Carbon nanotube-doped polymer optical fiber

Sho Uchida,[1,*] Amos Martinez,[2] Yong-Won Song,[3] Takaaki Ishigure,[1] and Shinji Yamashita[2]

[1]*Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan*

[2]*Department of Electronic Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

[3]*Center for Energy Materials Research, Korea Institute of Science and Technology, Seoul 136-791, Korea*

**Corresponding author: shouchida@a2.keio.jp*

Received May 21, 2009; revised August 25, 2009; accepted September 8, 2009; posted September 14, 2009 (Doc. ID 111665); published October 5, 2009

We present a method to fabricate graded-index multimode polymer optical fibers doped with carbon nanotubes (CNTs). Such fiber structures provide the means to fully utilize the exceptional optical properties of the CNTs. The core region of the fiber is composed of CNTs and polymethyl methacrylate (PMMA) with the addition of diphenyl sulfide (DPS), which acts as the dispersion stabilizer of CNTs in PMMA as well as the dopant to increase the refractive index of the core. Utilizing 2.5 cm of the fiber as a saturable absorber, passively mode-locked lasing with duration of 3.0 ps and repetition rate of 30.3 MHz was demonstrated.

OCIS codes: 160.5470, 140.4050, 190.4400, 190.4370.

Carbon nanotubes (CNTs) have attractive optical functionalities that could be derived from their one-dimensional structure, such as large third-order nonlinearity and saturable absorption. Moreover, they have ultrashort recovery time ($\sim$500 fs) [1]. Thus there have been many reports on photonic applications of CNTs, such as passively mode-locked lasing [2], noise suppression [3], all-optical switching [4,5], and wavelength conversion [6]. For effective operation of such photonic devices, it is important to develop a method to fabricate CNT-based components with homogeneous CNT dispersion. In addition, there is a need for CNT-based devices to intensify the CNT-lightwave interaction while maintaining the low background loss. The fabrication of CNT-incorporated waveguides is a promising approach toward intensifying the interaction. Such waveguides offer a longer interaction length as well as the chance for CNTs to "feel" the peak power of the guided lightwave. Recently, several CNT-based waveguides sprayed with CNTs have been fabricated [6–8]. However, these devices depend on the interaction between CNTs and the evanescent field of guided lightwave, which leads to the weak interaction intensity. Furthermore, polymer waveguides doped with CNTs in their core have been fabricated [9]. However, those waveguides still seem to suffer from the limitation of the interaction length that the devices allow.

In this Letter, we focus on graded-index (GI)-type polymer optical fibers (POFs) doped with CNTs, which are fabricated by utilizing a method for fabricating CNT-polymethyl methacrylate (PMMA) composites that we previously reported [10]. There are several advantages associated with these CNT-doped POFs, such as (a) mechanical flexibility, (b) symmetric cross-sectional structure, (c) connectivity to optical fiber, (d) efficient interaction between the doped CNTs and guided lightwave, and (e) adjustable interaction length; using this fabrication process, several tens of meters of CNT-doped POF is obtained, and thus the interaction length between CNTs and lightwaves can be customized over a range from a few millimeters to several meters.

First, we briefly explain the fabrication process of CNT-doped POFs. Next, we show the optical characteristics of the POFs and then demonstrate passively mode-locked lasing by employing the POF as a saturable absorber.

We used PMMA for the cladding of the POF and CNT–PMMA composite with the addition of diphenyl sulfide (DPS) for the core. Here, DPS is expected to play two roles: one as the dispersion stabilizer of CNTs in PMMA [10] and the other as the dopant to increase the refractive index of core. DPS has higher refractive index (n_d=1.633) than PMMA (n_d=1.492), and thus it has been utilized as a dopant for the core of GI-POFs [11]. The absorption spectra of CNTs in CNT-PMMA composites with and without the addition of DPS have been shown elsewhere [10]. Strong absorption peaks over the wavelength range of 1300–1600 nm were observed, which are derived from electronic transition of semiconductor CNTs.

To utilize the CNT-PMMA-DPS composite as the core material for CNT-doped POFs, we adopted the interfacial-gel polymerization process [11] described as follows. First, we make a PMMA tube by heat polymerization of methyl methacrylate (MMA) monomer in a glass tube. Here, MMA has a liquid state before polymerization reaction to solid-state PMMA. Next, the PMMA tube is filled with a viscous mixture of MMA and DPS in which specified amount of CNTs are uniformly dispersed, followed by polymerization reaction to obtain a preform. Here, we used CNTs made by high-pressure CO conversion. The concentration of DPS was 10% by weight. The viscous mixture of MMA-DPS-CNT is prepared as described in [10]. A mixture of MMA-DPS-CNT with the addition of a polymerization initiator is heated while it is exposed to ultrasonication in a water bath. As the polymerization reaction progresses, the mixture becomes viscous, and then we inject it into the PMMA tube before the polymerization reaction is completed. Finally, the CNT-doped POF is obtained by heat drawing the preform at a temperature of 240°C, which is low enough for CNTs to maintain their physical characteristics. Cross sections of the obtained fibers are

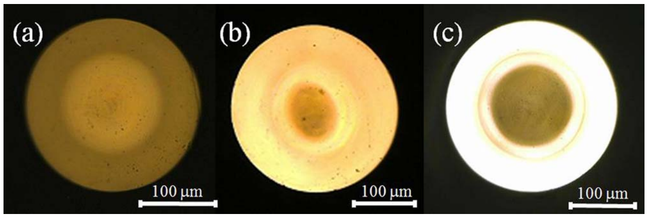

Fig. 1. (Color online) Cross sections of the obtained POFs doped with different CNT concentrations: (a) 0 ppm, (b) 15 ppm, (c) 25 ppm.

shown in Fig. 1. The darker colored core is clearly observed with increasing the CNT concentration. The attenuation values at a wavelength of 1550 nm were 0.88 dB/cm, 1.39 dB/cm, and 2.34 dB/cm for the POFs doped with 0 ppm, 15 ppm, and 25 ppm of CNTs, respectively.

We measured the refractive index profile of the POFs by using interference microscopy. The inset of Fig. 2 shows the interference fringe pattern observed on the cross section of the POF shown in Fig. 1(b). The monochrome concentric contour fringe pattern expresses a parabolic refractive index distribution. Figure 2 depicts the refractive index profiles of the POFs doped with various CNT concentration, which are measured on the radial direction as indicated by the white broken line in the inset.

Quasi-parabolic refractive index profiles are formed in all the POFs, although the index shape and index difference vary slightly, probably owing to the difference of polymerization velocity depending on the amount of doped CNTs. This GI profile can be attributed to the distribution of high refractive index dopant DPS in the core region [11]. It is expected that the GI profile enables to confine the guided lightwave tightly into the core center of the POFs. Therefore, the spot size of the output optical field from the POFs could be significantly smaller than the core size. We verified the spot diameter of the output near-field pattern (NFP) from the POFs. Figure 3 shows the NFPs from the POFs shown in Fig. 1 with a length of 2.5 cm, and the image observed from 15 ppm CNT-doped POF is shown in the inset. For comparison, Fig. 4 shows the NFPs from three samples of PMMA-DPS slab doped with 25 ppm CNTs with thicknesses of 1 mm, 1.5 cm, and 2.5 cm and the image observed from the 1.5-cm-thick slab is shown in the inset. Here, the incident cw light with a wavelength of

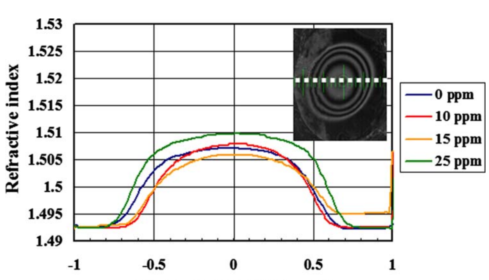

Fig. 2. (Color online) Refractive index profiles of the obtained POFs measured on the horizontal axis. Inset, interference fringe pattern observed from the POF shown in Fig. 1(b).

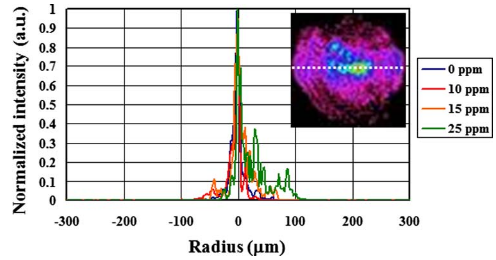

Fig. 3. (Color online) NFPs from the obtained POFs with a length of 2.5 cm. Inset, NFP image observed from fiber (b) in Fig. 1.

850 nm is coupled to the POFs or slabs via a 1 m single-mode fiber (core diameter is approximately 9 μm) and guided through them.

The NFP results indicate that the spot size of output NFP is broader with increasing the CNT concentration, due to the light scattering by the slightly agglomerated CNTs. However, the FWHM of the spot size is over a range in 20–30 μm for all the POFs. On the other hand, even after a 1.5 cm transmission through the slab sample, the NFP expands to the whole area. Thus, the core-cladding structure, particularly GI core, is important to maintain the small mode field and to reduce the insertion loss of the POF, which is preferable to the application of passive mode-locked devices mentioned later in this Letter.

One of the most major photonic applications incorporating CNTs is passive mode-locked lasing based on its nonlinear saturable absorption [2]. For this application, the POFs doped with higher concentration of CNTs would show better saturable absorption. Therefore, the POF shown in Fig. 1(c) was cut into 2.5 cm in length, and inserted into a ring cavity laser, as illustrated in the inset of Fig. 5(a); an erbium-doped fiber amplifier (EDFA) was used as a gain medium. With a 10/90 coupler, 10% of propagating light is taken out as the laser output, while the 90% remaining is fed back into the cavity, and several meters of single-mode fiber was inserted to optimize the intracavity dispersion. A polarization controller is used to match the state of polarization in the fiber cavity, and isolators guarantee unidirectional operation. Continuous lightwave emitted from the EDFA was coupled to the POF using two pairs of lenses. Here, the value of the insertion loss was approximately 10 dB. Due to the intensity-dependent saturable absorption of CNTs, low-intensity cw light is absorbed by the doped CNTs, while high-intensity

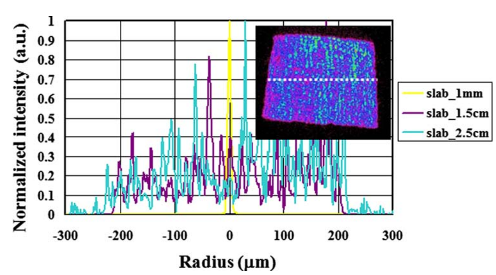

Fig. 4. (Color online) NFPs from three CNT-doped slabs with thicknesses of 1 mm, 1.5 cm, and 2.5 cm. Inset, NFP image observed from the 1.5-cm-thick slab.

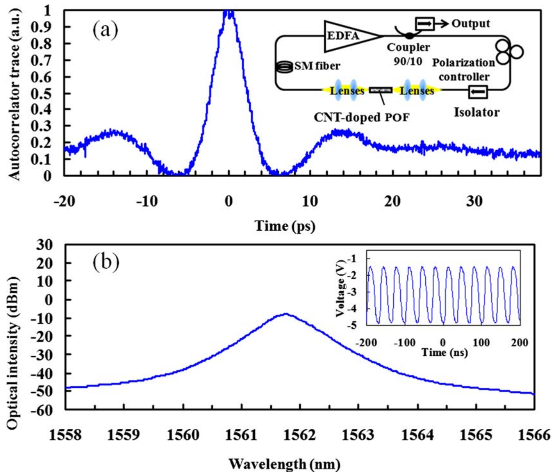

Fig. 5. (Color online) (a) Autocorrelator trace of the laser output. Inset, passively mode-locked laser configuration. SM, single-mode. (b) Optical spectrum of the laser output. Inset, pulse train of the laser output.

pulses propagate through them (i.e., the POF). Consequently, continuous pulses with duration from a few picoseconds to several hundred femtoseconds can be generated.

The autocorrelator trace in Fig. 5(a) shows the pulse duration of 3.0 ps. Figure 5(b) shows the optical spectrum of the laser output centered at 1561.8 nm with a FWHM of 0.5 nm. The inset of Fig. 5(b) describes a pulse train with 33 ns intervals between each pulse, corresponding to the repetition rate of 30.3 MHz. The average output power was 3 dBm. Because of the large core of the POF, the optical power density injected into the POF could be reduced. Thus, we did not observe any deterioration of the POF characteristics after a high-power pulsations demonstration.

It is confirmed by the results that the fiber structure allows the doped CNTs to act as a saturable absorber. Lasing performance is expected to be enhanced after optimization of various factors, such as CNT concentration, surface condition of both input and output fiber ends, and light coupling conditions at both fiber ends. In particular, single-mode POFs doped with CNTs are expected to intensify the interaction between CNTs and lightwaves as well as to reduce insertion loss due to free-space coupling using lenses in current cavity setup.

In conclusion, polymer optical fibers doped with CNTs were fabricated for the first time to the best of our knowledge. Such fibers allow the interaction between the CNTs and the guided lightwave through the center of the waveguide and hence allow the interaction with the propagating lightwave at its peak power. Furthermore, since the fabrication process allows the fabrication of several meters of fiber, the interaction length can be easily customized to fit any application requirement. By employing the fiber as a saturable absorber, passively mode-locked lasing was demonstrated. We successfully generated 3.0 ps pulses with a repetition rate of 30.3 MHz.

This work was partially supported by Ogasawara Science and Technology Foundation.

References

1. Y.-C. Chen, N. R. Raravikar, L. S. Schadler, P. M. Ajayan, Y.-P. Zhao, T.-M. Lu, G.-C. Wang, and X.-C. Zhang, Appl. Phys. Lett. **81**, 975 (2002).
2. S. Y. Set, H. Yaguchi, Y. Tanaka, and M. Jablonski, IEEE J. Sel. Top. Quantum Electron. **10**, 137 (2004).
3. S. Y. Set, H. Yaguchi, Y. Tanaka, M. Jablonski, Y. Sakakibara, A. Rozhin, M. Tokumoto, H. Kataura, Y. Achiba, and K. Kikuchi, in *Optical Fiber Communication Conference*, Technical Digest (Optical Society of America, 2003), paper FL2.
4. Y. W. Song, S. Y. Set, and S. Yamashita, in *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*, Technical Digest (CD) (Optical Society of America, 2006), paper CMA4.
5. K. Kashiwagi, S. Yamashita, H. Yaguchi, C. S. Goh, and S. Y. Set, in *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*, Technical Digest (CD) (Optical Society of America, 2006), paper CMA5.
6. K. K. Chow, S. Yamashita, and Y. W. Song, Opt. Express **17**, 7664 (2009).
7. Y. W. Song, K. Morimune, S. Y. Set, and S. Yamashita, Appl. Phys. Lett. **90**, 021101 (2007).
8. K. Kashiwagi, S. Yamashita, Y. Nasu, H. Yaguchi, C. S. Goh, and S. Y. Set, Appl. Phys. Lett. **89**, 081125 (2006).
9. T. Oomuro, R. Kaji, T. Itatani, H. Ishii, E. Itoga, H. Kataura, M. Yamashita, M. Mori, and Y. Sakakibara, *Conference on Lasers and Electro-Optics/Quantum Electronics and Laser Science Conference and Photonic Applications Systems Technologies*, OSA Technical Digest Series (CD) (Optical Society of America, 2007), paper CThV1.
10. A. Martinez, S. Uchida, Y. W. Song, T. Ishigure, and S. Yamashita, Opt. Express **16**, 11337 (2008).
11. T. Ishigure, A. Horibe, E. Nihei, and Y. Koike, J. Lightwave Technol. **13**, 1686 (1995).