Optimizing and Applying Graphene as a Saturable Absorber

Jonah Miller

Defense Fall 2011

1 Background

Over the last decade, a variety of exciting applications have been found for lasers that generate ultra-short pulses of light with durations of just a few femtoseconds [1]. Optical frequencies [2, 3], atomic and molecular spectra, lengths, distances [4], and displacements [5] are nowadays routinely measured with femtosecond lasers, or fs-lasers. Optical coherence tomography using fs-lasers as light sources can achieve noninvasive, in-vivo 3D imaging of the human retina, epidermis, and blood vessels, with resolutions comparable to what can be obtained from histological samples [6]. Optical frequency combs produced by fs-lasers are a key technology for probing and manipulating the quantum state of atoms and molecules [7], as well as for exciting or probing electronic processes in solids and novel nanomaterials (such as carbon nanotubes) [8]. Femtosecond lasers have even found their way to astrophysics [9, 10, 11], where they are used to calibrate spectrometers. Such calibration allows measurements of Doppler shifts of stellar objects with unprecedented accuracies of 1 cm/s. In high-energy physics, ultrashort lasers are not only interesting candidates for timing synchronization in large-scale accelerators [12], but they will likely play an important role in generating ultra-bright, coherent X-ray pulses in free-electron laser facilities—a tool that could bring several generations worth of improvements to precision spectroscopy at very high energies.

Optical pulses of such short duration are obtained from passively mode-locked lasers—that is, lasers in which the longitudinal standing electromagnetic waves in the laser cavity, or "modes," are locked into phase with each other [13]. An optical cavity, which in its simplest form is a pair of parallel mirrors facing each other, allows only an integer number of wavelengths in a standing wave inside it. The number of wavelengths in specific wave is known as the wave, or mode, number. All allowed waves can exist in a cavity at once, and without mode-locking, their relative phase oscillates such that they interfere with each other and average out to a constant intensity. However, when a laser is mode-locked, this phase is fixed such that the modes all constructively interfere with each other at regular intervals, producing extremely short high-intensity pulses, and destructively interefere with each other to "cancel out" at all other times. [13] A laser can be mode-locked by placing a material inside

the laser cavity that absorbs light at low intensities, but allows higher intensity light to pass right through with low absorption; such a material is called a saturable absorber. When a laser is not mode-locked, the intensity of the light that bounces around the cavity is unstable and it can fluctuate by about 3% of the total output power. These are the fluctuations that start the mode-locking process. When a saturable absorber is placed in the cavity, it will attenuate the higher intensity fluctuations to a lesser degree than the lower intensity ones. After many such attenuations, the low intensity fluctuations are absorbed away entirely and a pulse train forms. Even then, the saturable absorber improves the pulses. For each pulse, the low-intensity leading and trailing parts of the pulse or fluctuation are attenuated more strongly than the high intensity pulse center; making the newly formed pulses shorter and shorter over several iterations until a pulse-width of just a few femtoseconds is attained [13].

2 Goals

A semiconductor saturable absorber is usually opaque, but becomes transparent after it has absorbed a certain amount of energy (usually in the form of light). After it has absorbed this prerequisite amount, it cannot absorb any more energy until it emits energy and loses its saturation. This is where the term saturable absorber comes from. This property comes from the molecular structure of the material and the quantum interactions between its electrons. As a saturable absorber absorbs light, its electrons enter into an excited state—i.e., they transition from the valence band in the material to the conduction band. Later this electron relaxes back down to its ground state by emitting a photon—either through phosphorescence or stimulated emission. When the electron populations of the excited and non-excited states of the material are equal, we reach a steady-state between electrons becoming excited through absorption and relaxing through stimulated emission, and the saturable absorber effectively ceases to absorb more light. Usually, a semiconductor can only absorb a specific color of light because there is an energy gap between the set of unexcited states, the valence band, and the set of excited states, the conduction band. This energy gap is known as the bandgap. If the energy associated with an incident photon is less than the energy associated with the bandgap, the material won‘t absorb the photon. Thus, since different wavelengths of light are associated with different energies, only specific colors of light are able to make an electron "jump" the bandgap of a particular semiconductor and absorb into it.

My work is focused on finding the ideal growth parameters to produce synthetic, single atomic layer graphite, or graphene, as a semiconductor saturable absorber, then later apply the graphene as a novel saturable absorber in a laser cavity. Graphene is a zero bandgap material with a conical band structure. Because it has a zero band gap, graphene can absorb any color of light, which makes it a broadband saturable absorber [14, 15, 16]. My goals are twofold. First, I want to produce graphene that is ideal for use as a semiconductor saturable absorber, as opposed to electronic applications, where a bandgap is desirable. We can produce graphene by growing it on copper foils through a technique known as chemical vapor deposition (CVD). At high temperatures, copper catalyzes the breakdown of methane gas so that the carbon in the methane deposits on the copper foils and the hydrogen passes

by. This process is self limiting: we always get a single layer of carbon atoms (a graphene sheet) rather than multiple layers, which would form thin chunks of graphite [17]. Second, I want to apply an electric field to the graphene to turn the saturable absorption properties on and off. By applying an electric field, I change the Fermi level of the graphene and thus change the population of graphenes conduction and valence bands. By populating the conduction band with this technique, I should be able to saturate the graphene electrically rather than optically so that it no longer behaves like a saturable absorber in a laser cavity. This will allow me to precisely control when graphene behaves like a saturable absorber and thus quench instabilities in the laser cavity. This device is known as an electro-optic modulator.

3 Current Progress

Currently, I am creating the ideal conditions for growing graphene. There are many variables that need to be optimized for growth, including total pressure in the reaction chamber, partial pressure of methane and any other desirable gasses, temperature of the reaction, cooling time, and the transfer and etching process to move the graphene from a copper foil to an optical substrate. So far, Ive constructed a device to test graphenes optical properties using a technique known as differential reflectivity. I spent the previous summer building the differential reflectivity experiment, and presented my techniques at the annual meeting of the Four Corners Section of the American Physical Society [18]. By shining high intensity laser light on a graphene sample and measuring both the transmitted light and the incident light, I can measure the absorption of the sample in terms of incident intensity to an accuracy of better than 0.1% signal after calibration over three orders of magnitude of incident intensity. I can achieve such high accuracy by subtracting the laser noise away from the light transmitted through the samplehence, the differential of differential reflectivity [18].

Our lab now also has access to a device for pump-probe spectroscopy. Using the pump-probe setup, I can measure the time it takes for graphene to saturate and then to relax and begin to transmit light again. A high intensity pump pulse excites the sample and then a lower intensity probe pulse passes through the sample after a user-controlled time delay. I measure the transmission of the sample in terms of the time delay of the probe pulse, which allows for an accurate characterization of the ultrafast carrier dynamics of graphene.I have also discovered that graphene needs to be grown at extremely low pressures (less than a millitorr). Using this low pressure setup, I've discovered that the best recipes for graphene involve a very low flow rate of methane and a very high flow rate of hydrogen. I think that this is because the hydrogen atoms washe away the hydrogen ions left over after the methane has broken up, so that it cannot recombine. Hopefully I will soon have an ideal recipe and I can move on to work on electro-optic modulator.

References

[1] T. Kobayashi et al. In *Proceedings of the 145th International Conference*, pages 13–15. Springer Series in Chemical Physics, 2005.

[2] R. Holzwarth et al. Optical frequency synthesizer for precision spectroscopy. *PRL*, 2000.

[3] D.J. Jones et al. Carrier-envelope phase control of femtosecond mode-locked lasers and direct optical frequency synthesis. *Science*, (288):365–365, 2000.

[4] K. Minoshima and H. Mataumoto. High-accuracy measurement of 240-m distance in an optical tunnel by use of a compact femtosecond laser. *Applied Optics*, (39):5512–5517, 2000.

[5] T.R. Schibli et al. Displacement metrology with sub-pm resolution in air based on a fs-comb wavelength synthesizer. *Optics Express*, (14):5984–5993, 2006.

[6] W. Drexler et al. Ultrahigh resolution optical coherence tomography of the human retina. *Nature Medicine*, (7):502–507, 2001.

[7] M.C. Stowe, F. C. Cruz, A. Marian, and J. Ye. High resolution atomic coherent control via spectral phase manipulation of an optical frequency comb. *Physics Review Letters*, (96):153001–153001, 2006.

[8] Z. Zhu et al. Pump-probe spectroscopy of exciton dynamics in (6,5) carbon nanotubes. *Physical Chemistry*, C(111):3831–3835, 2007.

[9] T. Steinmetz et al. Laser frequency combs for astronomical observations. *Science*, (321):1335–1337, 2008.

[10] T.R. Schibli. Combs for dark energy. *Nature Photonics*, (2):712–713, 2008.

[11] C.-H. Li et al. A laser frequency comb that enables radial velocity measurements with a precision of 1 cm/s. *Nature*, (452):610–612, 2008.

[12] J. Kim et al. Drift-free femtosecond timing synchronization of remote optical and microwave sources. *Nature Photonics*, (2):733–736, 2008.

[13] Ursula Keller. Ultrafast solid-state lasers. *Progress in Optics*, 2004.

[14] Qiaolang Bao et al. Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers. *Advanced Functional Materials*, (19):3077–3083, 2009.

[15] Sunil Kamar et al. Femtosecond carrier dynamics and saturable absorption in graphene suspensions. *Applied Physics Letters*, (95):191911–1–191911–3, 2009.

[16] Chien-Chung Lee et al. Ultra-short optical pulse generation with single-layer graphene. *Journal of Nonlinear Optical Physics and Materials*.

[17] Xuesong Li et al. Transfer of large-area graphene films for high-performance transparent conductive electrodes. *Nano Letters*, (9):4359–63, 2009.

[18] Jonah M. Miller, Chien-Chung Lee, and Thomas S. Schibli. A systematic study of techniques to directly measure the saturable absorption of graphene. In *Annual Meeting of the Four Corners Section of the American Physical Society*, volume 55, 2010.

[19] Sukang Bae et al. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology*, (132), 2010.

[20] Jahan M. Dawlatey et al. Measurement of ultrafast carrier dynamics in epitaxial graphene. *Applied Physics Letters*, (92):042116–1–042116–3, 2008.

[21] Andy Geim and Alan H. Macdonald. Graphene: Exploring carbon flatland. *Physics Today*, (60):35–41, 2007.

[22] M. Haiml et al. Optical characterization of semiconductor saturable absorbers. *Applied Physics*, B(79):331–339, 2004.

[23] T.R. Schibli et al. Ultrashort pulse-generation by saturable absorber mirrors based on polymer-embedded carbon nanotubes. *Optics Express*, (13):8025–31, 2005.

[24] Zhenxing Wang et al. A high-performance top-gate graphene field-effect transistor based frequency doubler. *Applied Physics Letters*, (26):173104–1–3, 2010.

[25] Xuesong Li et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*, (324), 2009.

[26] Xuesong Li et al. Large domain graphene. *eprint arXiv:1010.3903*, 2010.

[27] Xuesong Li et al. Graphene films with large domain size by a two-step chemical vapor deposition process. *Nano Letters*, 10(11):4328–4334, 2010.