman scattering band of curve b comes from quartz substrate, indicating that $BaTiO_3$ in Sample B should be amorphous. So, the Raman results are consistent with the result of x-ray diffraction. In addition, Raman spectrum of Sample A has peaks at 140.7 and 190.1 cm^{-1}, which could be attributed to the radial breathing modes of carbon nanotubes.[13] But the freestanding CNTs and Sample B do not show the Raman radial breathing modes.

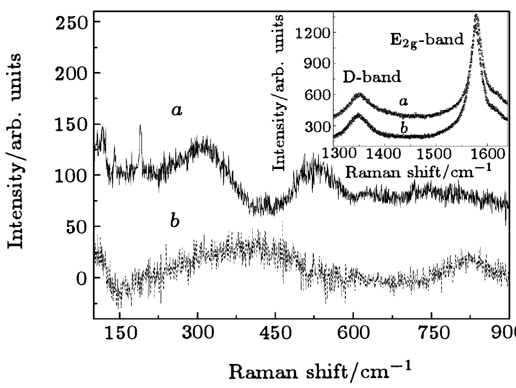

Fig.2. Raman spectrum of CNTs/$BaTiO_3$ composite film prepared at 600°C (a) and room temperature (b).

The optical extinction spectra of the samples as a function of the photon energy are shown in Fig.3.

Besides the composite films of Samples A and B, the absorption spectrum of pure CNTs film and $BaTiO_3$ film are also shown together for comparison. The extinction spectra of the composite films are similar to the results reported for CNTs in visible range;[14] light extinction properties of the samples mainly come from the CNTs because of the transparency of $BaTiO_3$. In the ultraviolet light range, the absorption peak of the composite film should be mainly attributed to $BaTiO_3$ layers. The results indicate a major characteristic feature of the CWNTs/$BaTiO_3$ composite film. The absorption intensity of Sample A is obviously smaller than that of Sample B. This means that the composite film prepared at high temperature has a better transmittance. The absorption spectrum of Sample A seems to be the combination of those of CNTs and $BaTiO_3$. High temperature treatment and crystallized $BaTiO_3$ may be beneficial for light transparency. The high absorption of Sample B possibly is attributed to the amorphous disorder of $BaTiO_3$ and a large number of interspaces among CNTs, which could scatter photons largely.

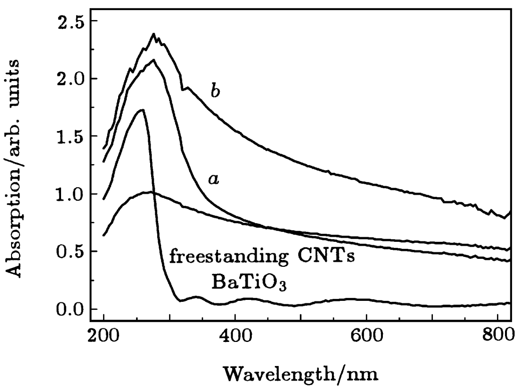

Fig.3. UV–vis extinction spectra of CNTs/$BaTiO_3$ composite film prepared at 600°C (a) and room temperature (b), $BaTiO_3$ thin film, and pure CNTs film with the same thickness.

The imaginary part of $\chi^{(3)}$ for the composite film was examined using the Z-scan technique. Normalized transmittance for open-aperture (OA) Z-scan profiles as a function of the sample position Z is shown in Fig.4 for the composite film prepared at high temperatures. Since fused quartz substrate has very small optical nonlinear response at wavelength of 532 nm, the high nonlinear optical properties observed here are attributed to the CNTs/$BaTiO_3$ composite film. The thickness of the composite film measured using SEM is about 500 nm. After calculation, the third-order imaginary parts of $\chi^{(3)}$ have a value about 1.5×10^{-7}esu, which means that CNTs/$BaTiO_3$ composite films also have large nonlinear optical properties.

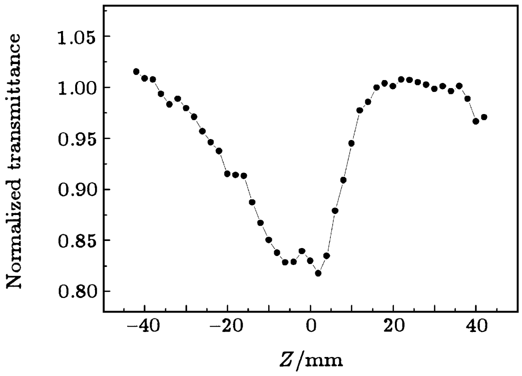

Fig.4. Z-scan normalized transmittance of CNTs/$BaTiO_3$ composite film prepared at 600°C with open aperture.

Another important result about the optical nonlinearity is the different sign of the imaginary parts between composite films prepared at room temperature and at a high temperature of 600°C. The normalized transmittance shows valley for open-aperture Z-scan profiles, as compared with our previous work,[12] in which the open-aperture profiles showed a peak and the imaginary part took a negative value. But the CNTs/$BaTiO_3$ composite prepared at high temperature has a positive imaginary part. We consider that CNTs/$BaTiO_3$ composite materials prepared at room temperature are similar to the relevant experimental investigations of CNTs,[15,16] in which the films containing freestanding CNTs were investigated and a negative imaginary part was obtained. They suggested that there should have few interactions between CNTs and $BaTiO_3$ when composite films were prepared at room temperature. However, XRD and absorption spectrum show some different behaviours when composite films prepared at high temperature. Especially, Raman spectrum of Sample A shows that annealing treatment of the composite films influences both CNTs and $BaTiO_3$. Likely, the microstructure of the composite film prepared at high temperature has a fundamental change, which induces the more contact and interaction between CNTs and $BaTiO_3$ grains just like the behaviour of CNT suspensions or solid nanocomposites.[17,18] The nonlinear absorption mechanism could be the governing principle. So, nonlinear optical transmission is strongly dependent on the microstructure of composite films. This means that we can control the value and sign of imaginary part simply by the amount of CNTs and annealing temperature.

4. Summary

In summary, CNTs/$BaTiO_3$ composite films were prepared by pulsed-laser deposition technique. XRD, Raman and absorption results show that the composite films prepared at a high temperature of 600°C showed different behaviours as compared with the samples prepared at room temperature. The composite films produced at high temperature have crystalline phase $BaTiO_3$, better transmittance, and show large optical third-order nonlinearity. Moreover, the different sign of the imaginary part of the nonlinearity has been discussed.

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