Ultrafast Optical Responsive SWNT/Polymer Thin Films in Guided Wave Mode Geometry

Jang-Hyun Ryu, Toshihiko Nagamura, Masahiro Shigeta, Naotoshi Nakashima*

Summary: Single walled carbon nanotubes (SWNT) having good optical and electrochemical properties were solublized by aromatic polymers. The polymer-wrapped SWNT film cast from solution showed transient bleaching with a time constant of recovery less than 1 ps in both the visible and optical telecommunication wavelength region. Polymer thin film containing SWNT was assembled into the guided wave mode geometry with a low refractive index polymer.

Keywords: femtosecond laser; guided wave mode; optical responses; polymer-wrapped carbon nanotubes; thin films

Introduction

Recently there have been increasing demands for much faster speed and larger capacity in the information processing technology. New materials and devices are needed for such optical data processing.[1] Many studies have been reported for ultrafast optical processing devices by using organic materials in the visible and near infrared (IR) region.[2–8] We demonstrated ultrafast or persistent optical property changes in the near IR region by ion pair charge transfer complexes, phthalocyanines and photochromic compounds.[9–14]

Single walled carbon nanotubes (SWNT) which have good optical and electrochemical properties are expected for the optical applications. It shows ultrafast absorption changes in the optical telecommunication wavelength region by femtosecond fs laser excitation.[4–8]

A problem of carbon nanotubes for the case in thin film state is that fully reproducible optical properties are not so easy to obtain. This problem results from inhomogeneity of thin film affected by the strong interaction between aromatic carbon atoms.[15]

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There are many studies for SWNT in the field of the ultrafast optical responses. Chen *et al*. have reported that SWNT showed not only less than 1 ps optical responses but also the third-order nonlinear polarizability.[4] Ichida *et al*. have made a detailed investigation on the relation between the electron-hole coupling constant and a diameter of SWNT. They said that the relaxation time by electron-hole recombination was affected by a diameter and a chirality of SWNT.[5] Tatsuura *et al.* reported SWNT thin film which was spray-coated had ultrafast optical relaxation in the near IR region to fabricate an all-optical data processing device based on ultrafast transient bleaching and recovery.[6]

We achieved all optical spatial light modulation by the guided wave mode (GWM) geometry for ultrafast information processing.[1,9–12] With such devices, we can control reflected light by changes of imaginary and/or real parts of complex refractive index caused by photoexcitation of dyes. Change of reflectance in this geometry, which is sensitive to subtle absorption or refractive index changes, will give increased sensitivity for all-optical data processing as compared with simple transmittance type devices.[12]

Aromatic compounds and polymers have been added to control carbon-carbon interactions and to make homogeneous dispersion

of SWNT.[16] In this study, well-dispersed SWNT/aromatic polymer was assembled with a low-refractive index polymer to form the GWM thin film and was excited at 800 nm by femtosecond laser to observe a transient reflectance change.

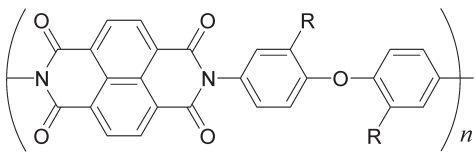
Materials and Experimental Methods

To make more homogenous thin film, polymer wrapped SWNT was employed in this experiment. According to Shigeta *et al.*, who have proved that totally aromatic polyimides with sulfonate groups are highly capable of solubilizing a large amount of SWNT in some organic solutions,[16] we prepared good quality thin films by spin-coating and casting of polyimide-wrapped SWNT in dimethylsulfoxide (DMSO). The GWM device was consisted of glass substrate, cladding layer (Cytop®, Asahi Glass Co., Ltd., Japan), SWNT/polyimide layer and a 60° prism. The chemical structures of the polyimide containing sulfonate and Cytop® are shown in Fig. 1.

The thickness of thin films was measured by a laser microscope. The refractive index of the polyimide ($n = 1.6074$ at 632.8 nm, $n = 1.5569$ at 1320 nm) was measured by a prism coupler (METRICON, Model 2010). The absorption spectra of films containing SWNT were recorded at room temperature on a Hitachi U-4100 spectrophotometer. The reflection behavior was calculated by a transfer matrix method with several parameters, such as thickness of layers, refractive index, wavelength, incident angle of light source and extinction coefficient.

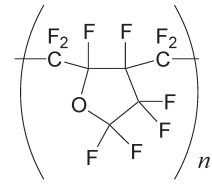
Femtosecond (fs) laser photolysis system was reported in details previously.[8,14,17] Figure 2 shows a simple diagram of the fs laser photolysis system. A fs time-resolved transient absorption spectrometer was consisted of an optical detection system (dual Si-photodiode array for the visible and InGaAs array for the near IR region), 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 fs Ti:sapphire laser (Spectra-Physics, TSUNAMI). An amplified Ti:sapphire laser has 3 mJ/pulse at 800 nm and the repetition is 10 Hz. 800 nm pulse from the amplified Ti:sapphire laser shows about 250 fs of a full width at half maximum.

For 800 nm excitation, output from Ti:sapphire regenerative amplifier was divided by a 800 nm beam splitter. Then the residual 800 nm light was focused into a 10 mm cell filled with D_2O:H_2O (2:1) mixture for visible range measurements and CCl_4 for near IR range measurements to obtain a fs white probe light. The pump and probe beams were focused on a sample film to about 1 mm diameter. The power of pump beam was adjusted by using a variable neutral-density (ND) filter to avoid damage of samples. Laser excitation was performed by pump-probe measurement with 30 fs/step time resolution of an optical delay stage. Additionally, probe beams were detected by Hamamatsu Photonics, C6140-PMA50 and C8147-PMA11 through optical fibers. Probe light was accumulated



R = $SO_3^-N^+HEt_3$

Polyimide containing sulfonate groups



Cytop®
(Asahi Glass Co., Ltd)

Figure 1.
The chemical structures of polyimide and Cytop®.

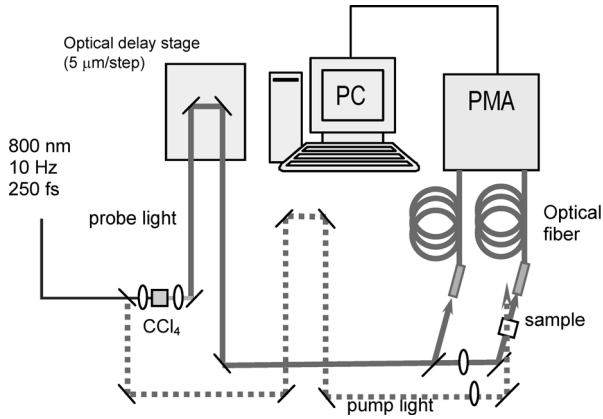


Figure 2.
The block diagram of fs laser photolysis system (detector: Hamamatsu Photonics, PMA).

for 24 times for PMA50 and 36 times for PMA11 in this experiment. Pump beam was set at about 200 μJ/pulse.

Results and Discussion

Two types of films containing polyimide-wrapped SWNT were prepared as shown in Fig. 3. A cast film is for a simple transmission type. 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 reflection type measurement. The cladding layer, Cytop® was spin-coated on the substrate and SWNT/polyimide was covered on the Cytop® layer by subsequent spin coating. Sample solution used 1 wt% of polyimide/DMSO solution containing 1 wt% of SWNT was applied for transmission type of cast film. And 5 wt% of polyimide/DMSO solution containing 0.5 wt% of SWNT was applied for reflection type of spin-coated film. Then a prism was attached on the opposite side of glass substrate with a matching oil.

Figure 4 shows the absorption spectra of two sample films. Two broad absorption bands were observed. They are attributed to the optical transitions from the valence

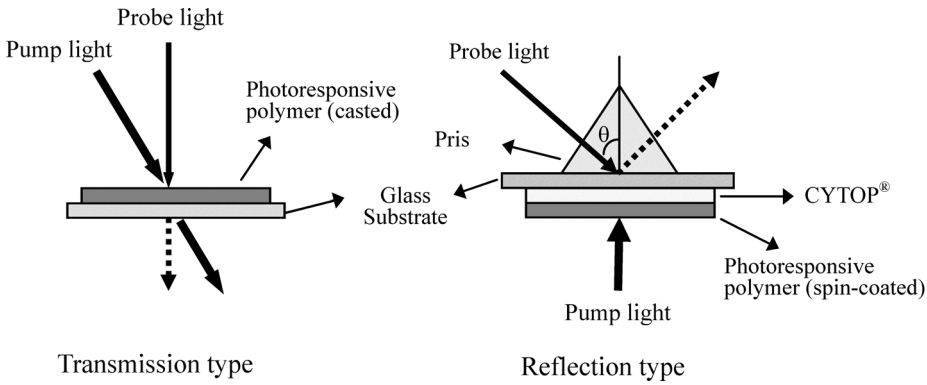


Figure 3.
Schematic representation of two measurement systems (Thickness of films : 1.5 μm for casted layer, 0.42 μm for Cytop® layer, 0.8 μm for spin-coated layer, θ : incident angle).

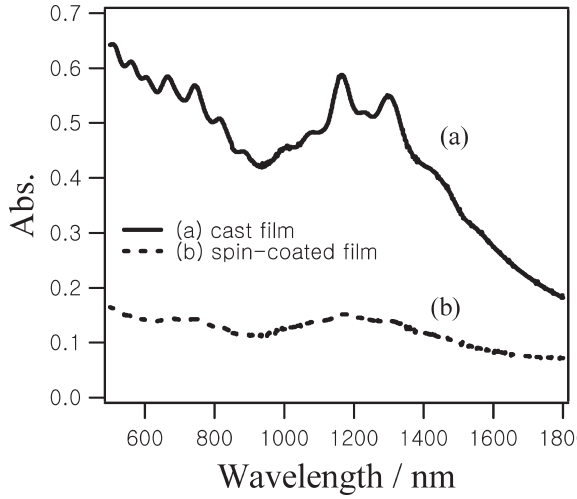


Figure 4.
Absorption spectra of sample films ; (a) cast film (Abs. = 0.5 at 800 nm), (b) spin-coated film (Abs. = 0.13 at 800 nm).

to the conduction bands in semiconductive SWNT. In the case of cast film, its absorbance was set higher than that of a guided wave mode thin film to be measured by a simple transmission type.

First, the 1.5 μm thick cast film was excited by 800 nm femtosecond laser to study their excited behaviors. The transient spectra are generally composed of two phenomena. One is transient bleaching, and another is transient absorption. The transient bleaching is due to transient decrease of the ground state by the formation of excited states or any higher energy states. In the mean time, transient absorption is caused by transition from the excited state to higher states. In this study, transient bleaching was observed.

Figure 5 shows the results of time-resolved transient bleaching spectra of SWNT cast film in the visible and near IR region upon 800 nm fs laser excitation. Transient bleaching was observed where two broad bands appeared in steady state absorption spectra from 600 to 800 nm for the visible region and from 1100 to over 1300 nm for the near IR region. Time profiles are plotted in Figure 6 at 750 nm and 1200 nm, where transient bleaching was observed. Time profiles were analyzed by following double exponential equation (1), slow (τ_1) and fast components (τ_2);

$$\Delta A(t) = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

In the case of visible range, the recovery was analyzed by a single exponential equation. Their time constants of bleaching recovery were less than 1 ps order at both visible and near IR regions. This means that the photo-excited electrons turn back to the ground state in such a short time.

The ultrafast relaxation time is well known for considerable non-equilibrium electron distribution in a valence band due to hot electrons. Tatsuura *et al.* reported that non-equilibrium electron distribution due to hot electrons with 1350 nm excitation gives transient absorption changes.[6,18] After SWNTs which have the same band-gap as the excitation photon energy are excited, Fermi levels of excited SWNTs are lowered and SWNTs becomes photoconductive transiently. The transient bleaching of absorption is affected by holes generated due to excited electrons transferring momentarily to the other SWNTs. At that time, generated holes which have a low

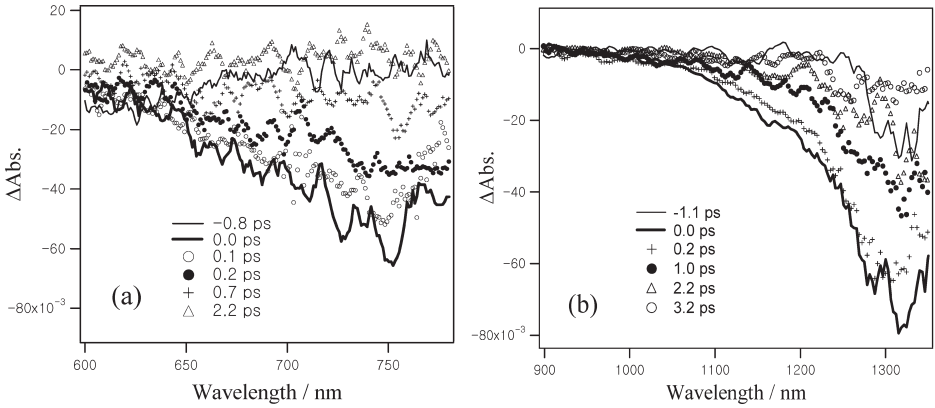


Figure 5.
Transient bleaching spectra of SWNT/polyimide cast film in the visible (a) and near IR region (b) by 800 nm fs laser excitation by transmission measurement.

charge transfer capacity are left. After then the interaction between SWNTs helps the returning of the excited electron. When the excited electrons move back again to the initial state, the temperature of the electrons rises in the valence band. These hot electrons bring about the non-equilibrium electron distribution.[6,18–20]

These ultrafast optical responses showed about 10 % transient bleaching of the ground state absorption upon excitation with 230 μJ/pulse pump beam as shown in Fig. 7. Reflection type measurement was then performed with the GWM thin film composed of low refractive index polymer, Cytop® for cladding layer. The reflectance behavior of the GWM sample upon light excitation was first calculated with parameters obtained from transmission experiment.

The calculated incident angle dependence of reflectance is shown in Fig. 8(a) at 1200 nm for the 800 nm thick photoresponsive polymer with complex refractive index,

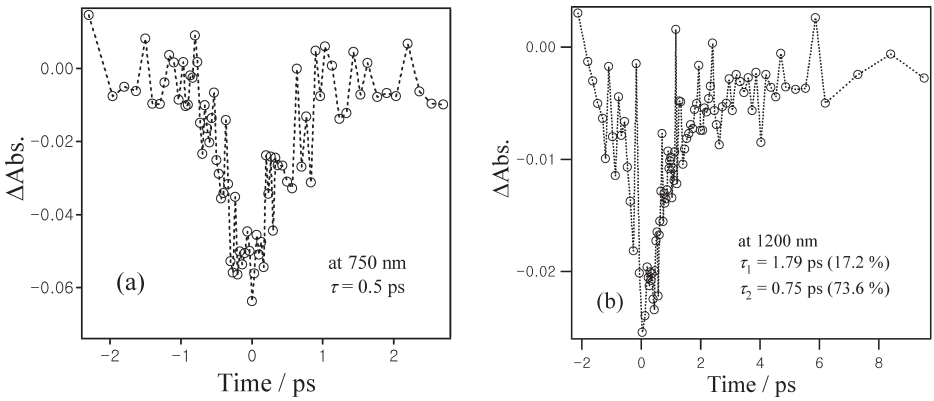


Figure 6.
Time profiles of bleaching recovery at 750 nm (a) and 1200 nm (b), respectively; (a): 230 μJ/pulse of pump beam, (b): 220 μJ/pulse of pump beam.

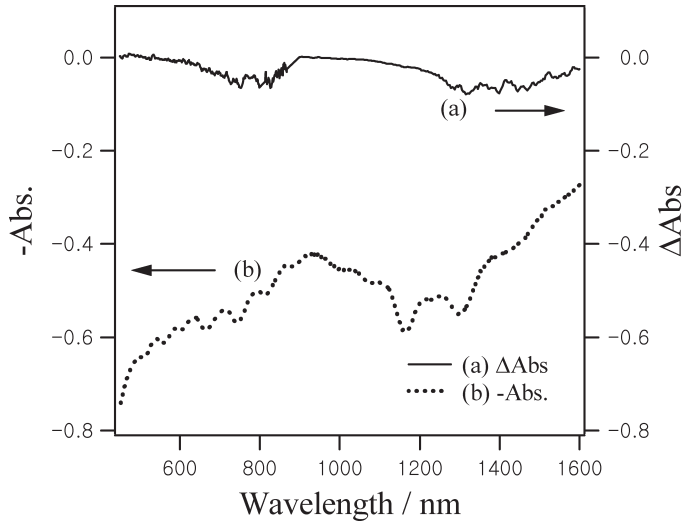


Figure 7.
Comparison of absorption spectra before and after excitation by 800 nm femtosecond laser (a: transient bleaching spectrum, b: reversed steady state absorption spectrum).

$n = 1.564 + ki$, on 420 nm thick Cytop® film with *p*-polarization. The *k*-value, extinction coefficient, was increased from 0.0001 to 0.1.

If there is no absorption in the photoresponsive layer, very high reflectance due to total reflection is observed at entire incident angle range. According to this simulation, a dip of reflectance appeared at 73.64° of incident angle with a critical *k*-value ($k_c = 0.003$). The reflectance first decreases to almost zero at the critical *k*-value, then increased again as shown in Fig. 8(b). In the reflection type measurement, if there is transient change of *k*-value upon excitation, reflectance should show transient changes according to Fig. 8(b). Much larger change in reflectance can be expected by the guided wave mode as composed with simple transmission,

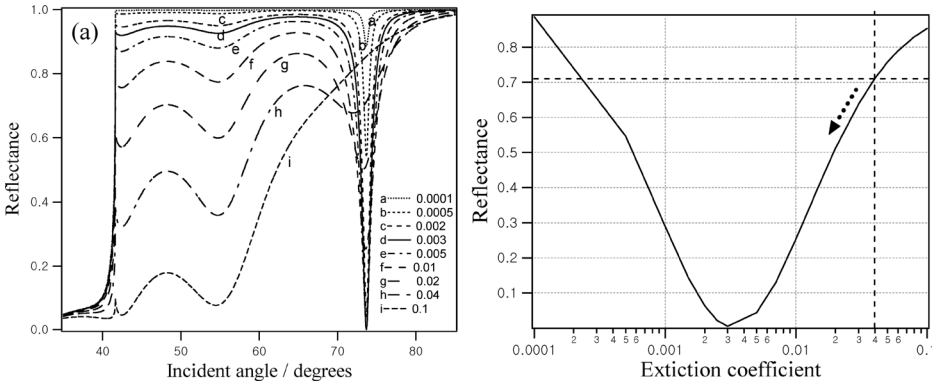


Figure 8.
The calculated incident angle dependence of reflectance at 1200 nm; photoresponsive layer 800 nm thick with complex refractive index, $n = 1.564 + ki$, on Cytop film ($n = 1.3354$) 420 nm thick and a BK7 substrate ($n = 1.505$).

because the GWM is based on a kind of resonance. The k-value of actual sample film at 1200 nm was calculated to be 0.04 by following equation, (2);

$$k = \frac{2.303 \times A \times \lambda}{4\pi d} \quad (2)$$

Where A is absorbance of the film with thickness, d, at the wavelength, λ.

Then reflection spectra of sample thin films were observed by fs white probe beam in the near IR region as shown in Fig. 9 using a glass slide as a reference. A polarizer was set in front of a detector to use the p-polarized incident beam. Broad decrease of reflectance was detected at around 1200 nm. The wavelength of minimum reflectance shifted to a longer wavelength side with decreasing incident angles. Since fs IR probe beam was used, the spectral profile is broadened by the uncertainty principle. The roughness of actual thin film also make the observed dips broader than those simulated.

According to these results, the sample film attached prism was set at specific incident angle around $66 \sim 76^\circ$. The ultrafast optical response of polyimide wrapped SWNT thin film in the GWM geometry upon fs laser excitation to observe transient reflectance spectra is under way.

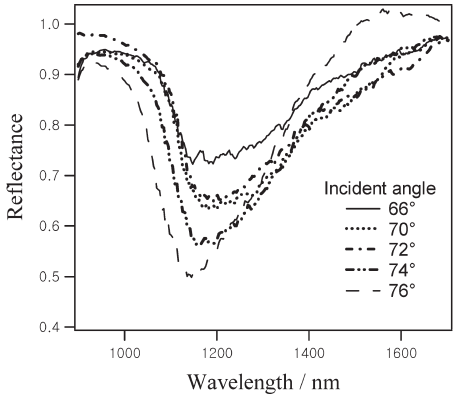


Figure 9.
Observed relative reflectance of SWNT/polyimide on Cytop® thin film by fs white probe beam at the near IR region with various incident angles.

Conclusion

To find new organic ultrafast photoresponsive materials for the information processing, polymer-wrapped SWNTs thin films, which was prepared from solution state with greatly improved homogeneity, were measured by fs laser. Transient bleaching spectra were observed by fs laser excitation. Durability of SWNT against repeated fs laser excitation was confirmed. It was durable against high power laser irradiation over 200 μJ/pulse. Polyimide-wrapped SWNTs thin film showed the ultrafast recovery in the near IR region caused by interband relaxation. The reflectance dip of fs white light in the near IR region depending on the incident angle was observed by composite thin films consisted of SWNT/polyimide as a photoresponsive layer and Cytop as a cladding layer which was due to the GWM formation. A possibility of new way of highly sensitive ultrafast all-optical data processing was demonstrated in the telecommunication region. Detailed studies for ultrafast reflectance control with optimized condition of sample thin films are in progress. This is due to the GWM formation which will give.

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