Ultrashort pulse-generation by saturable absorber mirrors based on polymer-embedded carbon nanotubes

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Abstract: We demonstrate passive mode locking of solid-state lasers by saturable absorbers based on carbon nanotubes (CNT). These novel absorbers are fabricated by spin-coating a polymer doped with CNTs onto commercial dielectric laser-mirrors. We obtain broadband artificial saturable absorber mirrors with ultrafast recovery times without the use of epitaxial growth techniques and the well-established spin-coating process allows the fabrication of devices based on a large variety of substrate materials. First results on passive mode locking of Nd:glass and Er/Yb:glass lasers are discussed. In the case of Er/Yb:glass we report the to our knowledge shortest pulse generated in a self-starting configuration based on Er/Yb:bulk-glass: 68 fs (45 fs Fourier-limit) at 1570 nm wavelength at a pulse-repetition rate of 85 MHz.

OCIS codes: (140.7090) Ultrafast lasers; (160.4330) Nonlinear optical materials; (190.4710) Optical nonlinearities in organic materials; (230.4170) Multilayers.

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1. Introduction

Just a few years after the first demonstration of lasing action in a rod of ruby it was realized, that lasers could generate pulses much shorter than the round-trip time of the laser cavity when a specific dye was brought into the laser resonator. It was known that these dyes reveal an optical absorption that decreases with increasing optical energy flux. The introduction of such saturable absorbing dyes into the laser resonator forced the laser to operate in a pulsed- ('mode-locked') rather than in a continuous mode. Up to now a large variety of saturable absorbers for the ultrashort pulse generation were developed with properties much more suitable for the today's needs compared to these early dye-based absorbers.

For the ultrafast pulse-generation saturable absorbers with ultrafast recovery times are needed [1]. Up to date, artificial saturable absorbers for femtosecond pulse generation are mainly based on semiconductors (SESAM: semiconductor saturable absorber mirror) with ultrafast recovery times [2-4]. However, such absorbers have to be fabricated by very complex and costly processes such as metal-organic vapor-phase epitaxy (MOVPE) or metal-organic chemical vapor deposition (MOCVD) and further treatment is often required for reducing the recovery time of the absorbing layer [5]. Substrate removal is another technically challenging process that is required if the SESAM ought to be combined with a broadband dielectric or metallic mirror.

In recent years, several groups [6-9] have reported saturable absorption in carbon nanotubes (CNT) with ultrafast recovery times (~ 1 ps). With this new type of saturable absorbing material first mode locking of Er fiber lasers was soon demonstrated in 2003 [10]. For solid-state lasers, Q-switched mode locking using CNT solutions has been reported [11] but continuous mode locking with CNT-based absorbers has not yet been demonstrated.

For solid state lasers the requirements for the saturable absorbers (such as device uniformity, insertion loss, controllability of the saturable absorption and thermal durability) are usually more stringent and subtler than for fiber lasers, and those requirements seem to be very difficult to be met with conventional CNT materials made by the deposition of bundled and entangled CNTs. Recently, Sakakibara et al. [12] demonstrated that carbon nanotube-polymer composite materials are well suited for reproducible construction of mode locked Er fiber lasers and the generation of sub-200 fs from a fiber oscillator was demonstrated [13]. The merit of such CNT-polymer composite materials is that they can be fabricated as large area thin films with excellent optical uniformity and fine controllability of the saturable absorption. In addition, the CNTs in these materials can be suspended in an isolated state. This isolation seems advantageous for self-starting the mode locking process [1], because isolated CNTs have a long-lived (several picoseconds or more) saturation recovery component in addition to the ultrafast (~ 1 ps) saturation recovery component [14]. These properties of the CNT-polymer composite materials make them also well suited for mode lockers for solid-state lasers. In this paper we describe the fabrication of an artificial saturable absorber mirror

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structure based on such composite materials that can be used in similar ways as SESAMs, and we discuss our first applications of these novel CNT-based saturable absorber mirrors in various solid-state lasers based on Nd- and Er/Yb:glass.

2. CNT based saturable absorber mirrors

In order to be able to build a bulk laser in a similar configuration to a SESAM based cavity we developed reflective type saturable absorbers based on the above-mentioned CNT-polymer composite materials. Our current absorbers consist of commercially available dielectric mirrors based on TiO_2/SiO_2 on a fused silica substrate with a broad reflectivity bandwidth. These mirrors were coated with a thin layer (a few microns thick) of the CNT-polymer composite material by spin coating. For the polymers we used polyimide and carboxymethyl cellulose (CMC).

To achieve efficient saturation of the CNTs, the wavelength of the CNT absorption should coincide with the emission wavelength of the laser. Because the wavelength of the CNT absorption is a function of tube diameter [15], we adopted two types of CNT materials with different diameter distributions. With a mixture of slightly different nanotubes broad absorption bands can be realized. For 1.5 μm use, CNTs were prepared by the laser ablation method [16]. For 1.0 μm use, commercial CoMoCAT CNTs (SouthWest NanoTechnologies, Inc.) were purchased. Both CNTs were sonicated in solution and then mixed with polymer solutions. Figure 1 shows the absorption spectra of cast films made from these solutions. The amount of saturable absorption of each sample was controlled by the concentration of CNTs in the polymers and by the rotation speed of the spin coater. Thin single layers of CNT-polymers were coated onto the TiO_2/SiO_2 dielectric mirrors designed for use in Nd- and Er/Yb:glass based solid lasers.

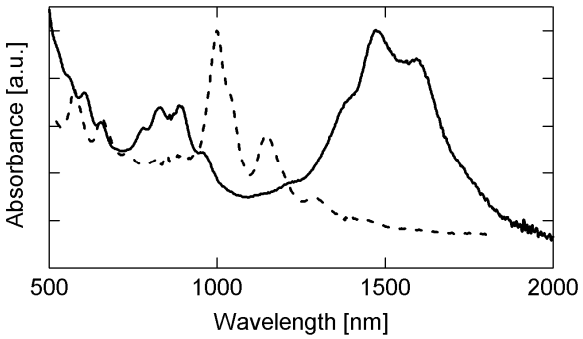

Fig. 1. Absorption spectra of the CNT-polymer composite films. Solid line: CNTs made by the laser ablation method were dispersed into polyimide for use in Er/Yb:glass lasers. Dashed line: CoMoCAT CNTs were dispersed into CMC for Nd:glass use.

Despite this technically simple fabrication process we obtain broadband, reflective type saturable absorber mirrors with ultrafast recovery-times. Thanks to the well-established spin-coating process high quality large area coatings onto a large variety of substrates become possible and samples in transmission, reflection or partially reflecting samples (‘output coupling absorbers’) can be obtained on a huge variety of optical surfaces. This technique might even allow for mode locking of monolithic cavities such as microchip lasers or non-planar ring oscillators (NPRO) by directly applying the coating to the laser crystal.

Owing to the excellent surface quality and durability of these spin-coated composite materials (particularly being true for polyimide), post-processing, such as applying anti-reflection (AR)-coatings or partial reflection (PR)- or high reflection (HR)-coatings on the spin-coated polymer layer, is possible. In cases where very thick absorber layers are required AR-coatings might be desirable to avoid interference effects between the polymer-air and polymer-mirror interfaces that could lead to strong variations of the dispersion of these

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saturable absorber mirrors comparable to a Gires-Tournois interferometer. AR-, PR- or HR-coatings might also be of interests to tailor the saturation properties of the absorber. Furthermore, such coatings might be of interests for applications, where the absorber layer is directly brought onto the surface of a laser crystal. In such cases, the laser crystal could serve as the heat sink for the absorbing layer. The direct coating of the laser crystal would allow very compact cavity designs, and no additional focusing on the absorber would be required as the laser mode is usually already tightly focused inside of the gain medium. For the experiments shown in the following we used absorbers without any additional AR- or HR-coatings. However, even without any such coatings we succeeded in generating sub-70 fs pulses at 1570 nm in a laser based on Er/Yb:glass as described in the next section. However, a protective coating might be required to passivate the polymer films and to protect the CNTs against atmospheric oxygen (see section 4 in this paper).

3. Ultrashort pulse generation in solid state lasers.

To test these absorbers in bulk lasers we have built several cavities based on Nd:glass (QX/Nd, Kigre Inc.) and Er/Yb:glass (QX/Er, Kigre Inc.). For both types of laser materials we chose astigmatic compensated X-fold cavities with an additional focus on one of the end mirrors, which was replaced by one of the CNT-based saturable absorber mirrors (see Fig. 2). In the case of the Er:glass laser, the focal spot on the saturable absorber was ~120 μm in diameter. This resulted in peak-intensities of about 35 to 700 MW/cm^2 depending on the pulse duration (68 fs – 2.3 ps) and the average intra-cavity power (0.5 – 3 W). To control the intra-cavity dispersion we could replace the mirror M3 by a GTI mirror (Gires–Tournois interferometer) if required. However, in the case of the Er:glass laser we obtained the shortest pulses without any such dispersion compensation since the laser glass provided sufficient anomalous dispersion at the emission wavelength to obtain soliton-like pulse shaping. The Er:glass laser was directly diode pumped by a pigtailed single transversal and single longitudinal-mode 980 nm laser diode (2900-series LD, JDS Uniphase Corp.). This diode delivered up to 500 mW of output power through a polarization maintaining fiber. However, due to the limited transmission of the coupling-mirror M1 and the collimating optics, only about 400 mW of pumping power were available at the position of the laser glass. The Nd laser was pumped by a tapered laser diode (Eagleyard photonics EYP-TPL-0808) that delivered up to about 1.5 W of pumping power at 805 nm wavelength in a near diffraction limited beam ($M^2 \approx 1.5$).

For both types of lasers (Nd:glass and Er/Yb:glass) we obtained very stable self-starting mode locking with pulse-durations in the fs and ps regimes. However, we achieved higher performance in the Er-based (68 fs) laser compared to the Nd-laser (~200 fs). In this report we shall therefore focus on the description of the Er-based laser.

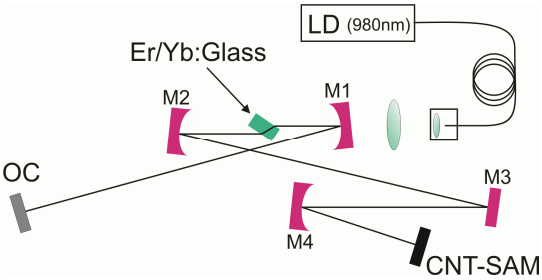

Fig. 2. Experimental setup of the Er/Yb:glass laser. OC: output coupler; M1-M4: standard Bragg-mirrors; CNT-SAM: Saturable absorber mirror based on carbon nanotubes; LD: pigtailed laser diode for pumping the Er/Yb:glass (QX/Er, Kigre Inc., 4.8 mm path-length).

The first sample we produced had a saturable absorption of about 0.4% and about 1-2% insertion loss. With this sample we already achieved reliable self-starting mode locking of the Er:glass laser shown in Fig. 2 with pulse-durations around 100 fs at 1560 nm with an average

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output power of ~10 mW from cavities with 90 MHz to 200 MHz fundamental pulse-repetition rates. In a 500 MHz cavity we observed thermal damage of the absorber due to the higher heat-load caused by the higher average power. For such high repetition rates we might therefore need to use substrates and mirror coatings with higher thermal conductivities compared to the present fused-silica mirrors and/or thermal conductivity-enhancing co-dopants in the polymer layer (see below).

In order to achieve even shorter pulse-durations we opted for a sample with higher saturable absorption. We achieved this by increasing the CNT concentration in the polyimide layer without changing its thickness. Due to the higher absorption of this sample the repetition rate could no longer be increased to 200 MHz. However, we obtained reliable and stable self-starting mode locking at 85 MHz pulse-repetition rates with intra-cavity powers around 1W. With this second sample we readily obtained shorter pulses. Without any extra-cavity chirp compensation we currently obtain pulse durations as short as 68 fs (45 fs Fourier limit) and spectra covering more than 200 nm at –30 dBc from the 85 MHz cavity shown in Fig. 3. This is the to our knowledge shortest pulse [17] generated in an Er/Yb:bulk-glass laser even though we didn't employ any intra- or extra-cavity dispersion compensation. It is interesting to note that these short pulses were obtained without the use of Kerr-Lens mode locking (KLM). This was made possible by the ultrashort recovery time of the CNTs. Currently the pulse-duration is limited by the reflectivity bandwidth (~1450-1700nm) and the resulting dispersion of the cavity mirrors. The sharp spike on the short wavelength side is due to the dispersion roll-off of those mirrors. With mirrors with a broader bandwidth even shorter pulses might be obtained with the very same saturable absorber layer.

As mentioned above one might want to increase the thermal conductivity of the polymer film by co-doping the polymer with thermally enhancing dopants or to increase the thermal conductivity of the substrate material in order to scale up the output power or the repetition rate of these lasers. For the third absorber we therefore co-doped the CNT-doped polymer with 50 wt% of alumina. With this absorber we succeeded in producing up to 80 mW of average output power from the same 85 MHz cavity in the single pulse regime. This value was solemnly limited by the available pumping power of 400 mW corresponding to an optical-to-optical quantum efficiency of more than 30 percent at an output-coupling ratio of 3%. We think that the combination of the alumina co-doping and the use of substrate materials with higher thermal conductivities will greatly increase the range of applications of these absorbers. However, even the current samples with alumina co-doped polyimide on a fused-silica substrates can already withstand several watts of power with spot sizes as small as 10^{-4} cm^2 corresponding to heating densities exceeding 0.5 MW/cm^3.

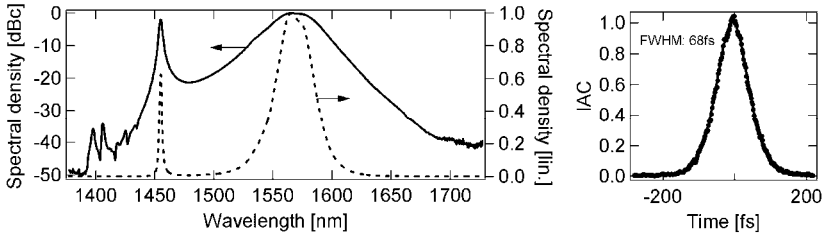

Fig. 3. Left side: Optical spectrum emitted by the Er:Yb:glass laser mode-locked by the CNT-based saturable absorber mirror on a linear (dotted line) and logarithmic (solid line) scale. The Fourier-limit of the spectrum corresponds to 45 fs. Right side: Background-free auto-correlation. The solid line is a sech^2 fit with a corresponding FWHM pulse-duration of 68 fs.

4. Long-term stability of CNT saturable absorbers

Due to the excellent adhesion and mechanical properties of the polyimide films we never observed de-lamination or cracking of the absorber layer nor could we find any limitations in the self-life. However, during the first experiments we observed a gradual reduction of the

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saturable loss in all of these samples. To investigate this issue we conducted some additional experiments.

Firstly, we operated the laser in the continuous-wave (cw) regime right below the mode-locking threshold for about 100 hours. Under these conditions we obtained nearly the same average optical power on the sample as in the mode-locked case. We therefore can assume that the heat-load on the sample was about comparable to the one during the mode-locked operation. To compensate slight misalignments of the laser-cavity and possible changes in the sample we used a PID-loop to control the laser's output power by adjusting the current of the pump-diode. After 100 hours of continuous operation we slightly increased the pump power to achieve mode-locked operation. However, we didn't find any significant difference between this pre-illuminated sample position and a non pre-illuminated position on the same sample. We therefore concluded that the heating due to the average power or the average intensity wasn't the cause for the slow degradation of the saturable absorption.

Next, we operated the laser with different pulse durations from 2.3 ps down to about 100 fs. In order to keep the average power on the sample constant we could either vary the intra-cavity dispersion or the position of the laser glass. If we, for instance, slightly moved the laser glass out of the focus in the X-fold cavity we obtained less non-linear phase-shifts, which lead to longer pulses at the same pulse energies. During these experiments, we found that the rate of the reduction of the saturable loss of the sample nonlinearly depends on the peak intensity on the absorber. Up to date we cannot yet fully identify the exact process of this degradation. However, we have reasons to believe that reactive oxygen $O_2(^1D_g)$ (also known as 'singlet oxygen') might destroy the CNTs. Singlet oxygen can be generated from atmospheric oxygen, which is usually in the much less reactive triplet state $O_2(^3S_g^-)$, by electronic energy transfer from photoexcited sensitizers. The required energy for this transition is approximately 94 kJ/mol, corresponding to roughly 1 eV/molecule. The energy of the photons of the laser at 1.55 μm is at about 0.8 eV per photon. Therefore, a multi-photon excitation of either the CNTs (for instance through excited-state absorption) or of the polymer or one of its additives (through multi-photon absorption) would be sufficient to convert a rather stable triplet oxygen molecule from the atmosphere into a highly reactive singlet oxygen molecule that might react with the CNTs.

To verify this assumption we blew a weak jet of nitrogen gas towards the sample. As soon as we used this nitrogen rich atmosphere we couldn't observe any degradation of the saturable absorption even under strong illumination intensities (75 fs pulses; corresponding to $0.5 \sim 1$ GW/cm^2 peak-intensities at 85 MHz pulse-repetition rate) over extended periods of time (>30 hours). This is a strong indication that the degradation was caused by the combination of multi-photon excitation and the presence of atmospheric oxygen. We found, that if at least one of these two factors is removed the samples do not show any degradation or ageing.

It is well known that gas molecules can penetrate and pass polymer films. Therefore, inorganic layers are often used to cover the polymer films in order to form gas barriers. Fortunately, an additional thin-film coating of dielectric materials on the surface of the polyimide absorber layer is possible due to the robustness and the high thermal durability of polyimide. Such a protective coating could simultaneously serve as an anti-reflection coating for the absorber. This finally paves the way towards robust and high performance artificial saturable absorbers based on polymer-embedded carbon nanotubes.

5. Conclusions

In conclusion we have introduced a novel type of artificial saturable absorber mirrors based on polymer-embedded carbon nanotubes. These mirrors can be produced in a much less costly way than the current sate-of-the-art semiconductor based saturable absorber mirrors (SESAM). Further, they enable the fabrication of new types of broadband saturable absorber mirrors with ultrashort recovery times without the requirement of the very challenging substrate-removal and ion-implantation processes. In this paper we demonstrated a few applications for these saturable absorber mirrors and we succeeded in producing 68 fs pulses

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at 1570 nm directly from a diode-pumped all-Bragg-mirror Er/Yb:glass laser. In the end we discussed the initial stability issues of these CNT-polymer based saturable absorber mirrors and we presented a way how to obtain long-term stable saturable absorber mirrors based on polymer-embedded carbon nanotubes.

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