Large Energy Pulse Generation Modulated by Graphene Epitaxially Grown on Silicon Carbide

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ABSTRACT Graphene grown by thermal decomposition of a two-inch 6H silicon carbide (SiC) wafers surface was used to modulate a large energy pulse laser. Because of its saturable absorbing properties, graphene was used as a passive Q-switcher, and because of its high refractive index the SiC substrate was used as an output coupler. Together they formed a setup where the passively Q-switched neodymium-doped yttrium aluminum garnet (Nd: YAG) crystal laser was realized with the pulse energy of 159.2 nJ. Our results illustrate the feasibility of using graphene as an inexpensive Q-switcher for solid-state lasers and its promising applications in integrated optics.

KEYWORDS: graphene · laser · Q-switcher · composites

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raphene possesses layers of carbon atoms forming honeycomb crystal lattices and a twodimensional structure, which determines unique promising characteristics such as electronic, topological, and optical properties, etc.,¹⁻⁵ and shows promising applications in high speed electronic devices based on its high mobility of electrons.^{6–11} Different from traditional semiconductors, graphene is a zero-bandgap material. Recently, it was found that, beside its linear absorbing property, this material also possesses nonlinear absorption due to the filled states by the electrons and holes in both the conduction and valence bands near the Dirac points when it is pumped by highintensity optical power, which generates its saturable absorbing properties.^{5,12} Unlike the traditional saturable absorbers, including Cr:YAG, semiconductor saturable absorber mirrors (SESAM), and GaAs, graphene is wavelength insensitive. With graphene as a mode-locker, Bao et al.⁵ and Sun et al.12 demonstrated mode-locked fiber lasers and Tan et al.¹³ reported a modelocked ceramic neodymium-doped yttrium aluminum garnet (Nd:YAG) laser with the pulse width of 4 ps, which showed promising applications in ultrafast lasers.

Beside mode-locking, Q-switching is another technology to generate a pulse with

short pulse width and high peak power. Compared with mode-locking, Q-switching can obtain a laser with much larger pulse energy (generally, 2 or 3 orders of magnitude). In this field, the passive Q-switching has a compact and simply structure and is easily operated. This technique is of practical importance in many areas, such as industry, medicine, military applications, and basic scientific research, where compact, reliable, and cost-effective nanosecond pulsed lasers are required. The passive Q-switcher is a necessary component, and its saturation intensity is one of the deterministic parameters that determines the performance of Q-switched laser and its applications. Graphene has a saturation intensity of about 0.7 MW cm⁻², 1 order of magnitude lower than SESAM.⁵ On the basis of the analysis by Keller,^{14,15} the low saturation intensity is favorable for a passive Q-switcher.

In the passive mode, the heat in the Q-switcher is great due to the absorbing of the laser during the switching. Recently, Balandin et al. reported a thermal conductivity of single-layer graphene of 5.3×10^3 W/mK.¹⁶ Therefore, the thermal character of graphene's substrate becomes crucial. Fortunately, the graphene can grow from the silicon carbide (SiC) which has excellent properties. Motivated by the reasons shown above, we propose that the graphene grown from a SiC substrate can be used as a passive Q-switcher just like SESAM which has been indentified as an excellent modelocker and Q-switcher. In this paper, we demonstrate the passively Q-switched Nd: YAG lasers with graphene grown from SiC as a passive Q-switcher. Considering its high refractive index, SiC was also used as an output coupler (OC) in the laser process.

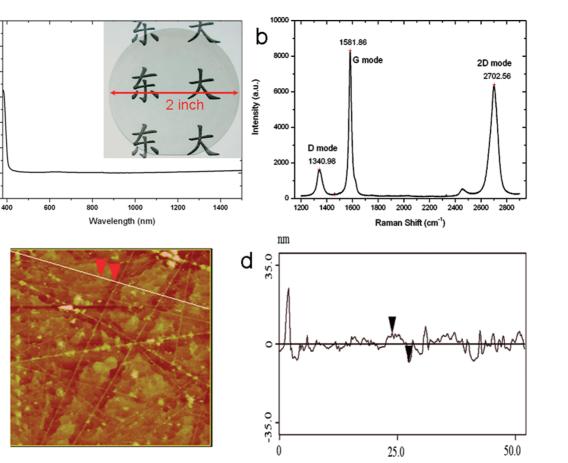


Figure 1. (a) Absorbance of graphene epitaxial grown on a SiC wafer. The inset shows a photograph of graphene sample; (b) Raman spectra of graphene sheet; (c) morphology of graphene obtained with AFM; (d) typical variation of the graphene height.

RESULT AND DISCUSSION

а

Absorbance

5

3

2

0

С

Graphene Q-Switcher. The linear absorption of a graphene sample epitaxial grown on a SiC substrate is presented in Figure 1a. Similar to the results reported by Tan et al.,¹³ the absorption of graphene is little wavelength dependent owing to its zero bandgap. The inset of Figure 1 a shows a photograph of the graphene on the 2-in. SiC. With a 532 nm laser, a typical Raman spectrum was achieved and plotted in Figure 1b. The D, G, and 2D modes are located at 1340.9, 1581.8, and 2702.5 cm⁻¹, respectively. The ratio of the intensities of G and D modes is about 5, which indicates that the graphene is disordered. Although the full width of half-maximum (fwhm) of 2D mode is 56 cm⁻¹, broader than one monolayer, it is still almost fitted by a single Lorentzian line shape, which implies that the grown graphene has similar electronic behavior to the single layers.11,17

With an atomic force microcopy (AFM), the morphology of graphene was achieved and shown in Figure 1c. From this figure, it can be found that the graphene shapes flakes. The typical variety of the graphene height is presented in Figure 1d. With the height change, we found that the layers of graphene were changeable from 10 to 40 layers. Because its saturable absorbing property changes with the layers numbers, the changeable layers are favorable for optimization of Q-switching operations.

Passively Q-Switched Laser. The laser experimental setup is sketched in Figure 2a, and its detailed description is shown in Methods. With a SiC wafer as OC, the continuous-wave (cw) Nd:YAG laser was achieved, which is shown in Figure 2b. The maximum output power is 2.01 W with a corresponding optical efficiency of 12% and slope efficiency of 20%. The cw laser output proved that the gain of Nd:YAG is sufficient. Replacing the SiC wafer with a graphene OC, the passively Q-switched Nd:YAG laser was observed when the pump power was above the threshold. The variation of the output power with incident pump power is also shown in Figure 2b. It can be found that the output power almost linearly increased with the rise of incident pump power. The threshold is measured to be 8.28 W, and the maximum output power is 105 mW at the pump power of 16.5 W. On the basis of the analysis on graphene,⁵ it can be found that absorption is increased by 2.3%. We believed that the large loss of graphene combined with the large transmission of SiC generated the large

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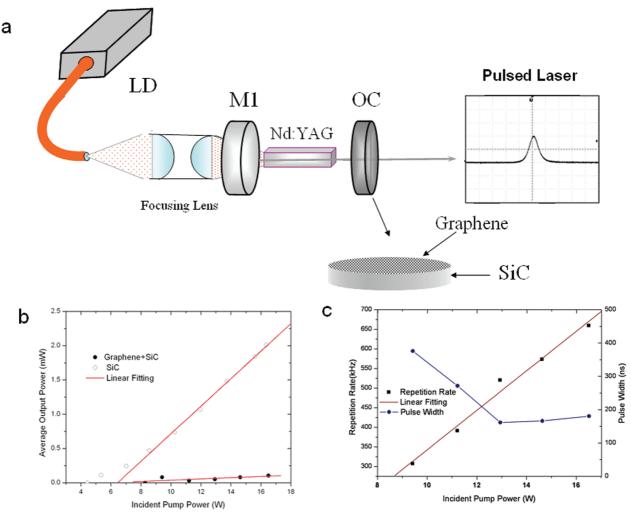


Figure 2. (a) Experimental setup of Nd:YAG pulsed lasers; (b) output power with the increase of incident pump power; (c) repetition rate and pulse width with the increase of incident pump power.

threshold (about 8.28 W) and low maximum output power.

With a digital oscilloscope, the pulse width and repetition rate of the passively Q-switched laser were measured. The dependence of the repetition rate and pulse width on the incident pump power is shown in Figure 2c. It is observed that the repetition rate almost linearly increases with increasing pump power, which agrees well with the passive Q-switching theory with a Cr:YAG as the saturable absorber.¹⁸ The maximum frequency is 660 kHz at a pump power of 16.5 W and the shortest pulse width is 161 ns at a pump power of 12.9 W. By the average output power and repetition rate, the pulse energy can be calculated. The maximum pulse energy is 159.2 nJ under the pump power of 16.5 W. The pulse energy is two orders higher than those obtained with graphene as a mode-locker.^{5,12,13} The display of the digital oscilloscope of the cw laser given in Figure 3a, shows that there is no pulse existing. The pulse profiles under the pump powers of 11.2, 12.9, 14.6, and 16.5 W are also shown in Figure 3 panels b, c, d and e, respectively. From this figure, it can also be observed that there is no mode-locking. It should be noted that there is no thermal damage observed on the graphene sample during the passively Q-switched laser operation, and after 20 min the output power instability of the Q-switched laser is less than 3% under the incident pump power of about 16 W. By the optical spectrum analyzer, the laser spectrum wavelength was found to be centered at 1064 nm.

CONCLUSIONS

Bao *et al.*⁵ proved that the modulation depth of graphene decreases with the increase of its layers due to the increased nonsaturable loss induced by enhanced scattering of graphene multilayers. By comparing our results with the results reported by them,⁵ we conclude that the modulation depth of the graphene used in the present experiment is less than 6%, and it can be believed that a much better result can be achieved by using a graphene with much fewer lays. We also proposed that an optimized Q-switching can be achieved if a microchip laser gain is used and the surface of SiC is suitably coated. Our results demonstrate

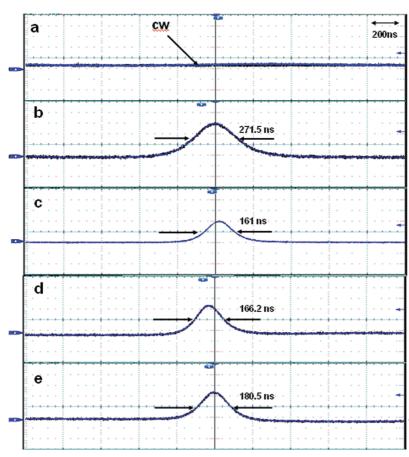


Figure 3. (a) Display of cw laser recorded by a digital oscilloscope. Q-switched pulse profile at a (b) width of 271.5 ns under the pump power of 11.2 W; (c) width of 161 ns under the pump power of 12.9 W; (d) width of 166.2 ns under the pump power of 14.6 W; (e) width of 180.5 ns under the pump power of 16.5 W.

that graphene is suitable to be used as a Q-switcher for solid-state lasers, and its easy fabrication and small-

ness in size show its promising applications in integrated optics.

METHODS

Material Preparation. The graphene used in the experiments is grown by thermal decomposition of a SiC surface at high temperatures of 1500–1600 °C. The SiC substrates used in this study were two-inch 6H-SiC wafers. By this technique, the layers of graphene can be controlled from a few to tens, and their structures and electronic properties are similar to those achieved by micromechanical cleaving techniques.^{10,19,20}

Laser Design. Based on the analysis by Keller¹⁴ and Haus,²¹ the condition for the Q-switching can be expressed as

$$\frac{\mathrm{d}R}{\mathrm{d}I}\Big|/\frac{T_{\mathrm{R}}(r-1)}{\tau}\tag{1}$$

where *R* is the absorber reflectivity, *I* is the laser intensity on absorber, T_R is the cavity round trip time, *r* is the pump parameter that determines how many times the laser is pumped above threshold, and τ is the upper state lifetime of the laser materials. Because *R* almost would not change with laser intensity and rise to a constant when the laser intensity becomes larger than the saturation one, the small saturation intensity determines the large slope |dR/dt|. Therefore, it can be derived that, in order to obtain optimized Q-switching, the selection should be a small saturation intensity determining a shorter T_{Rr} and a laser material with a long upper state lifetime τ .

During the laser experiments, Nd:YAG crystal has a Nd concentration of 1.1 atom %, and upper state lifetime of 230 μs was used as the gain material. It was cut to dimensions of 3 mm \times 3 mm \times 6 mm along its (111) direction. Its end-faces were polished but not coated. The cavity with the length of 1 cm was used corresponding a T_R of 67 ps.

The laser experimental setup shown in Figure 2 a is based on a simple plano-concave resonator. The concave input mirror M1 has a radius of curvature of 100 mm, and is AR coated at 808 nm on the flat face; and high-transmission (HT) coated at 808 nm, high-reflection coated at 1064 nm on the concave face. To remove the heat generated by the Nd:YAG under high pump power levels, the Nd:YAG was wrapped with indium foil and mounted on a water-cooled copper block. The temperature of the cooling water was controlled at 15 °C. The laser output power was measured by a power meter (EPM 2000, Molectron, Inc.), and temporal behaviors of the Q-switched laser were recorded by a TGS 3052 digital oscilloscope (500-MHz bandwidth and 2.5-Gs/s sampling rate, Tektronix, Inc.). With an optical spectrum analyzer (HR4000CG-UV-NIR, Ocean Optics, Inc.), their laser spectra were achieved.

Considering the high refractive index of SiC (n = 2.6), its reflectivity is calculated to be about 20% at the fundamental wavelength when the laser is normally incident on its face. If an output coupler (OC) is added behind SiC, there will be a Fabry–Perot (F-P) resonator generated between the face of SiC wafer and OC, which may induce the instability and lower the output power. Because the emission cross-section of Nd:YAG



is high, we believed that the laser gain can overcome the high transmission of SiC and the loss generated by graphene, and the SiC wafer was used as an OC.

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REFERENCES AND NOTES

- Nair, R. R.; Blake, P.; Grigorenko, A. N.; Novoselov, K. S.; Booth, T. J.; Stauber, T.; Peres, N. M. R.; Geim, A. K. Fine Structure Constant Defines Visual Transparency of Graphene. *Science* **2004**, *320*, 1308.
- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature (London)* **2005**, *438*, 197–200.
- Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. *Nature (London)* 2009, 457, 706–710.
- Dujardin, E.; Thio, T.; Lezec, H.; Ebbesen, T. W. Fabrication of Mesoscopic Devices from Graphite Microdisks. *Appl. Phys. Lett.* 2001, *79*, 2474–2476.
- Bao, Q. L.; Zhang, H.; Wang, Y.; Ni, Z. H.; Yan, Y. L.; Shen, Z. X.; Loh, K. P.; Tang, D. Y. Atomic-Layer Graphene as a Saturable Absorber for Ultrafast Pulsed Lasers. *Adv. Funct. Mater.* 2009, 19, 3077–3083.
- Liang, G.; Neophytou, N.; Nikonov, D. E.; Lundstrom, M. S. Performance Projections for Ballistic Graphene Nanoribbon Field-Effect Transistors. *IEEE Trans. Electron Devices* 2007, 54, 677–682.
- Williams, J. R.; DiCarlo, L.; Marcus, C. M. Quantum Hall Effect in a Gate-Controlled p-n Junction of Graphene. *Science* 2007, 317, 638–641.
- Gu, G.; Nie, S.; Feenstra, R. M.; Devaty, R. P.; Choyke, W. J.; Chan, W. K.; Kane, M. G. Field Effect in Epitaxial Graphene on a Silicon Carbide. *Appl. Phys. Lett.* **2007**, *90*, 253507.
- Rana, F. Graphene Terahertz Plasmon Oscillators. *IEEE Trans. Nanotechnol.* 2008, 7, 91–99.
- Dawlaty, J. M.; Shivaraman, S.; Chandrashekhar, M.; Rana, F.; Spencer, M. G. Measurement of Ultrafast Carrier Dynamics in Epitaxial Graphene. *Appl. Phys. Lett.* **2008**, *92*, 042116.
- Choi, D.; Choi, M.; Choi, W. M.; Shin, H. J.; Park, H. K.; Seo, J. S.; Park, J.; Yoon, S. M.; Chae, S. J.; Lee, Y. H.; *et al.* Fully Rollable Transparent Nanogenerators Based on Graphene Electrodes. *Adv. Mater.* **2010**, *22*, 2187–2192.
- Sun, Z.; Hasan, T.; Torrisi, F.; Popa, D.; Privitera, G.; Wang, F.; Bonaccorso, F.; Basko, D. M.; Ferrari, A. C. Graphene Mode-Locked Ultrafast Laser. ACS Nano. 2010, 4, 803–810.
- Tan, W. D.; Su, C. Y.; Knize, R. J.; Xie, G. Q.; Li, L. J.; Tang, D. Y. Mode Locking of Ceramic Nd:Yttrium Aluminum Garnet with Graphene as a Saturable Absorber. *Appl. Phys. Lett.* 2010, *96*, 031106.
- Keller, U. Recent Developments in Compact Ultrafast Lasers. *Nature (London)* 2003, 424, 831–838.
- Keller, U. Semiconductor Saturable Absorber Mirrors (SESAM's) for Femtosecond to Nanosecond Pulse Generation in Solid-State Lasers. *IEEE J. Sel. Top. Quantum. Electron.* 1996, 2, 435–453.
- Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett.* **2008**, *8*, 902–907.
- Latil, S.; Meunier, V; Henrard, L. Massless Fermions in Multilayer Graphitic Systems with Misoriented Layers: *Ab Initio* Calculations and Experimental Fingerprints. *Phys. Rev. B* 2007, *76*, 201402.
- Zhang, X.; Zhao, S.; Wang, Q.; Zhang, Q.; Sun, L.; Zhang, S. Optimization of Cr⁴⁺-Doped Saturable-Absorber Q-Switched Lasers. *IEEE J. Quantum Electron.* 1997, 33, 2286– 2294.

- Berger, C.; Song, Z.; Li, X.; Wu, X.; Brown, N.; Naud, C.; Mayou, D.; Li, T.; Hass, J.; Marchenkov, A. N.; *et al.* Electronic Confinement and Coherence in Patterned Epitaxial Graphene. *Science* **2006**, *312*, 1191–1196.
- Ohta, T.; Bostwick, A.; Seyller, T.; Horn, K.; Rotenberg, E. Controlling the Electronic Structure of Bilayer Graphene. *Science* 2006, *313*, 951–954.
- 21. Haus, H. A. Parameter Ranges for CW Passive Mode Locking. *IEEE J. Quantum Electron.* **1976**, *12*, 169–176.