Abstract: We characterize the saturable absorption of the second ($E_{22}$) electronic transition of a sample of single-walled carbon nanotubes and use it to mode-lock an ytterbium fiber ring laser. The modulation depth of $\sim 15\%$ was found to be similar to the corresponding $E_{11}$ transition ($\sim 13\%$), but the saturation intensity ($\sim 220$ MW cm$^{-2}$) about an order of magnitude larger ($\sim 10$ MW cm$^{-2}$). We achieved a 15 MHz mode-locked pulse train with an output pulse duration of 6.5 ps. For comparison we also demonstrate stable mode-locking on the $E_{11}$ transition, of the same nanotubes, with an erbium fiber ring laser, producing 1.1 ps pulses. Using the $E_{22}$ transition should enable the use of carbon nanotube saturable absorbers at shorter wavelengths than currently possible with the $E_{11}$ transition, which are limited by the smallest achievable nanotube dimensions.

Using the $E_{22}$ transition of carbon nanotubes for fiber laser mode-locking

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1. Introduction

The use of single-walled carbon nanotubes (SWNTs) as saturable absorbers for initiating and maintaining mode-locking has created wide interest [1–11], and fiber lasers utilizing SWNTs have been demonstrated at a range of operating wavelengths [9, 12–23]. This interest arises from the key properties of SWNTs for mode-locking lasers [6, 12]: sub-picosecond characteristic transition times; a high damage threshold; environmental stability; all-fiber integration. Combined, these properties make SWNTs competitive with conventional fiber mode-locking techniques such as nonlinear polarization evolution [24], or semiconductor saturable absorbers (SESAMs) [25, 26], and recent entrants such as graphene [27, 28].

The great majority of mode-locked lasers demonstrated use the fundamental ($E_{11}$) transition of semiconducting nanotubes, which corresponds to the single real gap in the electron density of states [29]. In contrast, only a few groups have reported saturable absorption and mode-locking of bulk lasers, using the second transition ($E_{22}$) [30, 31], corresponding to a pseudo-gap [29]. We recently expressly demonstrated that this transition can also be used to mode-lock fiber lasers [32], where the mode-locking dynamics differ from solid-state lasers, and larger modulation depths are required. It is of fundamental interest that

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Density of one-electron states

Valence band

Conduction band

Energy

EF E11 E22

Figure 1 (online color at www.lphys.org) Schematic of the levels involved in saturable absorption of E_{22}. E_F = Fermi level

Figure 2 (online color at www.lphys.org) Linear transmission spectrum of the carbon nanotube film used in the saturable absorption and mode-locking experiments. The wavelengths, at which the saturable absorption was measured, and mode-locking was achieved are shown by the red circles. The E_{11} and E_{22} transition absorptions are also indicated

(a)

(b)

Figure 3 (online color at www.lphys.org) (a) – overview of the Z-scan setup. (b) – close up of the Z-scan optics. CO – coupler, POW – power meter, SCF – small core fiber, SA – scanning arm, ATS – automated translation stage, R – reference, T – transmitted, L1 and L2 – focussing lenses, L3 – collection lens, and NT – nanotube sample

To further understand the potential use of the E_{22} transition, in this work, we report on detailed comparative measurements of the saturable absorption properties of both the E_{11} and E_{22} transitions in the same sample of highly-purified nanotubes, and realize a mode-locked ytterbium fiber laser operating at a wavelength of 1.06 μm. We also demonstrate an erbium fiber laser mode-locked on the E_{11} transition of the same set of nanotubes.

2. Nanotube sample

A transparent carboxymethylcellulose film with homogeneously dispersed individual SWNTs [35], was used as a saturable absorber. The same film already has been used in Er- and Tm- fiber lasers [9, 18]. In the Er case, a minimal pulse duration of 177 fs was achieved [9]. In the Tm case, the longest wavelength of operation was 1.9 μm [18]. The transmittance spectrum of this film is shown in Fig. 2. The clean two peaked spectrum is an indication of the purity of the nanotubes in the film, as the width of the absorption bands is related to the diameter distribution of the nanotubes. The absorption centered at 1.75 μm is due to the E_{11} transition, and was sufficiently broad to allow mode-locking at 1.55 μm. The peak around 1.0 μm is due to the E_{22} transition [36], even when taking into account excitonic effects [37].
3. Z-scan measurements

3.1. Experimental setup

The Z-scan setup is shown in Fig. 3. The pump light is passed through a fused fiber coupler to split 7% of the power to a reference power meter. The remaining power is then coupled into a small core, high NA fiber (Nufern UHNA 3), the output of which is imaged by a pair of identical aspheric lenses. An automated translation stage moves the sample arm and nanotube film through the focus. A third lens collects the light transmitted through the sample to a second power meter. To pump the $E_{11}$ transition we used an amplified mode-locked erbium fiber laser with a repetition rate of 14 MHz and pulse duration of 3 ps. For the $E_{22}$ transition we used a mode-locked ytterbium fiber laser followed by an amplifier and grating compressor system to produce 0.9 ps pulses at a repetition rate of 47.5 MHz. The resulting peak intensities at the Z-scan focus were approximately 125 MW cm$^{-2}$ and 2.6 GW cm$^{-2}$ for the $E_{11}$ and $E_{22}$ transitions respectively.

3.2. Results and discussion

The results of the Z-scan measurements are shown in Fig. 4. It should be noted that there is some uncertainty as to the accuracy of the intensity scale due to uncertainty in the exact pump pulse shape. The red fit curve is based on the instantaneous saturable absorption model:

$$\alpha(t) = \frac{\Delta\alpha}{1 + \frac{I(t)}{I_{sat}}} + (1 - \Delta\alpha).$$  \hspace{1cm} (1)

Due to the fact that for both the $E_{11}$ and $E_{22}$ transition the pump pulses are significantly longer than the transition lifetimes, by a factor of $\sim 8$ and $\sim 23$, respectively [34], the instantaneous model is appropriate. The normalized modulation depths ($\Delta\alpha$) of 13% and 15% for the $E_{11}$ and $E_{22}$ transitions, respectively, are very similar, however, the saturation intensities ($I_{sat}$) of $\sim 10$ MW cm$^{-2}$ and $\sim 220$ MW cm$^{-2}$ are different by an order of magnitude. This difference is expected, and can almost entirely
be accounted for, from the respective transition lifetimes of $\sim 400$ fs and $\sim 40$ fs [34].

The E\textsubscript{22} modulation depth ought to be sufficient to mode-lock a fiber laser, and the increased saturation intensity, although larger than the E\textsubscript{11} transition of nanotubes, and also of that of semiconductor saturable absorber mirrors (SESAMs), is still significantly smaller than required in nonlinear polarization rotation systems, and should not present a problem for fiber lasers.

4. Mode-locking results

4.1. Experimental setup

We constructed an erbium and ytterbium fiber ring laser to test mode-locking on both the E\textsubscript{11} and E\textsubscript{22} transitions. The experimental setups for the lasers are shown in Fig. 5. Both lasers were constructed from isotropic single-mode fiber. The polarization controllers were included to check the output pulse dependence on polarization state. The carbon nanotube films were sandwiched between two FC-APC connectors. In the ytterbium ring laser a fiber integrated circulator and chirped Bragg grating with a dispersion of 35.7 ps/nm were included to compensate for the normal dispersion of the other cavity components; due to this extremely high value the overall cavity dispersion was strongly anomalous. The erbium system was naturally anomalously dispersive and no compensation was required to operate in the soliton regime. The output coupler was 50% for the erbium laser and 15% for the ytterbium laser. In both setups exactly the same nanotube film was used.

4.2. Results and discussion

Both laser setups were self-starting upon reaching threshold, and mode-locking was maintained through approximately 10% tuning of the pump power. For increasing...
powers Q-switching was observed. The pulse trains exhibited no transient dynamics and remained stable with a single pulse per cavity round-trip during all experiments reported here. The polarization control had little effect on the pulse train and output characteristics.

Fig. 6 shows the results obtained with the erbium ring laser. The full width at half maximum (FWHM) of the second-harmonic intensity autocorrelator signal was 1.1 ps. From the close fit to a sech$^2$ pulse shape shown in Fig. 6, we deconvolve this to a pulse duration of 0.74 ps. No attempt was made to correctly tune the cavity dispersion and nonlinearity for short pulse operation, although that can lead to considerably shorter pulses [9]. The central wavelength of the pulse was 1.565 $\mu$m and the spectral width 3.16 nm. This leads to a measured time-bandwidth product close to 0.315, as expected for an unchirped sech$^2$ shaped pulse, indicating that we are indeed running in the soliton regime. From Fig. 2 it is clear that this laser was mode-locked using the short wavelength edge of the E$_{11}$ transition of the nanotubes.

Fig. 7 shows the results obtained with the ytterbium ring laser. For this system the FWHM autocorrelation duration was 10.1 ps, and the closely fitted sech$^2$ shape indicates a duration of 6.6 ps. Again, no attempt was made to fully dispersion compensate the cavity, rather the chirped Bragg grating ensured we were operating in the strongly anomalous regime. Full cavity dispersion compensation with bulk gratings or photonic band-gap fiber should lead to shorter pulse operation [14, 16]. The central laser wavelength was 1.066 $\mu$m and the spectral bandwidth was 0.19 nm. These values also correspond to a time-bandwidth product near to 0.315 indicating that this laser was also operating in the chirp free soliton regime. The average output power was 170 mW. The repetition rate of the laser was 15.2 MHz. The large spectral modulations observed in Fig. 7b are due to the very large third order dispersion of the chirped Bragg grating.

While the wavelength of the erbium laser clearly indicates it is operating on the E$_{11}$ transition (see Fig. 2), the ytterbium laser wavelength is too short for his transition and must be operating on the second absorption peak of the nanotubes, i.e. the E$_{22}$ transition. Despite this the laser exhibited similar qualitative behavior as the erbium system operating on the E$_{11}$ transition.

5. Conclusions

In conclusion we have characterized the saturable absorption properties of the E$_{11}$ and E$_{22}$ transitions of a high-purity film of single-wall carbon nanotubes. We found that the modulation depths were similar but the saturation intensity was one order of magnitude smaller for the E$_{11}$ compared to the E$_{22}$ transition. This is accounted for by the similar disparity in transition lifetimes. Mode-locking of a fiber laser was achieved on both transitions. The ability to saturate the fast E$_{22}$ transition raises a number of possibilities. Firstly, the larger transition energy of the E$_{22}$ level means that mode-locking at shorter wavelengths is viable, potentially into the visible spectral region. Secondly, because the electron falls to the E$_{11}$ level after E$_{22}$ excitation, the E$_{11}$ saturable absorption could be controllable via the E$_{22}$ transition. Finally, it may be possible to simultaneously mode-lock both transitions in a dual wavelength fiber laser.

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