Carbon Nanotube-Poly(vinylalcohol) Nanocomposite Film Devices: Applications for Femtosecond Fiber Laser Mode Lockers and Optical Amplifier Noise Suppressors

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Carbon Nanotube-Poly(vinylalcohol) Nanocomposite Film Devices: Applications for Femtosecond Fiber Laser Mode Lockers and Optical Amplifier Noise Suppressors

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We fabricated single-wall carbon nanotube (SWNT)/poly(vinylalcohol) (PVA) nanocomposite freestanding films and examined their application in devices in which the saturable absorption of SWNTs at near-infrared optical telecommunication wavelengths can be utilized. In a passively mode-locked fiber laser, we integrated a 30-μm-thick SWNT/PVA film into a fiber connection adaptor with the film sandwiched by a pair of fiber ferrules. A ring fiber laser with a SWNT/PVA saturable absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed. In examining noise suppression for optical amplifiers, mixed light of semiconductor absorber was operated very easily in the mode-locked short-pulse mode with a pulse width of about 500 fs. Reproducible stable device performance was confirmed.

KEYWORDS: carbon nanotube, single wall, saturable absorber, poly(vinylalcohol), nanocomposite, femtosecond fiber laser, mode lock, noise suppression, optical amplifier, amplified spontaneous emission

1. Introduction

Nonlinear optical functions of carbon nanotubes are of increasing interest1–9 because the unique electronic structures of carbon nanotubes, due to their tubelike structure, provide a characteristic nonlinear optical response. Among the various nonlinear optical functions investigated thus far, saturable absorption of single-wall carbon nanotubes (SWNTs) in the near-infrared optical telecommunication wavelength region around 1.55 μm7–9 is a particularly promising function, because various attractive applications, such as all-optical switching devices,7,9–11 saturable absorption mirrors9 usable for mode-locking lasers, pulse reshaping devices for ultrafast communication,10 and amplified stimulated emission (ASE) noise suppression filters for optical amplifiers12,13 have been proposed.

Saturable absorption is a function in which the absorption coefficient of a material decreases when the material is illuminated with intense light. This function is induced through a process in which the primary strong excitation causes the filling of excited states, and the absorption coefficient for the subsequent light is reduced during the period in which the primary excited states remain. For this process to occur efficiently, the material must have a large absorption cross section at the excitation wavelength. The existence of a strong S1 absorption band located in the near-infrared region in semiconductor SWNTs satisfies this need, and therefore is the essential advantage of this material. In addition, the saturation recovery time is very fast, less than 1 ps.7,9,16–19 This fast recovery time is promising for such applications as all-optical switches, pulse reshaping and mode lockers. In particular, since the first success of ~1 ps mode-locking pulse generation,20 mode-locked Er-doped fiber lasers using SWNT saturable absorber thin films have expanded various laser configurations,21,22 proving an excellent mode-locker properties of SWNTs comparable to or better than those of the semiconductor saturable absorbers that have been widely used for passively mode-locked fiber lasers.

The samples or devices used in previous investigations of SWNT saturable absorbers have been usually made by depositing SWNT films onto flat glass substrates8,9,18,21 or onto the ends of optical fibers.21 These deposited SWNT films are usually composed of bundled and entangled SWNTs (due to the strong van der Waals attractive forces between individual SWNTs) with sizes comparable to optical wavelengths. Therefore, these bundled and entangled SWNTs may cause considerable scattering loss. In the Er-doped fiber laser application,20–22 the scattering loss is not a crucial disadvantage because the high gain of the laser medium can overcome the scattering loss and enables mode-locking. However, for other important applications, scattering loss of the deposited SWNT film could be a severe disadvantage. Moreover, the direct deposition of SWNTs onto substrates greatly limits the variety of device structures that can be fabricated. In particular, the waveguide structure—one of the most promising device structures—cannot be fabricated by the direct deposition of SWNTs. A promising alternative form of material is a SWNT-polymer nanocomposite in which SWNTs with sizes smaller than optical wavelengths are uniformly dispersed in a transparent polymer matrix. In this form, scattering loss is expected to be considerably reduced and a variety of device structures—from a freestanding film to a waveguide—can be fabricated by various polymer processing technologies. We also point out a possible advantage of “nonlinear refractive index control” using these types of materials. By controlling the SWNT doping concentration, we can tune the nonlinear refractive index and therefore design advanced device structures using the controlled nonlinear interference of a propagating light wave.

From the above-mentioned description, the significance of optical materials made of SWNT-polymer nanocomposites is clear. However, although extensive investigations have been carried out on nanotube-polymer composites,23 only a few investigations have been carried out on optical appli-
cations, particularly those involving saturable absorption. Recently, Chen et al. fabricated a freestanding SWNT-polymide composite film with a thickness of 20 μm and observed ultrafast saturable absorption recovery at 1.55 μm.1) Our group fabricated a freestanding SWNT-poly(vinylalcohol) (PVA) nanocomposite film saturable absorber.2,3 In this film, a major area was made of a nanoscale SWNT/PVA mixture, as deduced from the fact that optical microscope observation of the area resulted in nominal recognition of SWNT bundles, but microscopic Raman observation established the existence of SWNTs in the area. The formation of this SWNT/PVA nanocomposite was achieved in two steps: (1) bundled SWNTs were strongly ultrasonicated with surfactant in water to unbundle the aggregated SWNTs,2,3 and (2) water-soluble PVA was dissolved into the SWNT solution and the mixture was gradually dried. The optical quality of our SWNT/PVA film saturable absorbers seems adequate and promising for some device applications. Therefore, in this study, we examined two applications—mode-locker and ASE noise suppressor—of the SWNT/PVA films. First, we describe how to prepare the SWNT/PVA films and microscopic structure of these films. Second, we demonstrate that the use of the SWNT/PVA film enables extremely easy construction of a passively mode-locked femtosecond fiber laser. Finally, we demonstrate that the SWNT/PVA film has the ability to suppress ASE noise.

2. SWNT/PVA Nanocomposite Film Preparation

To achieve efficient saturable absorption, we have proved that the peak wavelength of the SWNT absorption spectrum should coincide with the wavelength to be used.3) Because the wavelength of the absorption peak of SWNTs is controllable as a function of tube diameter,4,5 SWNTs were carefully prepared by the laser ablation method6,7 so as to have a mean diameter of 1.2 nm, which corresponds to a peak wavelength of about 1.55 μm. After purification, several milligrams of SWNTs were dispersed in 50 ml of 0.1% sodium dodecyl sulfate (SDS) aqueous solution2,3 or sodium dodecylbenzene sulfonate (NaDDBS) aqueous solution2,3 under strong ultrasonication (typical conditions, 28 kHz, 100 W and 1 h), and the aqueous solution was passed through a paper filter or a glass fiber filter (Advantec GC50, retaining diameter 0.5 μm) to remove large undispersed SWNT bundles. To this solution, several grams of PVA powder (Wako Pure Chemical Industry, absorptiometric grade, saponification degree 78–82%) was added and dissolved. The prepared suspension was then poured into a petri dish and the water was gradually evaporated over the period of one week. The black film formed was removed from the petri dish and a freestanding film was obtained. By altering the concentrations of SWNT and PVA in water, the thickness and absorbance of the SWNT/PVA film were controlled. Figure 1 shows the absorption spectra of the samples prepared using the processes described above.

We prepared two films of different thickness. For the mode-locking application, we prepared a 30-μm-thick SWNT/PVA film using NaDDBS surfactant. We chose a thickness of 30 μm because in this application, the film was to be sandwiched between two fiber ferrules, as described in the next section. As shown in Fig. 2, by observation using a VHX-100 Keyence digital optical microscope, we recognized a number of micron-scale particles of bundled SWNTs in the film, but in the major area, SWNTs were nominally observed because they were nano-dispersed in sizes smaller than optical wavelengths. In the practical situation, light is passed perpendicularly through the film with a beam diameter of about 10 μm (to achieve efficient saturable absorption). Therefore, the optical inhomogeneity due to the bundled SWNTs seems to be a minor disadvantage because the total cross-sectional area of the micron-scale particles that block the transmission of light is not critically large within the beam diameter. Therefore, even though we choose a beam transmission spot arbitrarily, device performance will not vary much. For ASE noise suppression, we prepared a 100-μm-thick SWNT/PVA film using SDS surfactant. We chose the thickness of 100 μm by considering the balance between the film strength and the focal depth (in which beam diameter is kept within \( \sqrt{2} \) times the beam waist) of about 100 μm in the adopted optics. Because the freestanding film was to be glued onto a metallic sample holder covering a 5-mm-diameter window for light transmission, a large film thickness was desired. On the other hand, to obtain sufficient light intensity for saturable absorption, we prepared two films of different thickness. For the mode-locking application, we prepared a 30-μm-thick SWNT/PVA film using NaDDBS surfactant. For ASE noise suppression, we prepared a 100-μm-thick SWNT/PVA film using SDS surfactant. We chose the thickness of 100 μm by considering the balance between the film strength and the focal depth (in which beam diameter is kept within \( \sqrt{2} \) times the beam waist) of about 100 μm in the adopted optics. Because the freestanding film was to be glued onto a metallic sample holder covering a 5-mm-diameter window for light transmission, a large film thickness was desired. On the other hand, to obtain sufficient light intensity for saturable absorption, we prepared two films of different thickness. For the mode-locking application, we prepared a 30-μm-thick SWNT/PVA film using NaDDBS surfactant. For ASE noise suppression, we prepared a 100-μm-thick SWNT/PVA film using SDS surfactant. We chose the thickness of 100 μm by considering the balance between the film strength and the focal depth (in which beam diameter is kept within \( \sqrt{2} \) times the beam waist) of about 100 μm in the adopted optics. Because the freestanding film was to be glued onto a metallic sample holder covering a 5-mm-diameter window for light transmission, a large film thickness was desired. On the other hand, to obtain sufficient light intensity for saturable absorption, we prepared two films of different thickness. For the mode-locking application, we prepared a 30-μm-thick SWNT/PVA film using NaDDBS surfactant. For ASE noise suppression, we prepared a 100-μm-thick SWNT/PVA film using SDS surfactant. We chose the thickness of 100 μm by considering the balance between the film strength and the focal depth (in which beam diameter is kept within \( \sqrt{2} \) times the beam waist) of about 100 μm in the adopted optics.
absorption, a film thickness desired was less than the focal depth. In this work, we determined the upper limit of the film thickness as the focal depth. We observed the 100-μm-thick film with the same optical microscope and found that the structures were similar to those in the 30-μm-thick film.

3. Passively Mode-Locked Femtosecond Fiber Laser Application

The passively mode-locked fiber laser using a SWNT saturable absorber\textsuperscript{20–22} is, at this stage, one of the most successful applications of carbon nanotubes. Thus far, SWNT saturable absorbers inserted into a laser cavity have been made by depositing SWNT films onto flat glass substrates,\textsuperscript{20,21} mirror substrates\textsuperscript{20} or the ends of optical fibers.\textsuperscript{21,22} When placing the SWNT saturable absorber inside the laser cavity, in the first two cases, to obtain high peak power of light at the saturable absorber and low insertion loss by the device, fine optical alignment with pair(s) of lenses is usually necessary. On the other hand, in the third case, when SWNT films are deposited onto the fiber ferrule surface, good optical alignment can be easily attained merely by bringing the two ferrules into contact inside the guiding sleeve.\textsuperscript{28,29} In this type of fiber connection technique, the gap width between the ferrule surfaces may be up to several tens of microns with permissible connection loss.\textsuperscript{28} Because our fabrication method for SWNT/PVA film is suited to controlling the thickness to several tens of microns, insertion of a SWNT/PVA film between two fiber ferrules (see Fig. 3) is expected to be a promising method for fabricating a mode locker for the fiber laser. In particular, the softness of the SWNT/PVA polymer film seems advantageous if we use physical contact (PC) ferrule surfaces.\textsuperscript{28} The PC surface is polished slightly spherically as shown in Fig. 3. When the soft SWNT/PVA polymer film is sandwiched between the two PC surfaces, the film is automatically fixed between the core center without an air gap. Therefore, we can expect very easy and good optical alignment.

The 30-μm-thick SWNT/PVA film, as described in §2, was cut into a small piece (about 2 mm × 2 mm), attached onto a FC/PC ferrule surface with index-matching gel, and sandwiched with another FC/PC ferrule surface. In the FC adaptor, surface contact is supported by a spring mechanism. Using this saturable absorber, we constructed the ring cavity laser shown in Fig. 4. A commercial Er\textsuperscript{3+}-ion-doped fiber amplifier (EDFA, Furukawa ErFA 1313) was used as a gain medium. We gradually increased the pumping power of the 980 nm semiconductor laser in the EDFA. Initially, the output light showed a broad Er\textsuperscript{3+}-ion luminescence spectrum. Next, the spectrum sharpened at around 1560 nm during cw lasing. Finally, the spectrum broadened at around 1560 nm with soliton sidebands,\textsuperscript{30} and at the same time, multiple-pulse mode-locking started, as observed using a high speed photodetector. Then, we gradually decreased the pumping power and achieved single-pulse mode-locking at a repetition rate of 7.26 MHz, as shown in Fig. 5. Figures 6 and 7 show an output spectrum measured with an optical spectrum analyzer (Ando AQ6317B) and an autocorrelation

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**Fig. 3.** Mode-locking device structure using a SWNT/PVA film. This diagram is a close-up of the essential part inside a FC adaptor. The ferrules are pushed by springs from both sides.

**Fig. 4.** Laser configuration constituting a ring cavity made of single-mode fibers and optical components.

**Fig. 5.** Repetition of the single-pulse mode-locked lasing. Repetition rate was 7.26 MHz.

**Fig. 6.** Output optical spectrum under the mode-locked lasing condition.
trace measured with an SHG-type autocorrelator (Femtochrome Research Inc. FR-103XL). Full width at half maximum (FWHM) of the autocorrelation trace was 700 fs, indicating that the inferred pulse duration was ≤500 fs. The average output power was 0.14 mW. Even when we shifted the SWNT/PVA film position at the ferrule surface, the mode-locking operation was almost unaffected.

These results demonstrate that the SWNT/PVA film is very promising as a passive mode locker for femtosecond Er-doped fiber lasers. The good controllability of film thickness and SWNT concentration will enable fine material tuning which will be advantageous for future laser improvements. The easy fabrication of devices with reproducible device performance using conventional fiber connection techniques will make the laser construction extremely easy.

4. ASE Noise Suppressor Application

Optical amplifiers utilizing stimulated emission of incident light under inverted population conditions are accompanied by ASE noise. This noise becomes a problem when short optical pulses are to be amplified to extremely high-peak-power pulses through a series of optical amplifiers at low repetition rates, or when telecommunication data are transmitted through a series of EDFAs or semiconductor optical amplifiers.31) Of late, ASE noise suppression devices using semiconductor saturable absorbers have been actively investigated for long-haul data transmission.32,33) The operating principle of these devices is based on the property of saturable absorbers that high-peak-power light is transmitted better than low-peak-power light such as ASE. Therefore, in addition to semiconductor saturable absorbers, SWNT saturable absorbers may be promising for this type of device. In particular, our SWNT/PVA material has attractive merits for the fabrication of uniform film devices with low scattering loss. In this study, we examined the ASE suppression effect using this material.

The 100-μm-thick SWNT/PVA film, as described in §2, was installed in the experimental setup shown in Fig. 8. In this setup, femtosecond laser pulses (IMRA Femtolite 780, model B-4-FC, 1.56 μm, pulse width 370 fs, repetition 50 MHz) and semiconductor ASE light (Fujitsu model AF-8101, output power 1.5 mW) were mixed into a single mode fiber with a 50:50 coupler, and the mixed light emitted from the fiber was 1:1 focused on the SWNT/PVA film using a pair of f = 11 mm aspheric lenses. The beam profile was measured with a beam profiler (BeamScope-P7, Data Ray Inc.), and a beam diameter of 6 μm (defined by a radial diameter of 50% intensity compared with the central beam intensity) was obtained at the focal position.24) The light transmitted through the film was collected into a single-mode fiber using a pair of lenses symmetrical to the focusing optics and analyzed with an optical spectrum analyzer (Ando AQ6317B).

Figure 9 shows the transmission loss spectrum of the SWNT/PVA film measured with only ASE light (ASE spectra with and without the film are also shown). The loss spectrum corresponds to the absorption spectrum shown in Fig. 1(b). (The small overlying ripple structure is due to the interference between the film surfaces with a distance of about 100 μm.) When the femtosecond pulse light (average power through the coupler was 1.5 mW) was added, the transmission loss decreased in the wavelength region of the
femtosecond pulse light, as shown in Fig. 10. With decreasing pulse light intensity, the decrease in transmission loss became smaller. These results demonstrate that the SWNT/PVA film has the ability to suppress ASE noise.

In this application, the noise suppression factor is strongly influenced by the ratio between the saturable loss and the nonsaturable loss. The former results solely from the saturable absorption of SWNTs. On the other hand, the latter has many sources such as (1) the scattering losses of the SWNTs and the PVA, (2) the reflection at the film surfaces, (3) the absorption components of the PVA film has the ability to suppress ASE noise. These results demonstrate that the SWNT/PVA nanocomposite can considerably reduce the scattering losses and therefore improve device quality. From the data reported thus far,7,8,24) to obtain large saturation in SWNT absorption, a pulse peak power of hundreds of MW/cm² seems to be necessary (though this value varies depending on the overlap condition between the S₁ absorption spectrum and the excitation laser wavelength90). Therefore, subpicos- or picosecond pulse applications at low repetition rates may be promising at first. Of course, in future ultrafast optical communication systems using subpicosecond- or picosecond-pulses, SWNT noise suppressors may play an important role.

5. Conclusions

We have demonstrated that SWNT/PVA nanocomposite films are very promising as saturable absorbers for passive mode-locking of femtosecond Er-ion-doped fiber lasers and for ASE noise suppressors. The good processibility of freestanding films increases the variety of device structures that can be fabricated. In particular, films with thicknesses of several tens microns are suited for use as mode lockers because they can be very easily inserted into conventional fiber connectors, making the laser construction extremely easy. The large area of nanoscale SWNT dispersion in the PVA matrix, in spite of the minor presence of micron-scale bundled SWNTs, permits arbitrary selection of the beam transmission position with a spot diameter of about 10µm with low scattering loss.

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