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Saturable absorber using single wall carbon nanotube-poly (vinylalcohol) deposited by the vertical evaporation technique

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ABSTRACT

We employed a vertical evaporation technique to fabricate saturable absorbers by embedding single wall carbon nanotubes (SWCNT) in polymer (vinylalcohol). Two fast recovery time constants, 250 fs and 1.13 ps, respectively, were measured for the absorbers using a transient absorption experimental setup. The saturation intensity of the absorber was found to be 300–400 μJ/cm^2 at 1060 nm, and a modulation depth as high as 3.5% was achieved.

1. Introduction

Over the past twenty years since the semiconductor saturable absorber mirrors (SESAMs) were successfully developed [1], the SESAMs have been commonly used for ultrashort pulse generation on the passively mode-locked solid-state lasers. Because the short pulse lasers are powerful tools for many applications in optics communication, laser machining, transient absorption experiments, etc., SESAMs have attracted a lot of attention. Furthermore, the advantages of SESAMs include their compactness, flexibility and suitable for a wide spectral range from the visible to the infrared. The SESAMs have been well proven as a promising device for passive mode locking in many kinds of solid-state lasers [2–5]. However, commercial SESAMs have been grown by expensive methods such as molecular beam epitaxy or metal-organic chemical vapor deposition on Bragg mirrors. Other than those strict fabrication requirements, the process of high-energy heavy-ion implantation is also needed to create defects and to reduce the recovery times [6]. Furthermore, the wavelength of the operation range in SESAMs is limited by the materials. Hence, a new material with stronger optical nonlinearity, a broader operation range and a simple procedure of fabrication is required.

The dissolved carbon nanotubes have been widely investigated by researchers to improve understanding of the unique electric mechanism and optical property [7]. Semiconducting SWCNT is a promising material for saturable absorbers in laser mode locking [11] because of the fast recovery time, which covers a broad spectral range in the near infrared, and excellent chemical stability [8–10]. Furthermore, SWCNT-based saturable absorbers can be fabricated by simple and economy-costed methods, such as spray [12], spin coating [13] or horizontal evaporation methods [14,15].

In 2002, Shimoda et al. [16] reported a method to fabricate carbon nanotubes at atmosphere by vertical evaporation, and they found that the carbon nanotubes possessed orientation on the hydrophilic substrate. Kim et al. [17] reported fabrication of carbon nanotubes with an in-plane orientation by the Langmuir–Blodgett method, and they also reported measurements of the polarized UV–VIS–NIR absorption spectra. However, in the Langmuir–Blodgett method, expensive instruments are required. In addition, vertical evaporation at atmosphere needs much longer time, about two to three weeks, to finish the growth procedure. Here, we used the rapid vertical evaporation technique to fabricate saturate absorbers and measured device parameters of the absorber by transient absorption techniques.

2. Fabrication and measurements

The SWCNTs were purchased from Golden Innovation Business Company, having a diameter about 1.5 nm and a length distributed from 1 to 5 μm. In order to dissolve SWCNTs into water, SWCNTs were processed with H_2SO_4/HNO_3. First, several milligrams of SWCNT powder were poured into a 10 ml 0.1% SDS (sodium dodecyl sulfate) aqueous solution. Here SDS was used as a surfactant. In order to obtain SWCNT aqueous dispersion with high absorption, a SWCNT aqueous solution was ultrasonically agitated for 10 h. After the ultrasonic process, the dispersed solution of SWCNT was centrifuged to remove sedimentation of large SWCNT bundles. After decanting the upper portion of the centrifuged

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solution, some PVA powder was poured into the solution and dissolved at 90 °C with ultrasonic agitation for 6 h. The SWCNT/PVA dispersion was poured into a 10 mm × 10 mm × 45 mm polystyrene cell. Then, we inserted a hydrophilic glass substrate into the cell as shown in Fig. 1. The polystyrene cell was placed inside a thermostatic oven for gradual evaporation. The oven was kept at 80 °C to prevent the PVA precipitated during the evaporation process. Comparing with the method of evaporation at atmosphere, the evaporation process which we used is much time saving, and it only takes about 2 days to get finished. We would like to point out that the dispersion of SWCNTs will aggregate after several weeks. Therefore, in order to have better quality for the sample, we need to speed up the evaporation time. For the horizontal evaporation method, the concentration of the SWCNT/PVA solution will be very high at the end of the evaporation process, which may lead to the aggregation of SWCNTs. On the contrary, for the vertical evaporation method, the SWCNT/PVA composition gradually deposited on the glass as the solution evaporates. Therefore, most SWCNTs on the glass are dispersed very well.

To identify the operating wavelength of the SWCNT/PVA absorber, a UV–VIS–NIR spectrophotometer, covering 300–2000 nm wavelength, was employed to measure the linear optical absorption of the SWCNT/PVA absorber of different compositions, as shown in Fig. 2. Because the transmittance of the sample was measured by the spectrophotometer, we needed to convert the transmittance to the absorption which was displaced in the vertical axis of Fig. 2. It means that the absorption includes the scattering, reflection of both surfaces and absorption of SWCNT, PVA and the glass substrate. As shown in Fig. 2, the absorption peak near 1000 nm decreases as the concentration of SWCNT is decreased. It indicates that the absorption peak corresponds to the second van Hove E_{11} of SWCNT, and the absorption peak is located at the gain window of Nd- and Yb-doped laser media.

For a pure SWCNT film, the bundled and entangled SWCNTs may cause considerable scattering losses [11]. Additional PVA was used to improve the optical quality and to decrease scattering losses for the SWCNT composite. From the absorption curves of SWCNT composites shown in Fig. 2, one could notice that the profiles of the absorption peak are similar in different PVA concentrations or without PVA because PVA is nearly transparent around the infrared. However, if the concentration of PVA far exceeds 1%, the absorption peak of SWCNTs will disappear and the absorption of the composite will significantly increase.

Fig. 3(a) shows the schematic of the transient absorption experimental setup for evaluating SWCNT/PVA absorbers. We used an ultrafast laser system from Spectra-Physics Corporation, including a Tsunami femtosecond laser, a Spitfire Pro amplifier and a TOPAS-C optical parameter amplifier, to provide 100 fs laser pulses with a wavelength from 300 nm to 2000 nm at a 1 kHz repetition rate. Corresponding to Nd- or Yb-doped gain media, we measured the device

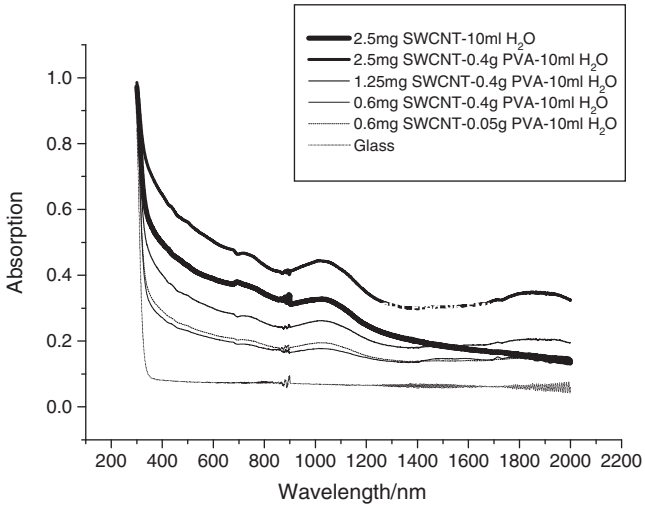

Fig. 2. Optical absorptions of four SWCNT/PVA absorbers which were fabricated by SWCNTs and PVA of different concentrations.

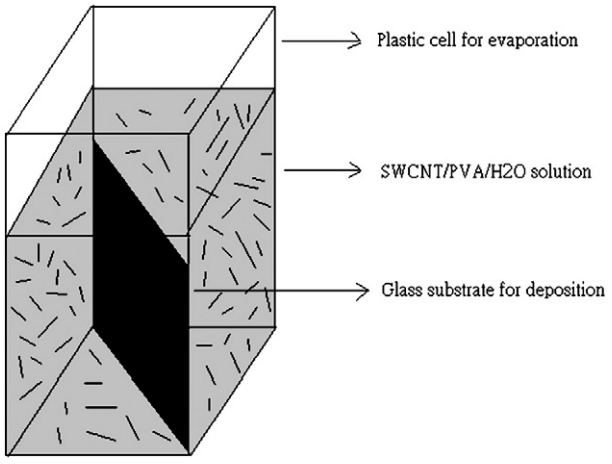

Fig. 1. A schematic illustration of the vertical evaporation process: SWCNTs were dispersed in the PVA aqueous solution to form suspension into which a hydrophilic glass was inserted along the diagonal line of the cell. With gradual evaporation of the water in an oven, the SWCNT and PVA stayed on the glass substrate around the air/water/substrate triple line [16].

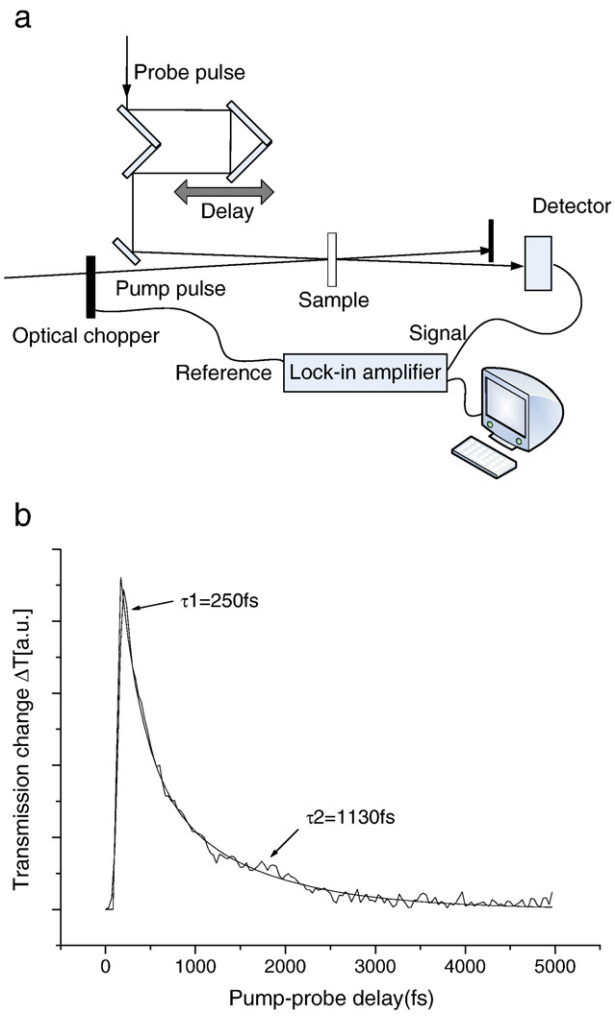

Fig. 3. (a) A schematic layout for the pump–probe setup for nonlinear parameter measurements of the SWCNT/PVA absorbers. (b) Modulated probe signal of the SWCNT/PVA plotted as a function of the time delay (1060 nm).

parameters of the SWCNT/PVA absorber at a wavelength of 1060 nm. In our experiments, the pump beam was employed to excite the SWCNT/PVA absorber to generate carriers of the excited state, and the delayed probe beam was then applied to measure carrier dynamics in time. In order to eliminate the influence of the probe beam, the ratio between the pump and the probe beam was set at 40:1 in the experiments.

Fig. 3(b) shows the dependence of the transmission change on the time delay as a result of the carrier dynamics of the SWCNT/PVA absorber. At the beginning or zero time delay, the electrons was photo-excited by the pump beam to occupy the excited state, the absorber will be bleached to allow the higher transmission of the probe beam. Subsequently, the carriers in the excited state are then relaxed to recover from the optical blench through the intraband or interband transitions. We used a biexponential function to fit the data in Fig. 3(b), and we obtained two carrier lifetimes which are 250 fs and 1.13 ps, respectively. The inverse of the carrier lifetime of the absorber represents the modulation speed when it works in the laser cavity. The lifetimes are sufficiently fast for generation of the ultrashort laser pulse.

3. Results and discussions

In this work the SWCNT/PVA absorbers were fabricated by different preparation conditions and the corresponding nonlinear transmission dependence on pump fluence was illustrated in Fig. 4, showing the transmission curves for the saturation characteristics of the absorbers. Similar to the transient absorption experiments, the optical chopper and lock-in amplifier were utilized to ensure that such a small transmission modulation could be detected. Comparing to Fig. 4(a) and (b), the modulation depth could decrease from 3.5% to 2% as the SWCNT concentration was decreased. These results are expected for the modulation depth to be directly proportional to the SWCNT concentration on the substrate.

In this study, we also found that SWCNTs competed with PVA to stick on the glass substrate during the deposition process. When the absorber is fabricated by 0.6 mg SWCNT, 0.4 g PVA and 10 ml H_2O, the modulation depth is small and difficult to measure. When we reduced the quantity of PVA to 0.05 g, a considerable modulation depth about 2% was observed, as shown in Fig. 4(c). The quantity of SWCNTs deposited on the glass would rapidly increase as the concentration of PVA remained below a certain value. In practice, the transmission of the absorber could increase by reducing the concentration of SWCNTs on the substrate to prevent too much loss. Schmidt et al. [18] reported a modulation depth of 0.5% at 1 μm for the SWCNT/PVA absorber by the horizontal evaporation technique. In our study, we could obtain the modulation depth as high as 3.5% (fabricated by 2.5 mg SWCNT, 0.4 g PVA and 10 ml H_2O). Here, we demonstrated a vertical evaporation method for fabrication of SWCNT/PVA absorbers with a higher modulation depth.

As a demonstration for the applicability of SWCNT-PVA absorbers for ultrashort solid-state laser mode locking, Fig. 5 shows the pulse train with a repetition rate of 58 MHz. The laser crystal Nd:YVO_4 was pumped by a 808 nm fiber-coupled diode laser. The maximum output is 30 mW at 7 W pump power. The pulses were not stable for us to measure the pulse duration. The output power varies from maximum to minimum and inverse periodically, which is due to the thermal effect of PVA. However, the maximum output power in every turn keeps the same. So we think the PVA was not damaged and only distorted under the laser illumination. Further investigation is under way.

4. Conclusions

In summary, we proposed SWCNT/PVA composites for saturable absorbers. From the transient absorption experiments, we obtained two recovery time constants, 250 fs and 1.13 ps. They are sufficiently short to validate the applications of SWCNT for ultrashort laser pulse generation. We used a vertical evaporation method to fabricate SWCNT/PVA absorbers which possesses adjustable modulation depth, high transmission and low non-saturable losses. These favorable

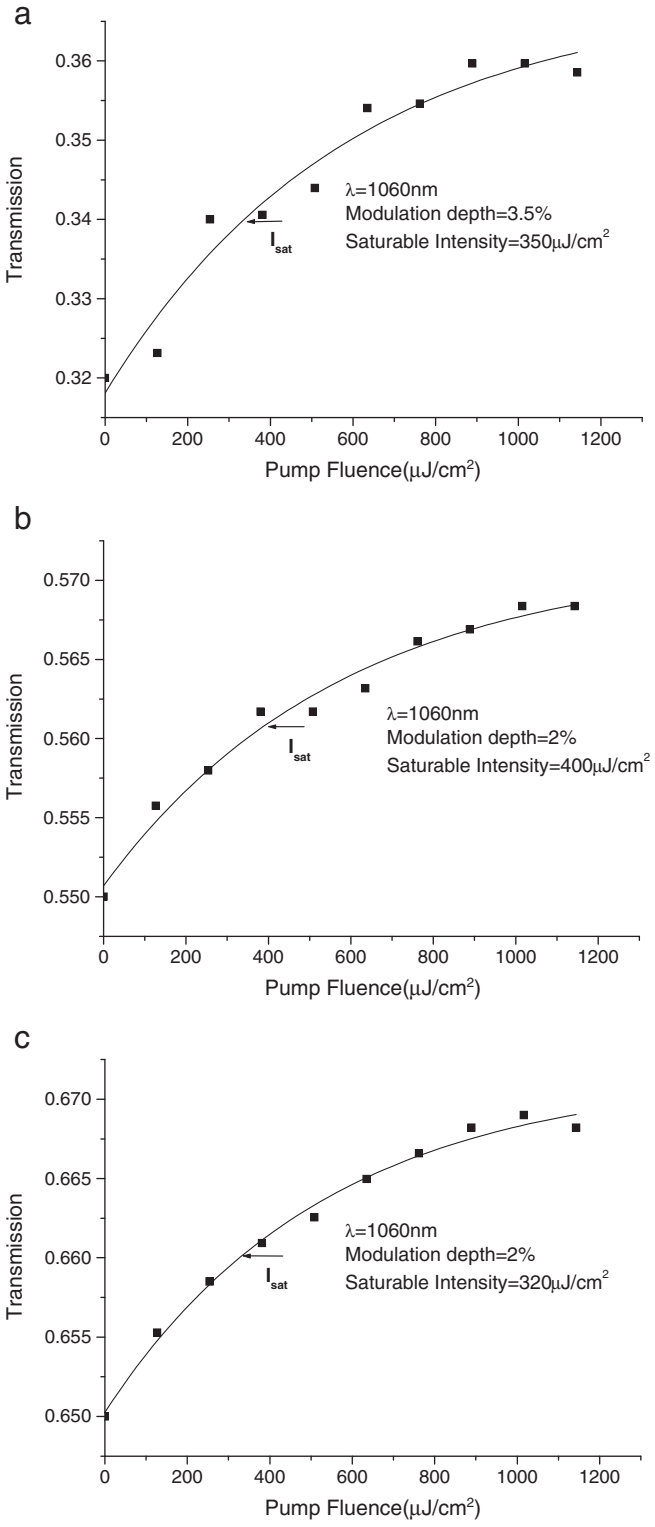

Fig. 4. Nonlinear transmission as a function of the pump intensity at 1060 nm (the diameter of the laser spot on the SWCNT absorber is about 100 μm, the repetition rate is 1 KHz and the pulse duration is about 100 fs). Fig. 4(a) represents the sample (a) which was fabricated by 2.5 mg SWCNT, 0.4 g PVA and 10 ml H_2O; Fig. 4(b) represents the sample (b) which was fabricated by 1.25 mg SWCNT, 0.4 g PVA and 10 ml H_2O; Fig. 4(c) represents the sample (c) which was fabricated by 0.6 mg SWCNT, 0.05 g PVA and 10 ml H_2O.

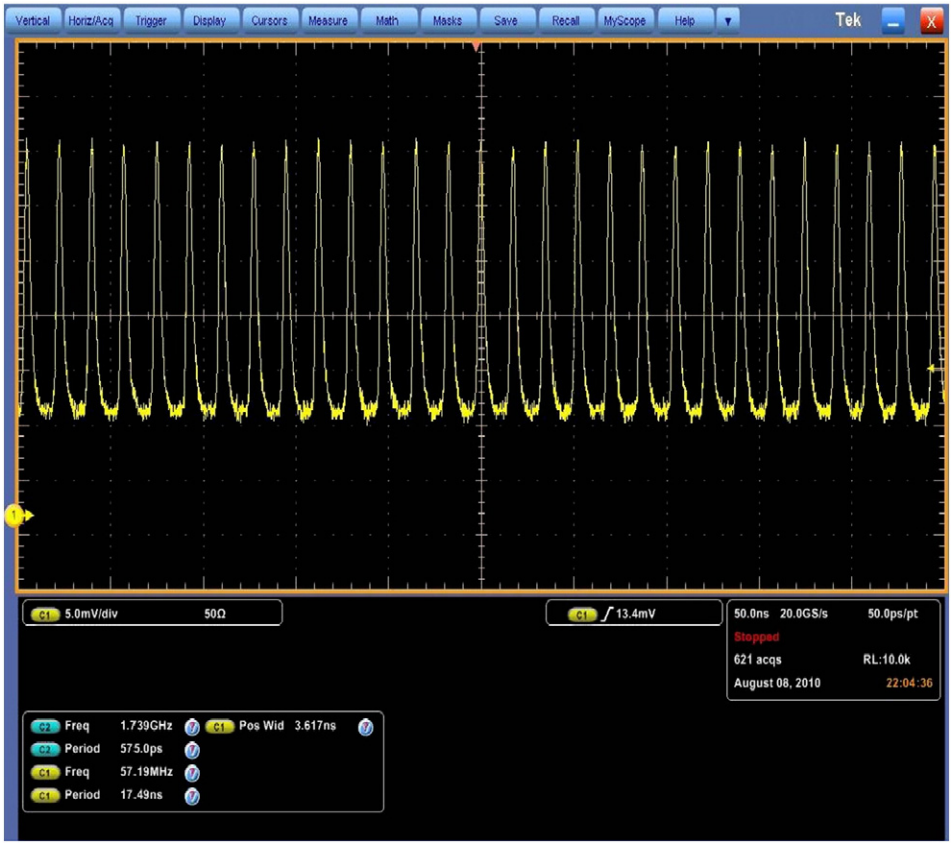

Fig. 5. Output pulse train with a repetition rate of 58 MHz.

optical properties of SWCNT/PVA composites could be achieved by inexpensive methods for applications in short laser pulse generation.

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