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Saturable absorber at 940 nm using single wall carbon nanotubes deposited by vertical evaporation technique

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ABSTRACT

The vertical evaporation technique allows us to fabricate aligned single wall carbon saturable absorbers. The nonlinear parameters of the absorber at the wavelength of 940 nm were measured. The measured bi-exponential lifetimes of the absorber are 330 fs and 850 fs, respectively. The saturation intensity and modulation depth were found to be 2000 μJ/cm^2 and 10% for SWCNT absorber at the direction of alignment, in comparison to 950 μJ/cm^2 and 7% for the SWCNT solution.

1. Introduction

Since the semiconductor saturable absorber mirrors (SESAMs) were successfully developed [1], there has been a great interest on the investigation of passively mode-locked solid-state lasers or fiber lasers from the visible to the infrared. SESAMs have been well proved as good devices for passive mode locking in many kinds of solid-state lasers [2–5]. Among these studies, directly diode-pumped ultrafast lasers, emitting in the range 900–950 nm, are very promising for developing blue laser by means of frequency doubling. Blue radiation has many applications in biology and medicine because many fluorophores have absorption band in this wavelength range. One of the most promising ways to achieve diode-pumped solid state laser between 900 and 950 nm is to use Nd-doped laser crystals on their $^4F_{3/2}$–$^4I_{9/2}$ transition line. Many continuous wave [3] or mode-locked lasers [4,5] with SESAMs as the absorbers at 900–950 nm were reported.

However, SESAMs have some shortcomings. SESAMs are grown by expensive devices such as molecular beam epitaxy (MBE) or metal–organic chemical vapor deposition (MOCVD) on Bragg mirrors and complex designation. In addition to these strict fabrication requirements, they often undergo high-energy heavy-ion implantation to create defects in order to reduce the recovery time. Furthermore, SESAMs typically cover a relatively narrow operation wavelength range and are not very successful in mode locking beyond 100 fs. Hence, new materials with stronger ultrafast optical nonlinearities, a broader operating range, a simpler fabrication procedure and a lower price are in great demand.

Due to their unique electric, mechanical and optical properties, carbon nanotubes (CNTs) are important nanomaterials widely investigated since their discovery [6]. Especially, single-walled CNTs (SWCNTs) exhibit fast recovery times, chemical stability, and a broad spectral range, roughly between 1 and 2 μm [7]. Semiconducting SWCNTs turned out to be a promising material for saturable absorbers for laser mode locking [8]. SWCNT-based saturable absorbers can be fabricated in a much simpler and more cost-effectively way with well-known techniques such as spray [9], spin coating [10] or horizontal evaporation methods [11,12].

In 2002, Shimoda et al. [13] fabricated carbon nanotubes at atmosphere by vertical evaporation and found out that the carbon nanotubes appeared to possess some extent of alignment. However, for vertical evaporation at atmosphere, too much time (about two to three weeks) would be needed to complete the whole growth procedure.

In this letter we used the vertical evaporation technique to fabricate carbon nanotubes with alignment. We measured their key

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nonlinear parameters at 940 nm to test potential applications in mode locking. We adopted evaporation in an oven at high temperature instead of evaporation at atmosphere in order to finish the deposition in short time. To our knowledge, SWCNT absorbers below 1 μm have not been reported by far.

2. Fabrication and measurements

The SWCNT material was purchased from Golden Innovation Business Company. The diameter of the SWCNTs is about 1.5 nm and the length distribution is from 1 to 5 μm. The SWCNTs were processed by H_2SO_4/HNO_3 so that they could be dissolved in water. First, several milligrams of SWCNT powder were poured into 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, SWCNT aqueous solution was ultrasonically agitated for 10 h. After the ultrasonic process, the dispersed solution of SWCNT was centrifuged to induce sedimentation of large SWCNT bundles. After decanting the upper portion of the centrifuged solution, the SWCNT dispersion was poured into 10 mm × 10 mm × 45 mm polystyrene cell inserted with a hydrophilic glass substrate as shown in Fig. 1. The polystyrene cell was then put into an oven for gradual evaporation. The oven was kept at 40 °C and the evaporation finished 2 days later, which appeared much shorter than evaporation at atmosphere which would usually take two to three weeks. Sometimes, the SWCNTs would aggregate in the dispersion after several weeks. Therefore, short evaporation time is necessary.

In Fig. 2, it is the schematic of transient absorption experiment for the SWCNT absorber. We use the ultrafast laser system of Spectra-Physics Corporation, which including the Tsunami femtosecond laser, Spitfire Pro amplifier and TOPAS-C OPA system, to provide 100 fs laser pulses with wavelength from 300 nm to 2000 nm at 1 kHz repetition rate. In our experiment, the pump beam excites the SWCNT absorber to generate carrier density of excited state, and the delayed probe beam measures carrier dynamics with time. In this report, we measured the nonlinear parameters of the SWCNT absorber at the wavelength of 940 nm, which represents the wavelength range 900–950 nm that corresponds to an important laser transition energy level of Nd-doped laser crystals. We measured the nonlinear parameters of SWCNT solution by using a peristaltic pump device, which could make a steady flow of SWCNT solution flowing so that the signal is very stable. Peristaltic pump through the flexible delivery hose pump alternating squeezing and releasing for pumping fluid. As two fingers, like the squeeze tube, with the finger movement, the formation of vacuum tube, the liquid flows along.

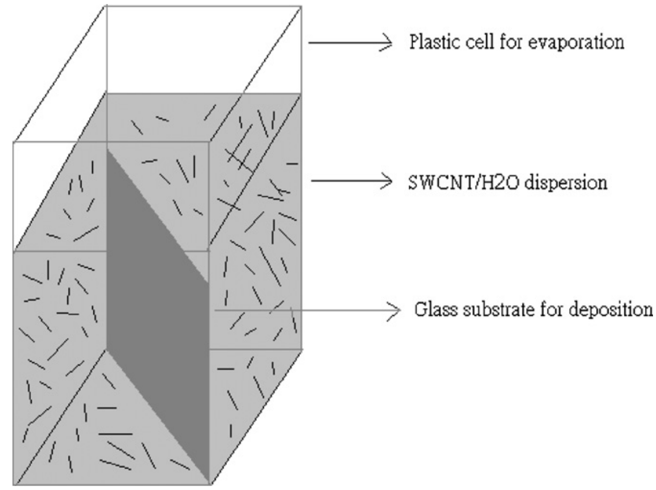

Fig. 1. A schematic illustration of the vertical evaporation process: SWCNTs were dispersed in SDS aqueous solution to form suspension into which a hydrophilic glass was inserted along the diagonal line of the cell. With gradual evaporation of the water in an oven, the SWCNT stayed on the glass substrate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

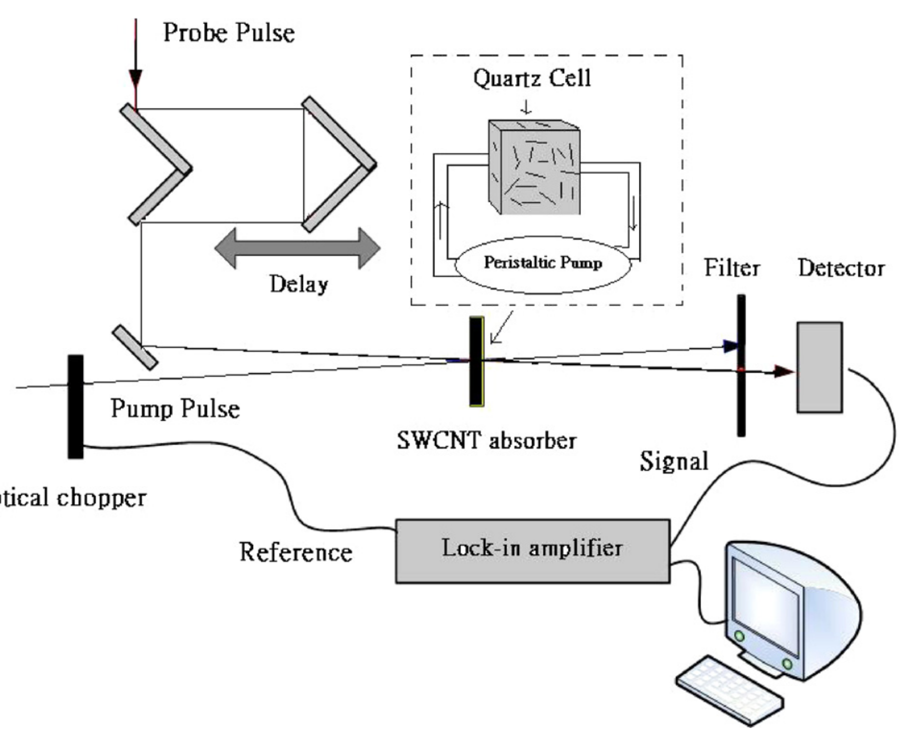

Fig. 2. A schematic layout for the pump–probe setup for nonlinear parameter measurements of the SWCNT absorbers and solution.

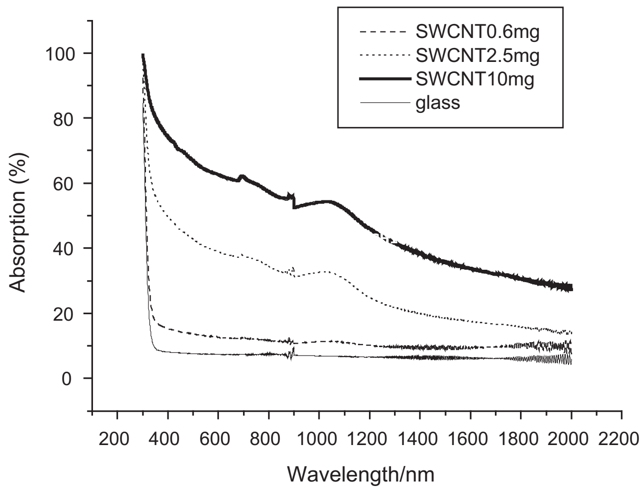

Fig. 3. Optical absorptions of three SWCNT absorbers which were fabricated by SWCNTs of different concentrations.

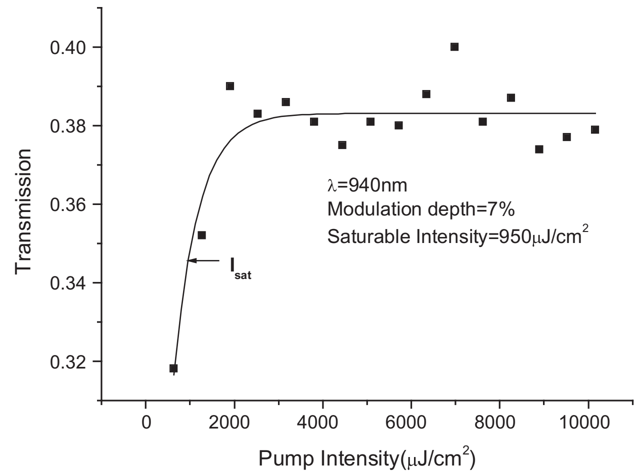

Fig. 5. Nonlinear transmission as a function of the pump intensity at 940 nm (the diameter of the laser spot on the middle of the SWCNT solution (10 mg in 10 ml SDS aqueous solution) is about 100 μm, the repetition fate is 1 kHz and the pulse duration is about 100 fs).

3. Results and discussion

To probe the operating wavelength of SWCNT absorber, a UV–Vis–NIR spectrophotometer was employed to measure the linear optical absorption of the SWCNT absorber of different compositions within 300–2000 nm wavelength, as shown in Fig. 3. It shows that the peak absorption wavelength of SWCNT absorber corresponds to the second van Hove E_{22} near 1000 nm, located at the neodymium and ytterbium gain window. The absorption of the absorber was observed to decrease as the concentration of the SWCNT in the dispersion decreased. We noted that the SWCNT absorber made by 0.6 mg SWCNT in 10 ml SDS aqueous solution has relatively small absorption and large transmission, which may help to the application in the mode locking solid-state laser as long as the modulation depth is not too low (>0.5%).

Fig. 4 shows the modulated probe signal of the SWCNT absorber versus the time delay. The shorter delay time of 330 fs corresponds to the intraband transition, whereas the longer delay time 850 fs corresponds to the interband transition. The latter is related to the behavior of passively mode locking lasers. Generally speaking, a fast lifetime is beneficial to the realization of a short laser pulse.

Fig. 5 shows nonlinear transmission as a function of the pump intensity (10 mg SWCNT in 10 ml SDS aqueous dispersion) at 940 nm. The diameter of the pump laser spot on the SWCNT is about 100 μm, the repetition rate is 1 kHz and the pulse duration is about 100 fs. The modulation depth is about 7% and the saturation intensity is about 950 μJ/cm^2. The thickness of the measured SWCNT dispersion is 1 cm. Fig. 6 shows nonlinear transmission as a function of the pump intensity at 940 nm (the measurement conditions are as similar to that of Fig. 5). Here, the direction of alignment (evaporation plane) of the SWCNT absorber is fixed and parallel to the probe polarization (■ represents the polarization of pump–probe and • represents that of pump–probe). We noted that the modulation depth is 10% at the case of the pump parallel to the probe and is 5% at the case of the pump perpendicular to the probe, which reflects the polarization absorption of the aligned SWCNTs. Generally speaking, SWCNT has more scattering losses so that they are mostly used in fiber lasers since the latter have relatively large gain. For aligned SWCNT absorber, we can use the advantage of large polarization absorption to get high transmission rate, low SWCNT concentration, low non-saturation losses, small but adequate modulation depth and relatively low saturation intensity, which would help us to realize mode locked solid-state lasers by using SWCNTs.

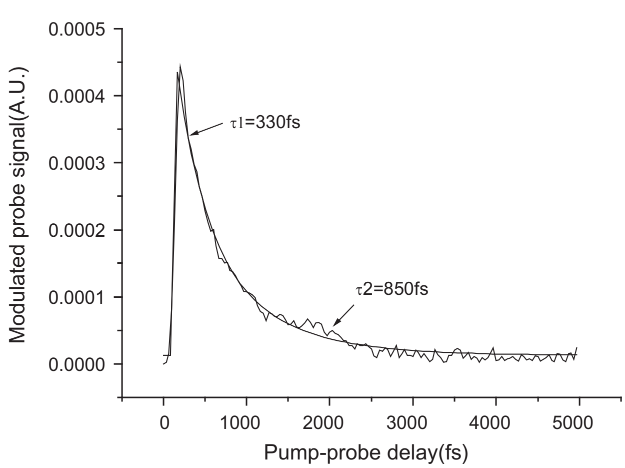

Fig. 4. Modulated probe signal of the SWCNT plotted as a function of the time delay (940 nm).

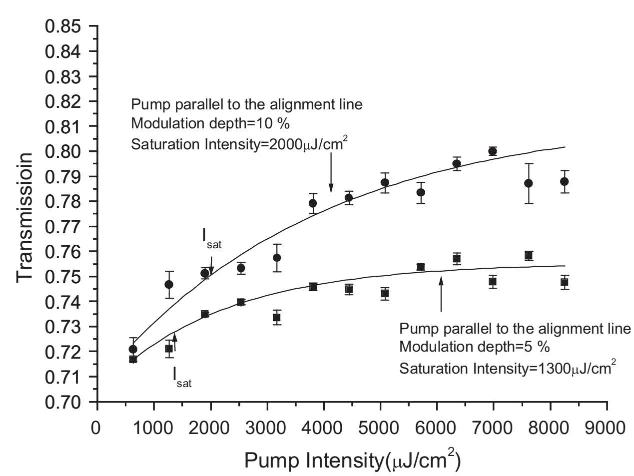

Fig. 6. Nonlinear transmission as a function of the pump intensity at 940 nm (the measured type of the SWCNT absorber is made by 2.5 mg SWCNT in 10 ml SDS aqueous dispersion). The diameter of the laser spot on the SWCNT absorber is about 100 μm, the repetition fate is 1 kHz and the pulse duration is about 100 fs. Here, the direction of alignment (evaporation plane) of the SWCNT absorber is fixed and parallel to the probe polarization (■ represents the polarization of pump–probe and • represents that of pump–probe).

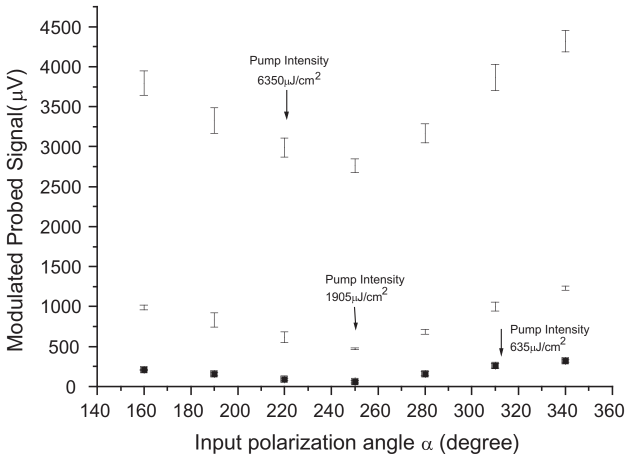

Fig. 7. Dependence of modulated probe signal on the input polarization angle α (the measured type of the SWCNT absorber is made by 2.5 mg SWCNT in 10 ml SDS aqueous dispersion). The signal is from phase lock-in amplifier, which reflects the extent of photo bleaching. Here, the direction of alignment (evaporation plane) of the SWCNT absorber is parallel to the probe polarization. The angle α is between the pump polarization and the evaporation plane of the SWCNT absorber. We can tune the angle α by tuning the polarizer in the pump branch.

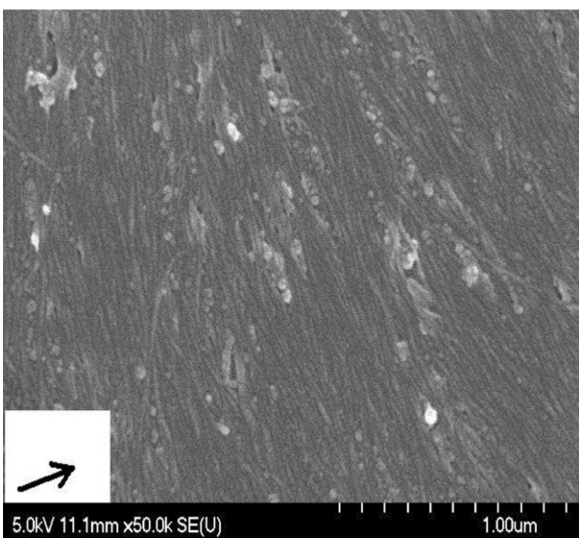

Fig. 8. SEM image of a SWCNT film on a glass substrate which is fabricated by vertical evaporation technique.

Fig. 7 shows the dependence of modulated probe signal on the input polarization angle α (the signal is from phase lock-in amplifier). Here the evaporation plane of the SWCNT absorber is parallel to the probe polarization. The angle α is between the pump polarization and the evaporation plane of the SWCNT. We could tune the angle α in the experiment by tuning the polarizer in the pump branch. Aligned SWCNT can show the polarization absorption characteristics. From Fig. 7 we considered that the SWCNTs in our absorber are aligned to some extent, which can help us get different modulation depths by rotating the SWCNT absorber.

Fig. 8 shows the SEM image of a SWCNT film on a glass substrate prepared by the vertical evaporation technique. The arrow corresponds to the evaporation direction. It is clear that many tubes are preferentially oriented vertical to the evaporation direction. The alignment of the carbon nanotubes has relation with the polarization characteristics in Figs. 6 and 7.

4. Conclusions

In summary, we presented in the work a vertical deposition method to fabricate SWCNT for the applications as saturable absorbers. We measured the nonlinear parameters of the absorber at 940 nm, which have not been reported by far. We demonstrated that such kind of SWCNT absorbers have some advantages, including large modulation depth as high as 10%, low non-saturable losses and adjustable modulation depth varied with polarization angle. Our studies showed that the transmission rate could be increased substantially by decreasing the SWCNT's concentration in the dispersion. Such a property of SWCNT could be useful as inexpensive saturable absorbers for mode locking applications in solid-state lasers.

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