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Carbon Nanotubes in Composite Polymer Guided Wave Mode Device for Ultrafast Molecular Photonics

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Single walled carbon nanotubes (SWNT) show excellent optical and electric properties. Ultrafast optical responses of SWNT were studied by femtosecond laser excitation in solutions and thin films. Such properties can be used for all optical data processing with our composite polymer guided wave mode geometry based on transient change of refractive index or extinction coefficient.

Keywords: guided wave mode; polymer thin film; single walled carbon nanotubes; ultrafast optical responses

INTRODUCTION

There have been studies for ultrafast optical processing devices by using organic materials in the visible and near infrared (NIR) regions [l–6]. We have been studying ultrafast optical responses of organic materials, such as ion pair charge transfer complexes, extended porphyrins and phthalocyanines [4–12]. Carbon nanotubes have also attracted much attention as one of the most promising materials for electrical and optical applications. SWNT showed ultrafast absorption changes in the, optical telecommunication wavelength region upon femtosecond laser excitation [13–16]. Carbon nanotubes, however, have weak points for optical application due to their strong interactions which causes low homogeneity in a thin film state. To make thin

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films with well-dispersed SWNTs, polymer wrapping was employed in the present experiments. Well-dispersion of SWNTs by polymer wrapping was reported by Shigeta *et al*. using aromatic polyimide with sulfonate groups [17]. They showed a large amount of SWNTs were solubilized in organic solution. Using this SWNT/polymer solution, thin films were prepared for measurement of ultrafast optical responses in solutions and in thin films. We also report the comparison of transmission type and reflection type measurements with a low-refractive index polymer to form the guided wave mode (GWM) thin film by 800 nm excitation.

EXPERIMENTS

Preparation of Sample Thin Films

We prepared good quality thin films by spin-coating and casting of polyimide-wrapped SWNT from dimethylsulfoxide (DMSO) solutions [17]. The GWM device was consisted of a 60° prism, BK7 glass substrate, Cytop® cladding layer (Asahi Glass Co. Ltd., Japan), and SWNT/polyimide layer. Figure 1 shows the chemical structures of Cytop® which is a low refractive index polymer for the cladding layer and the aromatic polyimide containing sulfonate groups.

Measurements of Absorption Spectra, Refractive Index and the Simulation of GWM

Absorption spectra of SWNT/polyimide thin film were observed by a Hitachi U-4100 spectrophotometer. The thickness of thin films was measured by a laser microscope (KEYENCE, VK-7810). The refractive index of aromatic polyimide was measured by a prism coupler (METRICON, Model 2010); $n = 1.6074$ at 632.8 nm and $n = 1.5569$ at 1320 nm. All measurements were performed at room temperature.

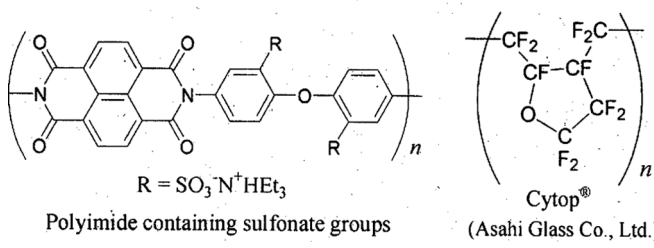

FIGURE 1 Structure of Cytop® and aromatic polyimide.

Reflectance and characteristics of complex thin films were calculated by a transfer matrix method with several factors, such as the thickness of two polymer layers, the refractive index, the extinction coefficient, the wavelength and incident angles of light source [18].

Femtosecond Laser Photolysis

Femtosecond laser photolysis system was reported in details previously [4,11]. A femtosecond time-resolved transient absorption spectrometer was consisted of an optical detection system (Dual MOS PMA 50 and InGaAs PMA 11), a pulse stretcher & compressor, a Ti:sapphire regenerative amplifier which was pumped by a Q-switched Nd:YAG laser (Quanta Ray) and a mode-locked femtosecond Ti:sapphire laser (Spectra-Physics, TSUNAMI). An amplified Ti:sapphire laser has 3 mJ/pulse at 800 nm at a repetition rate of 10 Hz. A 800 nm pulse from the amplified Ti:sapphire laser shows about 250 fs of a full width at half maximum. Pump-probe measurement was performed by fs laser excitation with an optical delay stage of 30 fs/step resolution. Probe beams were detected by a dual photodiode array system and two photodiode array systems in the visible and in the NIR regions (Hamamatsu Photonics, C6140-PMA50 and C8147-PMA11), respectively. The power of a pump beam was set at 210 μJ/pulse.

RESULTS AND DISCUSSION

Two types of films containing polyimide-wrapped SWNTs were prepared as shown in Figure 2. A cast film is for a simple reflection or

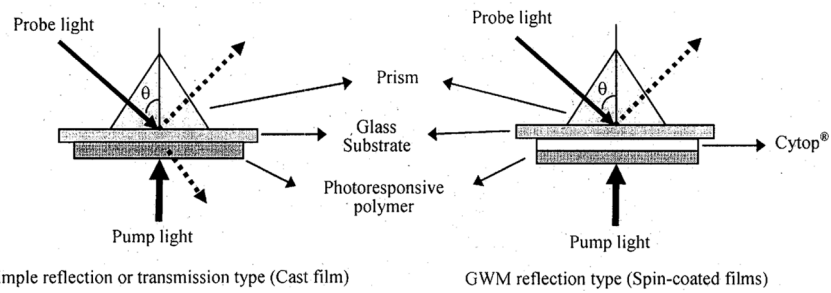

FIGURE 2 Schematic representation of two measurement system (Thickness of films: 1.5 μm for cast film, 0.42 μm for Cytop® layer, 0.8 μm for spin-coated layer, θ: incident-angle).

transmission type experiments. A GWM thin film, consisted of a glass substrate, Cytop® as a low refractive index material ($n = 1.3335$ at 1550 nm), and SWNT/polyimide layer, is for a GWM reflection type measurement. Details of GWM thin films were designed based on simulations. A 7 wt% Cytop® solution was spin-coated on a glass substrate and SWNT/polyimide was covered on the Cytop® layer by subsequent spin coating. A 1 wt% polyimide in DMSO solution containing 1 wt% SWNT was used to make cast films for transmission type measurement. A 5 wt% polyimide in DMSO solution containing 1.5 wt% SWNT was spin-coated for simple reflection type measurement. A prism was attached on the opposite side of glass substrate with a matching oil.

Figure 3 shows the absorption spectra of two sample films. Two broad absorption bands were observed in this region. They were attributed to the optical transitions from the valence to the conduction bands in semiconductive SWNTs. In the case of the cast film, its absorbance was high enough to be measured by a simple transmission type experiment. First, the 1.5 μm thick cast film was excited by 800 nm femtosecond laser to study their excited behaviors. In Figure 4, the transient bleaching reflection spectrum of SWNT cast film upon 800 nm fs laser excitation with 210 μJ/pulse was compared with the reversed steady state absorption spectrum. Transient bleaching observed at 600 to 800 nm for the visible region and at 1100 to 1600 nm for the NIR region almost corresponded with two broad bands in the absorption spectrum

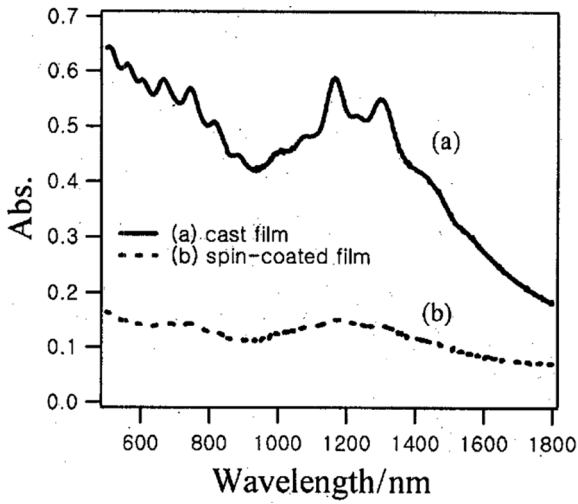

FIGURE 3 Absorption spectra of sample films ; (a) cast film (Abs. = 0.5 at 800 nm), (b) spin-coated film (Abs. = 0.13 at 800 nm).

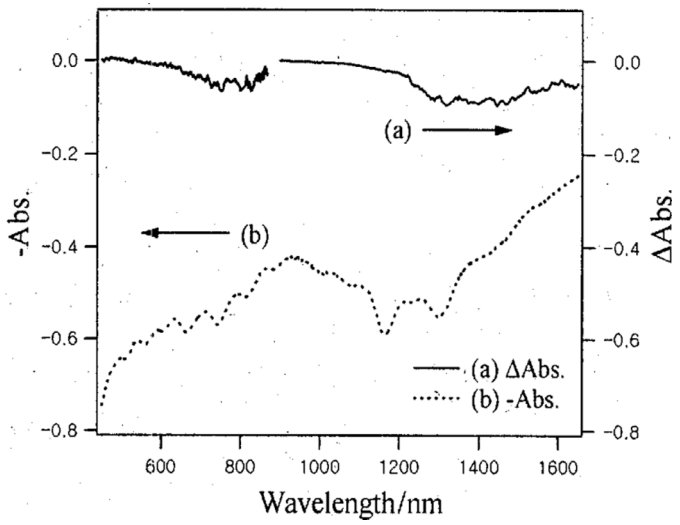

FIGURE 4 Comparison of reflection spectral change (a) after excitation by 800 nm femtosecond laser and (b) reversed steady state absorption spectrum.

at the ground state as previously reported for transient transmission [19]. The transient bleaching is due to transient decrease of the ground state by the formation of first excited state or any higher energy states. From femtosecond laser photolysis results, the ultrafast transient bleaching was estimated to be about 10% of the ground state absorption upon excitation with 210 μJ/pulse pump beam. The recovery dynamics at 750 nm was single exponential with a time constant of less than 1 ps. At 1200 nm, the time constants were evaluated to be 1.8 ps and less than 1 ps by a double exponential equation.

It means that the photo-excited electrons turn back to the ground state in such a short time by considerable non-equilibrium electron distribution in the valence band caused by hot electrons as reported by several authors [14,20–22] upon 534 ~ 1900 nm excitation.

The reflectance behavior of the GWM sample upon excitation was first calculated with parameters of refractive index (n) and extinction coefficient (k) obtained from ground state and transient absorption spectra. The calculated incident angle dependence of reflectance is shown in Figure 5A at 1200 nm for a 700 nm thick photoresponsive polymer with complex refractive index of, $n = 1.564 + ki$, on 600 nm thick Cytop® film at p-polarization. The minimum reflectance at the GWM was plotted as a function of the k-value from 0.0001 to 0.03 in Figure 5B. Figure 5B shows that about 10% decrease of k-value by

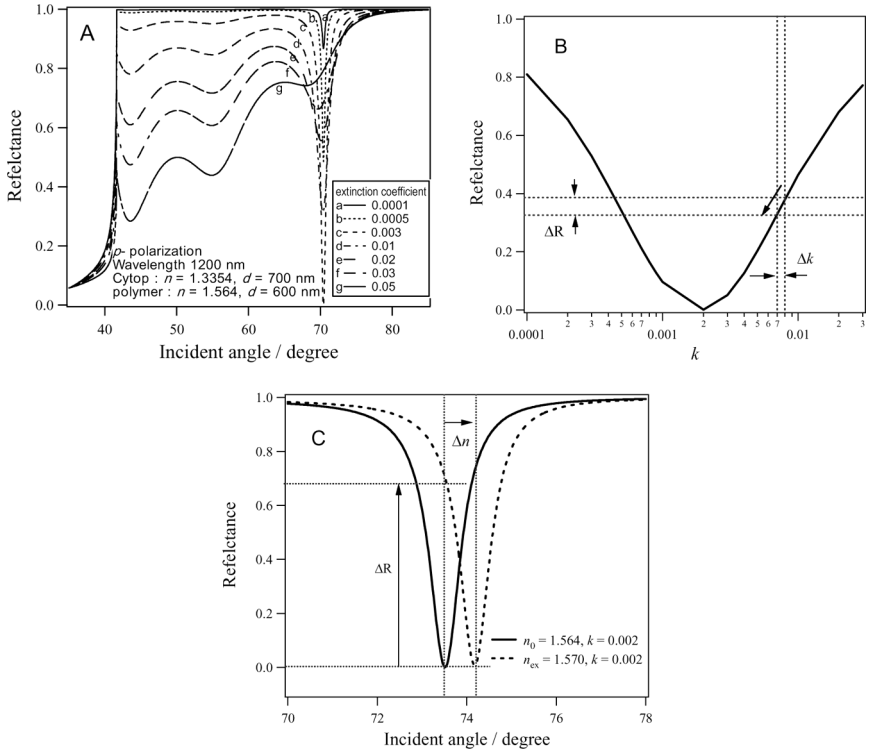

FIGURE 5 A: Calculated incident angle dependence of the reflectance, B: Extinction coefficient dependence of the minimum reflectance at the GWM; $\triangle$R is the change of reflectance due to $\triangle$k, C: Incident angle dependences of the reflectance for $\triangle$R is due to the change of refractive index, $\triangle n$.

laser excitation as mentioned above causes 16% change of reflectance in the GWM geometry. The change of refractive index ($\triangle n$) is also expected from absorption changes upon laser excitation depending on the wavelength due to the Kramers-Kronig relationship. Such changes can also be used for sensitive change of reflectance as shown in Figure 5C which predicts more than 700 fold reflectance change by 0.4% change of the n-value from 1.564 to 1.570. Highly sensitive ultra-fast optical responses by using these two methods with the GWM geometry upon laser excitation are under progress.

CONCLUSION

Promising results for information processing technology were obtained by femtosecond laser excitation of polymer-wrapped SWNT thin films

showing ultrafast time recovery and laser durability. Composite polymer GWM with SWNT thin film on Cytop layer is expected to become a key device for such purposes.

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