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Efficient Mode-Locking of Sub-70-fs Ti:Sapphire Laser by Graphene Saturable Absorber

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The efficient passive mode-locking of a Ti:sapphire laser with a monolayer graphene saturable absorber is demonstrated for the first time. High-quality and large-area (1 in.) monolayer graphene, synthesized by chemical vapor deposition, exhibits ultrafast recovery times and excellent nonlinear absorption behavior for bulk solid-state laser mode-locking near 800 nm. The continuous-wave mode-locked Ti:sapphire laser generates 63-fs pulses with output powers up to 480 mW under stable operation at 99.4 MHz.

The saturable absorber (SA) has been widely employed as efficient intracavity passive mode-lockers for ultrashort pulse generation. Over the last two decades, the semiconducting saturable absorber mirror (SESAM) has been proven as a standard mode-locker in ultrafast solid-state lasers, and its applications have been extended to vertical cavity surface-emitting lasers (VECSELs),[1)] thin-disk lasers,[2)] and even gigahertz pulsed lasers.[3)] Although few-cycle pulse generation with a broadband SESAM has recently been demonstrated,[4)] the spectral applicability of multiple-quantum-well semiconductor heterostructure-based SESAMs was still limited because of the relatively narrow band coverage and the index mismatch of semiconducting materials. As an alternative, single-walled carbon nanotube-based saturable absorbers (SWCNT-SAs) have recently been qualified for a broadband mode-locking device for bulk and fiber lasers thanks to the intrinsic semiconducting transitions of SWCNTs distributed between 800 nm and 2.0 μm.[5–9)] However, the absorption range of this device is also limited by the diameters and chiralities of currently available SWCNTs.

Graphene, a two-dimensional lattice of sp^2-hybridized carbon atoms in a honeycomb structure, has pushed the frontier of ultrafast photonics and optoelectronics because of its unique properties.[10,11)] The linear dispersion relation between energy and momentum around the Dirac point makes this low-dimensional carbon nanostructure a point bandgap semiconductor.[12)] Graphene also possesses extraordinary nonlinearities and ultrafast recovery times of photoexcited electrons in the picosecond and femtosecond timescales.[13)] Such characteristics enable the use of graphene as an ultrafast saturable absorber in a practically unlimited ultrawide spectral range.

For the synthesis of few-layer graphene and its subsequent use as a saturable absorber, several exfoliation methods have been reported recently.[14–17)] However, the structural purities of such graphene SAs cannot be assured because of atomic defects that arise because these SAs undergo harsh processes such as ultrasonication or reduction from graphene oxide.[18)] This also restricts the dimensions of uniform monolayer graphene flakes to just a few tens of microns, which is comparable to or smaller than the beam size on the absorber within the laser cavity.

The fiber laser mode-locking based on chemical vapor deposition (CVD)-grown graphene SAs has been reported previously,[19,20)] but the SAs used consist of a few graphene layers that were not exactly defined and had uncontrollable layer numbers, leading to high linear and nonsaturable losses. In addition, their dimensions were also limited. Therefore, such devices are not appropriate for bulk solid-state laser mode-locking, which requires low intracavity losses. We have recently demonstrated the first femtosecond bulk laser mode-locking near 1.25 μm utilizing graphene SAs and generated pulses of ~100 fs.[21)] In this work, we present nonlinear optical characteristics such as the modulation depth and saturation fluence, and make a quality evaluation of the high-quality 1 in. monolayer graphene SA. The first graphene-SA mode-locked bulk solid-state laser near 800 nm, employing the widespread broadband gain medium Ti:sapphire, delivers sub-70 fs pulses with average powers up to 480 mW in stable mode-locked operation.

The monolayer graphene SA is fabricated by CVD and the transfer technique. The graphene layer is synthesized on a Cu film of 700 nm in thickness at 1000 °C using a methane/hydrogen gas mixture. After rapid cooling, 5 wt % poly(methyl methacrylate) (PMMA) in chlorobenzene is spin-coated on the grown graphene as a supporting material. Subsequently, high-quality monolayer graphene on PMMA is separated from the Cu film through wet etching in 0.5 M aqueous $FeCl_3$ and transferred onto a quartz substrate of 1 in. diameter. Finally, the PMMA layer is removed using acetone. Figure 1 shows the Raman spectrum of the monolayer graphene SA and the uniformity evaluation at ten different positions along the x-direction on the sample with an image of the fabricated graphene SA (inset). The D peak, which is usually observed in defective graphene, is almost suppressed, whereas both the G peak and 2D peak, indicating a symmetric E_{2g} mode at the Brillouin zone center and a second-order scattering mode of two zone-boundary phonons, clearly appear at the frequencies of ~1600 and ~2700 cm^{-1}, respectively. In particular, the undistorted 2D peak is a clear evidence of the presence of monolayer graphene, whereas the broad 2D peak of multilayer graphene generally results from a superposition of individual 2D peaks originating from multiple band structures.[22)] Across the whole absorber region, the intensity ratio of $I(G)/I(2D)$ is almost constant at ~0.87. This indicates that the whole 1 in. substrate is well coated with a high-quality monolayer graphene.

Figure 2 shows the linear transmission spectrum of the monolayer graphene SA exhibiting about 2.7% absorption at 800 nm, which deviates slightly from the theoretical value of

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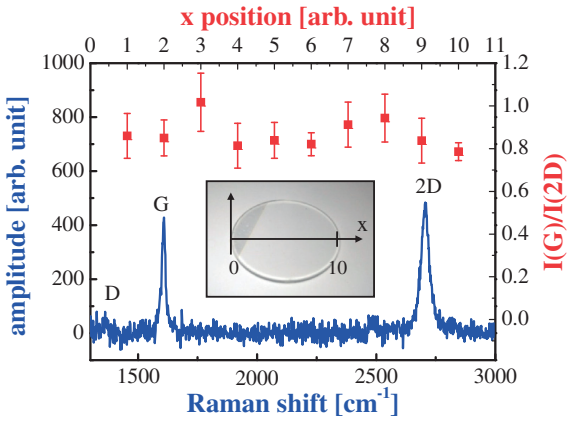

Fig. 1. Raman spectrum of monolayer graphene on quartz substrate and the amplitude ratios between the G peak and 2D peak at different locations (blue) in the sample along the *x*-axis. The photograph shows the monolayer graphene SA with the *x*-coordinate (inset).

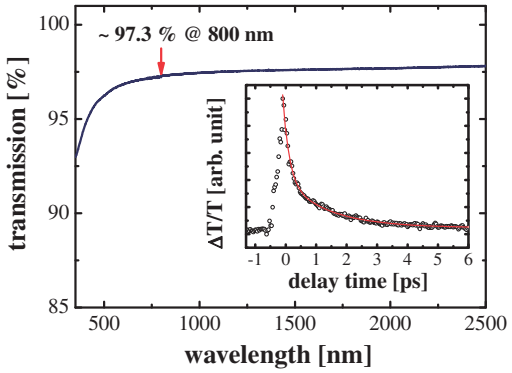

Fig. 2. Linear transmission spectrum and pump-probe trace of monolayer graphene SA with fit curve (inset).

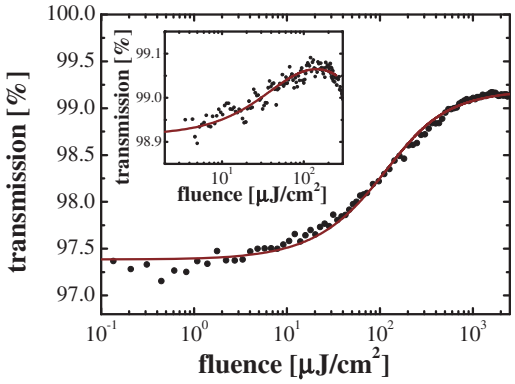

Fig. 3. Nonlinear transmission behaviors of monolayer graphene SA and SWCNT-SA (inset) measured at 800 nm.

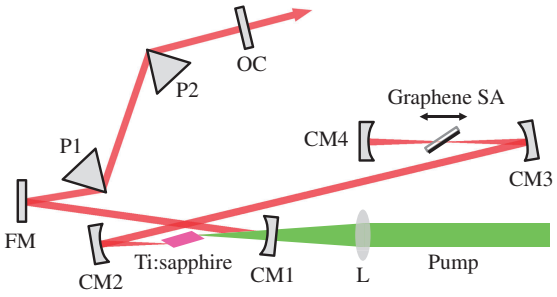

Fig. 4. Setup of the graphene-SA mode-locked Ti:sapphire laser. CM1, CM2, CM3, and CM4: concave mirrors with radius of curvature (ROC) = −100 mm; FM: folding mirror; P1, P2: SF10 prisms; OC: output coupler with 10% transmission.

universal absorption. The carrier relaxation dynamics in the monolayer graphene SA are characterized by time-resolved pump–probe measurements. As shown in the inset of Fig. 2, the nonlinear response of excited carriers comprises an instantaneous response of 203 fs and a slow $1/e$ recovery time of 1.47 ps, mainly associated with intraband carrier–carrier scattering and carrier relaxation with hot optical phonon cooling through the interband, respectively.[13] The nonlinear response times estimated are comparable to those of SESAMs and SWCNT-SAs.[4,6]

Other important nonlinear saturation characteristics such as the saturation fluence, modulation depth, and nonsaturable loss are measured by high-resolution nonlinear transmission experiments at 800 nm. It is known that the two-photon absorption (TPA) coefficient is two orders of magnitude smaller for monolayer graphene than for bilayer graphene. No significant sign of any induced nonlinear absorption is observed in our monolayer graphene SA near 800 nm at high fluences, as shown in Fig. 3, whereas a rollover of transmission is seen clearly in the SWCNT-SA at fluences exceeding 200 μJ/cm^2 (inset of Fig. 3), which is obviously caused by TPA.[5] From the fit to the data, we obtain a modulation depth of 1.8%, a saturation fluence of 66.5 μJ/cm^2, and a nonsaturable loss of <0.9% for the graphene SA. These values are comparable to those of other SAs that are often used for bulk laser mode-locking. Note that the value of the nonsaturable loss is the lowest, ever reported for graphene SAs, and therefore enables the application of our SA for high-power laser mode-locking.

To demonstrate bulk laser mode-locking utilizing the monolayer graphene SA near 800 nm, we adopt a similar resonator configuration to that previously used for SWCNT-SA mode-locking.[5] As depicted in Fig. 4, a Brewster-cut rod-type Ti:sapphire crystal (4 mm in length) is mounted in a water-cooled copper block and pumped using a continuous-wave (CW) optically pumped semiconductor laser (Coherent Verdi OPSL G5) operating at 532 nm with a maximum output power of 5 W. Two dielectric mirrors with a radius of curvature (ROC) of −100 mm are arranged in a folding angle to compensate the astigmatic aberration. The graphene SA is placed under Brewster's angle near the focus of the second folding cavity formed by two highly reflecting concave mirrors with the same ROC. Note that graphene only reflects <0.1%, and therefore the surface reflection loss of the SA can be neglected. The beam waist on the SA is varied between 30 and 70 μm by moving the sample position along the beam propagation axis. For dispersion compensation in the resonator, an SF10 prism pair is inserted in a separation of 16 cm into the shorter arm containing the output coupler with 10% transmission.

Figure 5 shows the output power versus the incident pump power. A slope efficiency of about 21% is obtained. The

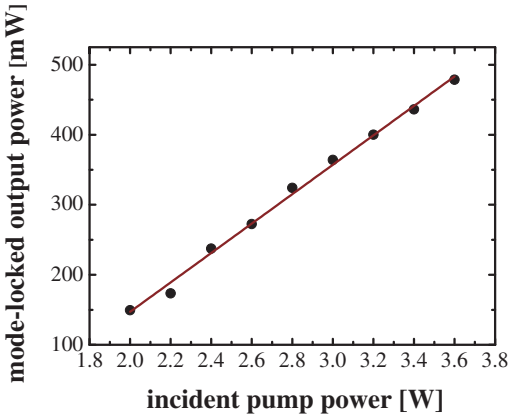

Fig. 5. Output power from the monolayer graphene-SA mode-locked Ti:sapphire laser versus incident pump power.

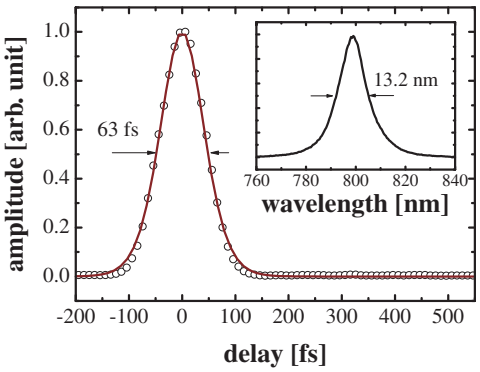

Fig. 6. Autocorrelation trace of the monolayer graphene-SA mode-locked Ti:sapphire laser and the corresponding optical spectrum (inset).

mode-locking first starts at an output power of 150 mW with 2.0-W pumping, because the energy fluence on the SA is not sufficient for saturable absorption to be reached in the absorber with pumping below 2.0 W when a 10% output coupler is used. A maximum average output power of up to 480 mW is achieved at 3.5-W pumping. The mode-locking is self-starting or easily initiated in the whole power range above the threshold by slightly tipping the absorber. The Ti:sapphire laser operates stably for several hours in the mode-locked regime. No damage or degradation of the graphene SA is observed.

Figure 6 shows the autocorrelation trace of the graphene-SA mode-locked pulses with the corresponding laser spectrum (inset). The second harmonic generation from a 0.1-mm-thick type-I BBO crystal is used for intensity autocorrelation. The pulse duration and spectral bandwidth are measured to be 63 fs and 13.2 nm, respectively, where a sech^2-shaped pulse is assumed. The time-bandwidth product of 0.389 leads to nearly Fourier-transform-limited pulses. Figure 7 shows the measured radio frequency (RF) spectrum of the graphene SA mode-locked pulses. The high extinction ratio of 65.4 dBc at the fundamental beam note of 99.4 MHz in a 400-kHz span with 1-kHz resolution bandwidth depicts

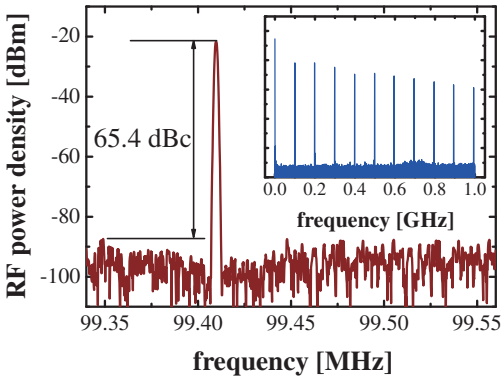

Fig. 7. Recorded RF spectrum at fundamental beam note and at 1 GHz span (inset) in the mode-locked regime.

stable CW mode-locked operation without any Q-switching modulation or multiple pulsing. The inset of Fig. 7 shows the recorded RF spectrum at a 1-GHz span.

In conclusion, a high-quality monolayer graphene was grown by CVD and transferred onto a 1 in. transparent substrate in order to fabricate an ultrafast passive mode-locking device applicable in bulk lasers. The Raman spectra measured at different positions of the SA indicate the high quality and uniformity of the monolayer graphene. We have demonstrated for the first time the monolayer graphene-SA mode-locking of a Ti:sapphire laser delivering the shortest pulses (63 fs) ever achieved with graphene SAs, and with average output powers as high as 480 mW at 99.4 MHz. Despite a 2.7% linear loss at the laser operation wavelength, the sufficient modulation depth of the monolayer graphene SA leads to a low nonsaturable loss and enables the achievement of efficient bulk laser mode-locking.

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1) S. Hoogland *et al.*: IEEE Photonics Technol. Lett. **12** (2000) 1135.
2) S. V. Marchese *et al.*: Opt. Express **16** (2008) 6397.
3) A. E. H. Oehler *et al.*: Opt. Express **16** (2008) 21930.
4) I. D. Jung *et al.*: Opt. Lett. **22** (1997) 1009.
5) I. H. Baek *et al.*: Opt. Express **19** (2011) 7833.
6) A. Schmidt *et al.*: Opt. Express **17** (2009) 20109.
7) W. B. Cho *et al.*: Opt. Lett. **33** (2008) 2449.
8) W. B. Cho *et al.*: Opt. Lett. **35** (2010) 2669.
9) W. B. Cho *et al.*: Opt. Express **17** (2009) 11007.
10) A. K. Geim: Science **324** (2009) 1530.
11) F. Bonaccorso *et al.*: Nat. Photonics **4** (2010) 611.
12) A. H. C. Neto *et al.*: Rev. Mod. Phys. **81** (2009) 109.
13) H. Wang *et al.*: Appl. Phys. Lett. **96** (2010) 081917.
14) D. Popa *et al.*: Appl. Phys. Lett. **97** (2010) 203106.
15) Y.-W. Song *et al.*: Appl. Phys. Lett. **96** (2010) 051122.
16) W. D. Tan *et al.*: Appl. Phys. Lett. **96** (2010) 031106.
17) J.-L. Xu *et al.*: Opt. Lett. **36** (2011) 1948.
18) E. Y. Polyakova *et al.*: ACS Nano **5** (2011) 6102.
19) Q. Bao *et al.*: Adv. Funct. Mater. **19** (2009) 3077.
20) Q. Bao *et al.*: Nano Res. **4** (2011) 297.
21) W. B. Cho *et al.*: Opt. Lett. **36** (2011) 4089.
22) A. C. Ferrari *et al.*: Phys. Rev. Lett. **97** (2006) 187401.