

Graphene-Based Fast Saturable Absorber Devices and Their Application to Mode Locking of Solid-State Lasers

by

Işinsu Baylam

A Dissertation Submitted to the
Graduate School of Sciences and Engineering
in Partial Fulfillment of the Requirements for
the Degree of
Doctor of Philosophy
in
Physics



**KOÇ
UNIVERSITY**

January 23, 2017

Graphene-Based Fast Saturable Absorber Devices and Their Application to
Mode Locking of Solid-State Lasers

Koç University

Graduate School of Sciences and Engineering

This is to certify that I have examined this copy of a doctoral dissertation by

Işınsu Baylam

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Committee Members:

Prof. Alphan Sennaroğlu (Advisor)

Asst. Prof. Aşkın Kocabaş

Asst. Prof. Coşkun Kocabaş

Prof. Alper Kiraz

Assoc. Prof. Sarper Özharar

Date: _____

ABSTRACT

Graphene and other carbon-based nanomaterials have emerged as alternative saturable absorbers to other semiconductor saturable absorbers due to their favorable optical characteristics and relatively simple growth schemes. It has been demonstrated that the graphene saturable absorbers (GSAs), can be used as effective modulators to generate femtosecond pulses from lasers, operating in the near and mid infrared. Therefore, it is of great interest to explore the mode locking performance of the GSAs, grown on different substrates, in power-scaled lasers. However, one possible drawback of a monolayer graphene saturable absorber stems from its small-signal optical insertion loss of 5%, which leads to challenges in operating low gain lasers. Such challenges can be obviated by using graphene-based supercapacitor structures so that when a voltage bias is applied, the Fermi level of graphene can be shifted to reduce the absorption via Pauli blocking.

The first part of this thesis focuses on the linear and nonlinear optical characterization of the GSAs grown on different substrates (quartz and YAG) and their application to mode locking of an energy-scaled multipass-cavity (MPC) Cr^{4+} :forsterite laser operating near 1250 nm. The Cr^{4+} :forsterite resonator, mode-locked with the GSA on quartz or the GSA on YAG, produced nearly transform-limited pulses with sub-100 fs durations and 53-kW pulse peak powers. To the best of our knowledge, both results report the highest peak powers obtained from a GSA mode-locked femtosecond solid-state laser.

The remaining parts of this thesis investigate the optical characterizations and mode locking applications of the graphene-based supercapacitors as fast saturable absorbers with voltage-controllable optical insertion losses.

The first supercapacitor design (voltage-controlled graphene saturable absorber, VCG-SA) consisted of a high dielectric electrolyte, sandwiched between two graphene electrodes. Linear and non-linear optical characterizations of the device were performed to explore its voltage-dependent optical properties and the results indicated that the

supercapacitor architecture enabled the modulation of absorption up to the visible region (2.4 eV) even with few volts (0-3V) of applied bias. The VCG-SA was further employed in the MPC Cr⁴⁺:forsterite laser to investigate the voltage-dependent mode-locked operation. The MPC Cr⁴⁺: forsterite laser produced, 84-fs pulses with a time-bandwidth product of 0.32 at 1V of applied bias.

To further reduce the insertion losses at zero bias, a second graphene-based supercapacitor architecture with the same electrolyte sandwiched between a graphene and a notched gold electrode was fabricated. Mode locking performance of the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) was investigated again in the MPC Cr⁴⁺:forsterite laser, operating near 1250 nm. Since one of the graphene electrodes of the previous design was replaced with a notched gold electrode, the optical insertion loss of the VCG-gold-SA was reduced at zero bias with respect to the previous design involving two graphene electrodes. In this case, the resonator generated 80-fs nearly transform-limited pulses with a pulse peak power of 42 kW at 0.8V of applied bias.

Finally, to push the mode locking capability of these supercapacitor devices to as low a wavelength as possible, a Ti³⁺:sapphire laser, operating near 800 nm was used. The Ti³⁺:sapphire resonator successfully produced femtosecond pulses at wavelengths as short as 795 nm. To our knowledge, this is the shortest wavelength, where a graphene-based supercapacitor was used as a fast saturable absorber to generate femtosecond pulses.

The novel graphene supercapacitor devices, first demonstrated as fast saturable absorbers in this thesis, have the potential to be used for femtosecond pulse generation from lasers operating over a broad wavelength range and with different levels of gain.

ÖZETÇE

Grafen ve karbon-tabanlı doyabilen soğurucular, ayrıcalıklı optik özellikleri ve düşük maliyetli üretim teknikleri nedeniyle, son yıllarda diğer yarı iletken doyabilen soğuruculara alternatif olarak ortaya çıkmışlardır. Son yıllarda yapılan çalışmalar, grafen doyabilen soğurucuların (GSA), yakın ve orta-kızılaltı dalga boylarında çalışan lazerlerin kip-kilitlenmesinde (mode locking) etkin doyabilen soğurucular olarak kullanılabileceğini göstermiştir. Bu nedenle, farklı alttaşlar üzerine aktarılmış grafen doyabilen soğurucuların, kip-kitleme performanslarının yüksek darbe tepe gücüne sahip lazerlerde de incelenmesi oldukça önemlidir. Fakat, tek katmanlı grafenin sahip olduğu %5 optik kayıp, düşük kazanç değerlerine sahip lazerler içerisinde grafenin çalışmasını zorlaştırmaktadır. Bu zorluklar, grafen-tabanlı süperkapasitörler kullanılarak aşılabilmektedir. Grafen-tabanlı süperkapasitörlere voltaj uygulandığı zaman, grafenin Fermi seviyesi değiştirilebilmekte ve optik soğurma miktarı Pauli bloklama prensibi sonucunda kontrol edilebilmektedir.

Tezin ilk kısmında, farklı alttaşlar üzerine aktarılmış grafen doyabilen soğurucuların (kuartz ve YAG) optik nitelendirme ölçümleri yapılmıştır. Her iki grafen doyabilen soğurucunun da kip-kitleme performansı, 1250 nm civarında çalışabilen ve yüksek tepe gücüne sahip darbeler üretebilen çok yansımali kovuklu (multipass-cavity, MPC) Cr^{4+} :forsterite katıhal lazeri ile test edilmiştir. Cr^{4+} :forsterite lazeri, grafen-kuartz ve grafen-YAG örneği ile kip-kilitli rejimde çalıştırıldığında, 100 fs civarında uzunluğa ve 53 kW tepe gücüne sahip darbeler üretmiştir. Bu çalışma sonucunda, grafen doyabilen soğurucuların yüksek darbe tepe gücüne sahip lazerlerde de etkin doyabilen soğurucular olarak çalışabildiği literatürde ilk kez gösterilmiştir.

Tezin geriye kalan bölümlerinde, grafen-tabanlı süperkapasitör yapıların optik karakterizasyonları ve farklı dalga boylarında çalışan katıhal lazerlerindeki kip-kitleme performansları incelenmiştir.

Bu çalışmalarda kullanılan ilk süperkapasitör yapısı (VCG-SA), iki grafen elektrottan ve bu elektrotların arasında yer alan yüksek dielektrik katsayısına sahip bir elektrolitten oluşmaktadır. Optik karakterizasyon deneyleri sonucunda, süperkapasitörün optik soğurma miktarının, görünür dalgaboylarında (2.4 eV) bile düşük voltajlar (0-3V) uygulanarak kontrol edilebildiği gösterilmiştir. Bu süperkapasitörün kip-kilitme performansı, bir önceki deneylerde de kullanılmış olan çok yansımali kovuklu Cr^{4+} :forsterite lazeri içerisinde incelenmiştir. Süperkapasitöre 1V uygulandığında, kip-kilitli lazer rezonatörü, 1250 nm civarında, 84 fs uzunluğa sahip ve zaman-spektral genlik çarpımı 0.32 olan darbeler üretmiştir.

Voltaj uygulanmadığı durumdaki optik kayıpları daha da azaltabilmek için, ikinci bir süperkapasitör tasarımı yapılmış ve grafen elektrotlardan biri, üzerinde ışığın geçişini sağlamak için bir delik bulunan altın elektrot ile değiştirilmiştir. Grafen-altın tabanlı süperkapasitörün doyabilen soğurucu olarak çalıştırılması, aynı Cr^{4+} :forsterite lazeri içerisinde araştırılmıştır. Bir önceki tasarımda yer alan grafen elektrotlardan biri altın ile değiştirildiği için, grafen-altın süperkapasitörün (VCG-gold-SA) rezonatör içerisindeki optik kaybı, bir önceki süperkapasitör tasarımına kıyasla daha düşük seviyelerde kalmıştır. 0.8V voltaj uygulanmış grafen-altın süperkapasitör ile kip-kilitli rejimde çalıştırılan Cr^{4+} :forsterite lazeri, 80 fs süreli ve 42 kW tepe gücüne sahip darbeler üretmiştir.

Grafen-tabanlı süperkapasitörlerin, daha düşük dalgaboylarında da doyabilen soğurucu olarak çalışabileceğinin gösterilmesi, 800 nm civarında çalışan Ti^{3+} :sapphire lazeri kullanılarak araştırılmıştır. Grafen-altın süperkapasitör ile bu rezonatörden, 795 nm civarında femtosaniye darbeler üretilmiştir. Bu dalgaboyu şimdiye kadar grafen-altın süperkapasitörün doyabilen soğurucu olarak çalışabildiğinin gösterildiği en düşük dalgaboyudur. Bu tez çalışmaları sonucunda, grafen-tabanlı süperkapasitör doyabilen soğurucuların, farklı dalgaboylarında çalışan ve farklı optik kazançlara sahip lazerlerde doyabilen soğurucu olarak kullanılabilme potansiyeline sahip oldukları gösterilmiştir.

ACKNOWLEDGMENTS

I would like to thank my advisor Alphan Sennaroğlu for giving me the opportunity to study under his supervision during my MSc and PhD studies. He was always willing to share his enormous amount of knowledge and experience with me. I learned a lot from his way of managing different situations in academic life. However, I believe that there is still plenty of advice, I should remember and learn from him to become an academician who cares about ethical research, creativity, and problems of the world we live in.

I would also like to thank Adnan Kurt and Sarper Özharar for their educational and friendly collaboration during my studies. I was very lucky to work with them and I gained incredible amount of skills in the laboratory from them. I present my deepest appreciation to my thesis committee members, Alper Kiraz, Aşkın Kocabaş, and Coşkun Kocabaş for their precious comments that will improve my research.

I am also grateful about the supports and the friendships of my lab-mates, Ferda Canbaz, İsmail Yorulmaz, Can Cihan, and Abdullah Muti and my friends Natali Sözüdoğru, Mine Toker, Müge Atış, and Betül Durmuş. I never hesitated to ask them questions and I learned many things from their experience. The hard times were not hard at all with them!

I present my deepest love to my parents, Neriman Baylam and Erdem Baylam for their endless support throughout my life.

Last but not least, I would like to dedicate my thesis to the founder of Modern Turkish Republic, Mustafa Kemal Atatürk who encouraged women to be a part of the modern society, and to the brave people who have been working for peace, protection of nature and progress of humankind.

“Our true mentor in life is science.” M. Kemal Atatürk

TABLE OF CONTENTS

Table of Contents	vi
List of Figures and Tables	ix
Nomenclature	xix
Chapter 1: Why Graphene?	1
1.1 Overview of Graphene	1
1.1.1 Optical Properties of Graphene	4
1.2 Optical Characterization Methods for Graphene	8
1.3 Novel Graphene-Based Modulators with Voltage Reconfigurable Absorption Levels	17
Chapter 2: Ultrashort Laser Pulses	25
2.1 Characteristics of Ultrashort Laser Pulses	25
2.2 Pulse Propagation in Nonlinear Media	27
2.2.1 Effects of Dispersion on Ultrashort Pulses	28
2.2.2 Self-Focusing and Self-Phase Modulation of Ultrashort Laser Pulses	29
2.2.3 Optical Solitons and Methods to Control Nonlinear Effects During Pulse Propagation in Nonlinear Media	33
2.3 Femtosecond Pulse Generation	43
2.3.1 Saturable Absorber Mode Locking	45
2.3.2 Kerr-Lens Mode Locking	51

Chapter 3: Solid-State Lasers: Operation Parameters and Design Principles	53
3.1 Operation Parameters of Solid-State Lasers	53
3.2 Design Principles for Solid-State Lasers with Multipass-Cavity Extensions	59
3.3 Cr^{4+} :forsterite and Ti^{3+} :sapphire Lasers	64
Chapter 4: Graphene Saturable Absorber Mode-Locked Multipass-Cavity Cr^{4+}:forsterite Laser	68
4.1 Fabrication and Optical Characterization of Graphene Saturable Absorbers	68
4.2 Experimental Setup	73
4.3 Continuous-Wave Operation Results	75
4.4 Mode-Locked Operation Results	78
Chapter 5: Mode-Locked Operation of a Femtosecond Cr^{4+}:forsterite Laser by Using Voltage-Controlled Graphene Saturable Absorber	84
5.1 Fabrication and Optical Characterization of Voltage-Controlled Graphene Saturable Absorber	84
5.2 Experimental Setup and Voltage-Dependent Continuous-Wave Operation Results	90
5.3 Mode-Locked Operation Results	94

Chapter 6: Mode-Locked Operation of a Femtosecond Cr⁴⁺:forsterite Laser by Using Voltage-Controlled Graphene-Gold Saturable Absorber	99
6.1 Fabrication and Optical Characterization of Voltage-Controlled Graphene-Gold Saturable Absorber	100
6.2 Voltage-Dependent Continuous-Wave Operation Results	103
6.3 Mode-Locked Operation Results	104
 Chapter 7: Mode-Locked Operation of a Femtosecond Ti³⁺:sapphire Laser by Using Voltage-Controlled Graphene-Gold Saturable Absorber	 109
7.1 Voltage-Dependent Continuous-Wave Operation Results Obtained with Dispersion Control Mirrors	110
7.2 Mode-Locked Operation Results Obtained with Dispersion Control Mirrors	113
7.3 Voltage-Dependent Continuous-Wave Operation Results Obtained with a Prism Pair	116
7.4 Mode-Locked Operation Results Obtained with a Prism Pair	120
 Chapter 8: Conclusions	124
Bibliography	132
Vita	143

LIST OF FIGURES AND TABLES

Figure 1.1.1. Illustration of the 2D hexagonal structure of graphene.	2
Figure 1.1.2. The energy-band diagram of a monolayer graphene. Fermi level is shown as (E_F).	2
Figure 1.1.3. (a) Honeycomb lattice structure of graphene. The two unit vectors define the unit cell. (b) Brillouin zone of graphene in the reciprocal space, which is defined by the two reciprocal lattice vectors. (c) Schematic of the six Dirac points in the reciprocal space.	4
Figure 1.1.4. Photograph of the single layer (left) and multilayer (right) graphene on quartz substrate. The samples were prepared via chemical vapor deposition (CVD) by C. Kocabas's group at Bilkent University.	6
Figure 1.1.5. Schematic of the interband and the intraband transitions of a monolayer graphene.	7
Figure 1.2.1. Optical transmission spectrum of our monolayer graphene grown on a quartz substrate.	9
Figure 1.2.2. The measured fractional change in the transmission of graphene as a function of the time delay. The measurement was performed by using the pump-probe setup at Koç University Surface Science and Technology Center (KUYTAM).	13
Figure 1.2.3. The measured saturation fluence and the modulation depth of our monolayer graphene on quartz sample by using the femtosecond transient spectroscopy system at Koç University Surface Science and	

Technology Center (KUYTAM).	14
Figure 1.2.4. The Raman spectrum of a monolayer graphene on a quartz substrate.	16
Figure 1.3.1. (a) Sketch of the absorption in graphene when the Fermi level is at the Dirac point and (b) the Fermi level position is shifted up.	19
Figure 1.3.2. Illustration of the Fermi-Dirac distribution at different temperatures.	20
Figure 1.3.3. Energy-band diagram for n-doped (left) and p-doped (right) graphene.	21
Figure 1.3.4. Schematic of the electrical double layer formation inside a supercapacitor.	22
Figure 2.2.1. A laser beam with a Gaussian intensity distribution passes through a medium and gets focused due to the Kerr effect.	30
Figure 2.2.2. (a) The temporal envelope and (b) the electric field distribution of an incident Gaussian pulse. (c) The evolution of the electric field in the presence of the second-order positive dispersion. (d) A phase shift occurs in the pulse due to the self-phase modulation and it can be balanced by introducing negative second-order dispersion.	33
Figure 2.2.3. (a) Schematic description of the diffraction from a reflective grating. (b) Photograph of the reflective diffraction grating that is used in our laboratory.	38
Figure 2.2.4. Schematic diagram for a pair of parallel diffraction gratings.	40
Figure 2.2.5. Propagation of the light through a pair of prism.	41

Figure 2.2.6. (a) The second-order negative group delay dispersion (GDD) introduced by different slab materials. (b) The resulting GDD obtained from a fused silica prism pair at different prism separations.	43
Figure 2.3.1. The high intensity laser beam (grey) gets more focused than the low intensity one (red) and overlaps better with the pump beam (green) inside the gain medium.	51
Figure 3.1.1. Description of the energy levels of the four-level solid-state gain media.	54
Figure 3.1.2. Efficiency curve of a solid-state laser.	57
Figure 3.2.1. The initial and the final q-parameters of the beam are equal after passing through a q-preserving cavity extension. Therefore, the extension has no effect on the q-parameter of the original resonator.	62
Figure 3.2.2. Photographs of the spot distribution on the flat MPC mirror of our Cr ⁴⁺ :forsterite laser (left) and the bouncing beams between the MPC mirrors (middle). These photographs were taken by using an infrared viewer and a camera. The MPC Ti ³⁺ :sapphire laser (right) (Photograph by Aref Mostafazadeh).	64
Figure 3.3.1. In our mode locking experiments, the Cr ⁴⁺ :forsterite (left) and the Ti ³⁺ :sapphire (right) gain media were used.	67
Figure 4.1.1. Measured Raman spectrum of the graphene on quartz substrate.	70
Figure 4.1.2. (a) Measured Raman spectra of graphene on YAG substrate and (b) the bare YAG.	70

Figure 4.1.3. The steady-state transmission spectrum of the graphene on quartz sample.	71
Figure 4.1.4. (a) The measured variation of the fractional transmission change at 1250 nm as a function the delay for the graphene on quartz and (b) the graphene on YAG samples.	72
Figure 4.1.5. (a) Measured change in the transmission of the graphene on quartz and (b) the graphene on YAG saturable absorbers at 1250 nm.	72
Figure 4.2.1. (a) Experimental setup of the x-cavity and (b) the multipass-cavity Cr^{4+} :forsterite laser.(c) The final resonator architecture consisted of the MPC and dispersion control optics.	75
Figure 4.3.1. Power efficiency curves for the short x-cavity and the MPC Cr^{4+} :forsterite laser with the 4.7% output coupler.	76
Figure 4.3.2. Power efficiency curves for the laser resonator with GSA samples on different substrates and with different output couplers (DCO: dispersion control optics, MPC: multipass-cavity).	77
Figure 4.4.1. Photograph of the MPC Cr^{4+} :forsterite laser (left) and the GSA-quartz sample, which was placed between the two curved mirrors (right).	79
Figure 4.4.2. (a) Collinear autocorrelation data for the GSA-quartz mode-locked Cr^{4+} :forsterite laser with the 4.7 % and (b) 2.4 % output coupler.	79
Figure 4.4.3. (a) Measured mode-locked spectra of the femtosecond MPC Cr^{4+} :forsterite laser for the 4.7 % and (b) for the 2.4 % output coupler.	80
Figure 4.4.4. (a) RF spectra of the GSA-quartz mode-locked MPC Cr^{4+} :forsterite laser. The sideband noise level was determined to be 68.7 dBc for the 4.7% output coupler and	

(b) 65.8 dBc for the 2.4% output coupler indicating stable mode-locked operation.	80
Table 4.4.1. Summary of the femtosecond laser parameters for the GSA-quartz mode-locked multipass-cavity Cr ⁴⁺ :forsterite laser.	81
Figure 4.4.5. (a) Autocorrelation trace, (b) mode-locked spectrum, and (c) RF spectrum of the GSA-YAG mode-locked Cr ⁴⁺ :forsterite laser with the 4.7% output coupler.	82
Table 4.4.2. GSA-YAG mode-locked multipass-cavity Cr ⁴⁺ :forsterite laser.	82
Table 4.4.3. Measured maximum intracavity peak powers and the estimated critical powers for the GSA-quartz and the GSA-YAG mode-locked MPC Cr ⁴⁺ :forsterite laser.	83
Figure 5.1.1. (a) Schematic of the graphene-based supercapacitor architecture. (b) The energy-band structure of graphene for the unbiased and the biased case. E _p and E _F are the photon and the Fermi energies, VB and CB are the valance and the conduction bands respectively.	85
Figure 5.1.2. Measured transmission spectrum of the electrolyte.	86
Figure 5.1.3. Normalized change in the transmission of the voltage-controlled graphene saturable absorber as a function of the wavelength at different applied voltages.	87
Figure 5.1.4. (a) Measured fractional change in the transmission spectrum of the VCG-SA as a function of the bias voltage at three selected wavelengths. (b) The Fermi level shift of the VCG-SA as a function of the bias.	88
Figure 5.1.5. Measured ultrafast response of the VCG-SA at the probe wavelength of 1250 nm for different bias voltages.	89

Figure 5.1.6. (a) Measured change in the transmission of the VCG-SA as a function of the incident fluence at 700 nm. (b) Measured variation in the modulation depth and the saturation fluence as a function of the applied bias.	90
Figure 5.2.1 Experimental setup of the multipass-cavity Cr^{4+} :forsterite laser with the voltage-controlled graphene-based saturable absorber (VCG-SA) and the 2.4% output coupler (OC).	91
Figure 5.2.2. Power efficiency curves of the multipass-cavity Cr^{4+} :forsterite laser with and without the voltage-controlled graphene saturable absorber (VCG-SA) by using the 2.4% output coupler.	92
Figure 5.2.3. (a) Measured variation in the output power of the laser with the VCG-SA as a function of the applied bias at a fixed input power of 7.1 W. (b) The estimated change in the single-pass optical insertion loss of the VCG-SA as a function of the applied voltage.	93
Figure 5.2.4. Measured output power of the multipass-cavity Cr^{4+} :forsterite laser with respect to the different output coupler transmissions at a fixed input power of 7.1 W.	94
Figure 5.3.1. Mode-locked operation range (blue) of the laser as a function of the applied voltage.	95
Figure 5.3.2. (a) Spectrum, (b) RF spectrum, and (c) autocorrelation trace of the VCG-SA mode-locked multipass-cavity Cr^{4+} :forsterite laser measured at 0.5V of applied bias.	96
Figure 5.3.3. (a) Spectrum, (b) RF spectrum, and (c) autocorrelation trace of the VCG-SA mode-locked Cr^{4+} :forsterite laser measured at 1V of applied bias.	97
Table 5.3.1. Summary of the laser parameters for the VCG-SA	

mode-locked multipass-cavity Cr^{4+} :forsterite laser at 0.5V and 1V of bias.	98
Figure 6.1.1. (a) Photograph of the voltage-controlled graphene-gold saturable absorber. (b) Schematic of the supercapacitor architecture comprising an electrolyte sandwiched between the graphene and the gold electrode.	100
Figure 6.1.2. Measured fractional change in the transmission of the voltage-controlled graphene-gold saturable absorber as a function of the wavelength at different applied voltages.	101
Figure 6.1.3. (a) Measured variation of the fractional change in the transmission spectrum of the VCG-gold-SA as a function of the voltage at three selected wavelengths and (b) near the operation wavelength of our laser.	102
Figure 6.1.4. Estimated Fermi level shift of the VCG-gold-SA as a function of bias voltage.	102
Figure 6.2.1. (a) Measured variation in the output power at a fixed input power of 7.1 W as a function of the applied voltage. (b) Estimated voltage-dependent optical insertion losses of the VCG-SA and the VCG-gold-SA.	104
Figure 6.3.1. Measured threshold pump power to initiate VCG-gold-SA mode-locked operation.	105
Figure 6.3.2. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.4V of applied bias.	106
Figure 6.3.3. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.6V of applied bias.	106

Figure 6.3.4. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.8V of applied bias. 107

Figure 6.3.5. (a) Measured RF spectra of the VCG-gold-SA mode-locked laser at 0.4V, (b) at 0.6V, and (c) at 0.8V of applied bias. During the measurements, the resolution bandwidth and the span were 1 kHz and 200 kHz respectively. 107

Table 6.3.1. Summary of the femtosecond laser parameters for the VCG-gold-SA mode-locked MPC Cr^{4+} :forsterite laser at 0.4V, 0.6V, and 0.8V of bias. 108

Figure 7.1.1. Sketch of the Ti^{3+} :sapphire laser consisted of only the dispersion control mirrors and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA). 111

Figure 7.1.2. Power efficiency curves for the Ti^{3+} :sapphire laser with and without the dispersion control mirrors (DCMs) and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) at zero bias. 112

Figure 7.1.3. (a) Measured variation in the output power of the Ti^{3+} :sapphire laser as a function of the applied voltage at a fixed input power of 1.6 W. (b) Estimated single-pass insertion loss of the VCG-gold-SA as a function of the applied bias. 112

Figure 7.2.1. (a) Measured mode-locked spectra, (b) autocorrelation traces, and (c) RF spectra (1 kHz resolution bandwidth) of the generated pulses at three different voltages. 114

Figure 7.2.2. Variation in the measured pulse widths and the corresponding time-bandwidth products (TBP) as a function of the applied voltage for the

resonator, which consisted of only the dispersion control mirrors. 114

Table 7.2.1. Mode-locking results obtained from the VCG-gold-SA mode-locked Ti^{3+} :sapphire laser. For this case, the resonator consisted of only the dispersion control mirrors. 115

Figure 7.3.1. Estimated negative group delay dispersion (GDD) introduced by the dispersion control mirrors (DCMs) and an SF-14 prism pair with 13 cm tip-to-tip separation. 116

Figure 7.3.2. Sketch of the Ti^{3+} :sapphire laser resonator consisted of the prism pair and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA). 117

Figure 7.3.3. Power efficiency curves for the empty cavity Ti^{3+} :sapphire laser, with the SF-14 prism pair, and with the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) at the zero bias. 118

Figure 7.3.4. (a) Voltage-dependent output power of the Ti^{3+} :sapphire laser with the SF-14 prism pair. (b) Estimated insertion loss of the voltage-controlled graphene-gold saturable absorber as a function of the applied voltage. 119

Figure 7.3.5. Measured output power of the laser across the 5-mm notch at a fixed voltage of 1.5V for 1.6 W of fixed input pump power. 119

Figure 7.4.1. (a) Mode-locked spectrum, (b) autocorrelation trace, and (c) RF spectrum (1 kHz resolution bandwidth) of the generated pulses at 0.8V of applied bias. 121

Figure 7.4.2. (a) Mode-locked spectrum, (b) autocorrelation trace, and (c) RF spectrum (1 kHz resolution bandwidth) of the generated pulses

at 1.2V of applied bias. 121

Figure 7.4.3. (a) Measured pulse durations and corresponding intracavity energies and (b) the time-bandwidth products (TBP) as a function of the applied voltage. 122

Table 7.4.1. Summary of the femtosecond laser parameters for the VCG-gold-SA mode-locked Ti^{3+} :sapphire laser with the prism pair. 123



NOMENCLATURE

α :	fine structure constant
α_s :	saturable absorption
α_{NS} :	non-saturable absorption
A :	area / absorption / element of the ray transformation matrix
$A_{eff.}$:	effective area
c :	speed of light in vacuum
C :	element of the ray transformation matrix
C_Q :	quantum capacitance
d :	distance
D :	group delay dispersion parameter / element of the ray transformation matrix
$\Delta\nu$:	bandwidth
e :	electron charge
E :	energy / energy level
E_F :	Fermi energy
E_p :	photon energy / pulse energy
f :	focal length
f_{rep} :	repetition rate of the pulses
g :	ground state energy level / gain
g_0 :	small-signal differential gain
G_0 :	quantum of conductance
γ :	Kerr nonlinearity (self-phase modulation) constant
γ_0 :	small-signal gain coefficient
$\hbar$:	Planck's constant
I :	light intensity

I_L :	laser intensity
I_p :	pump intensity
I_{sat} :	saturation intensity
J :	fluence
J_{sat} :	saturation fluence
$\mathbf{k}$:	wave vector
k_B :	Boltzman constant
K :	time-bandwidth product
L :	total loss of the resonator / cavity length
l_m :	length of the gain medium
M :	M-square parameter / mirror
N :	groove density / population density
n :	refractive index / carrier density
n_0 :	low intensity refractive index
n_2 :	nonlinear refractive index
η :	slope efficiency
η_a :	fractional pump absorption
θ_i :	incident angle
θ_B :	Brewster angle
λ_L :	laser wavelength
λ_p :	pump wavelength
ν_L :	laser frequency
ν_p :	pump frequency
v_F :	Fermi velocity
ν_{FSR} :	free spectral range
q :	q-paramater of the beam

P :	power
P_{cr} :	critical power
R :	reflectivity
σ :	Pauli matrices / optical conductivity
σ_a :	absorption cross section
σ_e :	emission cross section
τ :	recombination time
τ_f :	fluorescence lifetime
τ_p :	pulse width / cavity photon lifetime
T :	transmission / temperature
T_0 :	steady-state transmission
T_R :	cavity round-trip time
u_g :	group velocity
ϕ :	phase
ω :	angular frequency
$w(z)$:	spotsize function
w_0 :	beam waist
z_0 :	Rayleigh range

Chapter 1

WHY GRAPHENE?

Chapter 1 presents, optical properties of graphene, optical characterization tools that have been used to characterize graphene, alternative graphene-based structures, which have been utilized to modify unique optical properties of graphene, and our approach to overcome potential drawbacks of the alternative methods.

1.1 Overview of Graphene

Graphene is an atomic layer thick nanomaterial, which is formed by the 2D hexagonal arrangement of the carbon atoms as shown in Fig. 1.1.1. It was first theorized by P. R. Wallace [1] in 1947 to explore the electronic properties of 3D graphite. In 2004, Geim and Novoselov from Manchester University experimentally showed that graphene can be isolated from bulk graphite [2]. This study resulted in the two scientists winning the Nobel Prize in Physics in 2010.

Graphene has many remarkable properties [3], such as mechanical robustness [4], high carrier mobility [5], and broadband optical absorption [6]. Furthermore, availability of the simple and low-cost growth techniques, such as chemical vapor deposition (CVD) [7], exfoliation via adhesive tape [2], and graphite oxide reduction [8] makes graphene an easily accessible material for laboratories and industries. There are also other promising carbon-based nanomaterials (e.g. Single-walled carbon nanotubes [9], nanoribbons [10], quantum dots [11], and graphene oxides [12]), which have been produced and explored to extend the application border of graphene.

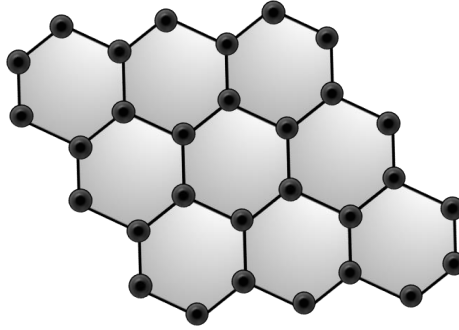


Figure 1.1.1. Illustration of the 2D hexagonal structure of graphene.

The unusual energy-band diagram of monolayer graphene (Fig. 1.1.2) has a zero band-gap and leads to the relativistic behavior of the charge carriers in graphene [13]. The zero band-gap structure is not commonly encountered in the field of condensed matter physics. Hence, apart from its cutting-edge technological applications, graphene has its own importance in terms of the exploration of the fundamental physics [3, 14].

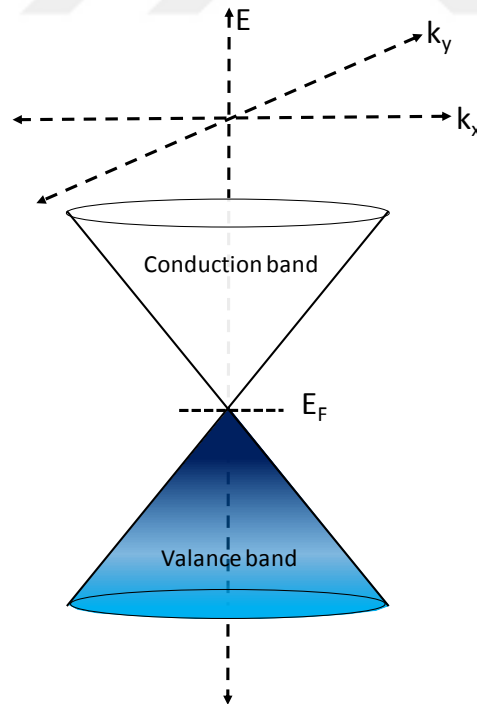


Figure 1.1.2. The energy-band diagram of a monolayer graphene. Fermi level is shown as (E_F).

The unit cell of graphene contains two atoms and defined by the two lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ as shown in Fig. 1.1.3 (a). In the reciprocal space, Brillouin zone of graphene is defined by the reciprocal lattice vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, which contain the points K, K', and Γ (Figure 1.1.3 (b)). The Γ point is at the center of the Brillouin zone in the reciprocal space. K and K' points are located at the corners. The symmetric energy bands in graphene are satisfied at these points, which are called as the Dirac points. In the momentum space, graphene contains six Dirac points (Figure 1.1.3 (c)), which give rise to the linear dispersion relation with gapless band structure as described in Ref. [13].

The linear dispersion relation arises as a solution of the Dirac equation for the massless Dirac fermions at the Dirac points. The charge carriers (electrons and holes) in graphene obey a linear dispersion relation given by [3]

$$E = \hbar v_F k \quad (1.1.1)$$

which is similar to the dispersion relation for a photon,

$$E = \hbar c k \quad (1.1.2)$$

In Eq. (1.1.1) and (1.1.2), $\mathbf{k}$ is the wave-vector, $\hbar$ is the Planck's constant, c and v_F are the speed of light in vacuum (3×10^8 m/s) and the Fermi velocity (1.1×10^6 m/s) respectively. Electrons and holes in graphene are called as relativistic Dirac fermions and they behave like massless particles near the Dirac point.

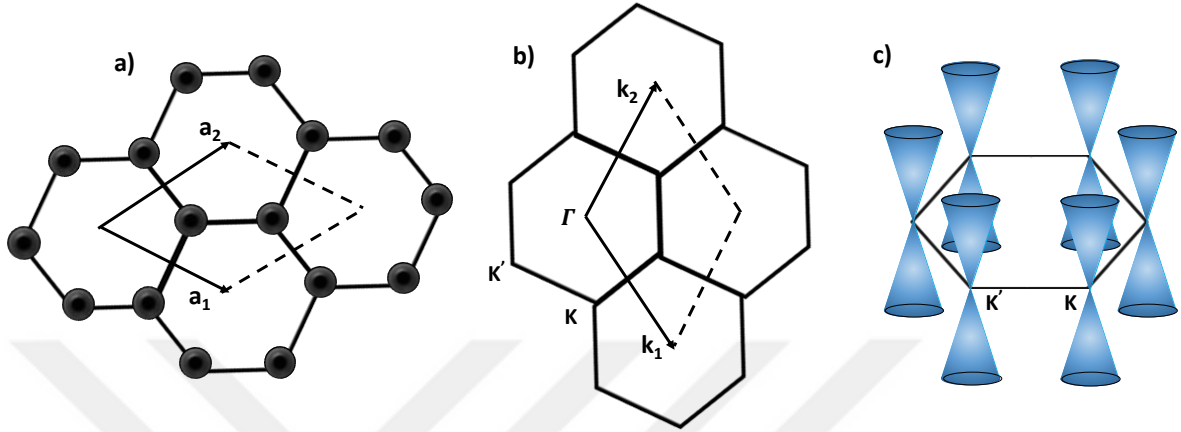


Figure 1.1.3. (a) Honeycomb lattice structure of graphene. The two unit vectors define the unit cell. (b) Brillouin zone of graphene in the reciprocal space, which is defined by the two reciprocal lattice vectors. (c) Schematic of the six Dirac points in the reciprocal space.

The novel optical properties of graphene stem from its unique zero band-gap and have been utilized by researchers in the fields of optics and photonics. The following sections of Chapter 1 will focus on the optical properties of graphene, optical characterization methods for graphene, different approaches that have been developed to control the optical properties of graphene, and operation principles of the novel graphene-based devices, which were demonstrated for the first time by our groups.

1.1.1 Optical Properties of Graphene

A monolayer graphene has a nearly wavelength-independent and constant absorption, which arises from the linear dispersion relation of the Dirac fermions. By following the analysis done by Geim et al. [15], absorption of light by graphene can be derived by calculating the interaction of light with graphene. The Hamiltonian, which gives this interaction can be written as

$$\hat{H}_{\text{int}} = -v_F \vec{\sigma} \cdot \frac{e}{c} \vec{A} \quad (1.1.3)$$

where v_F is the Fermi velocity, $\vec{\sigma}$ represents the Pauli matrices, e is the electron charge, and $\vec{A}$ is the vector potential, which is given in terms of the electric field $\vec{E}$ and the frequency ω of the incident light as

$$\vec{A} = \frac{ic}{\omega} \vec{E} \quad (1.1.4)$$

The absorbance A of graphene is defined as the absorbed energy divided by the incident flux $\left(\frac{\phi_a}{\phi_i} \right)$ [15], where

$$\phi_i = \frac{c}{4\pi} |\vec{E}|^2 \quad (1.1.5)$$

and

$$\phi_a = \eta \hbar \omega \quad (1.1.6)$$

In Eq. (1.1.6), η is the number of the absorption events, given by

$$\eta = \left(\frac{2\pi}{\hbar} \right) |M|^2 D \quad (1.1.7)$$

as described in Ref. [15]. Here, M is the matrix element which gives the interaction between light and graphene and D is the density of states at which the Fermi level E_F is equal to $\frac{\hbar\omega}{2}$. The matrix element for the interaction can be calculated by taking the average of the interaction Hamiltonian over all possible initial and final states. Furthermore, by inserting the value of $|M|^2$ in Eq. (1.1.7), the absorbed energy ϕ_a becomes

$$\phi_a = \frac{e^2}{4\hbar} \quad (1.1.8)$$

Hence, the absorbance A can be written as [15]

$$A = \frac{\phi_a}{\phi_i} = \frac{\pi e^2}{\hbar c} \quad (1.1.9)$$

In Eq. (1.1.9), $\frac{\pi e^2}{\hbar c} = 1/137$ is the fine structure constant α and hence, the absorbance A of monolayer graphene can be expressed in terms of the fundamental constants π and α as

$$A = \pi\alpha \approx 2.3\% \quad (1.1.10)$$

Due to the strong and wavelength-independent absorption, even a monolayer graphene, which is only an atomic layer thick, can be seen by the naked eye under the incident light (Figure 1.1.4).

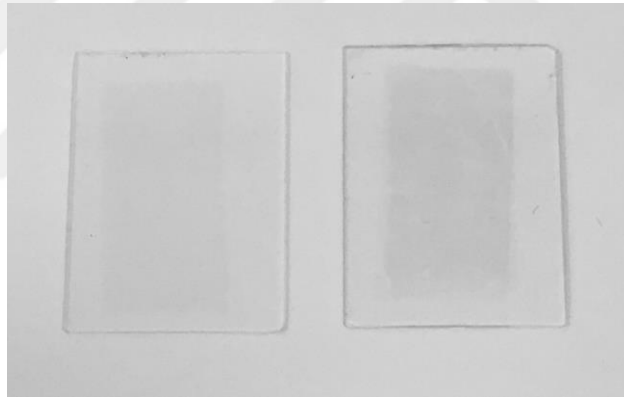


Figure 1.1.4. Photograph of the single layer (left) and multilayer (right) graphene on quartz substrate. The samples were prepared via chemical vapor deposition (CVD) by C. Kocabas's group at Bilkent University.

Optical properties of graphene are governed by the intraband and the interband transitions [16], which are illustrated in Fig.1.1.5. Interband transitions in graphene occur directly from the valance to the conduction band and they are described by the frequency-independent optical conductivity σ of graphene (i.e. absorbance of graphene) given as [6]

$$\sigma = \frac{\pi G_0}{4} \quad (1.1.11)$$

where G_0 is the quantum of conductance and equal to $\frac{e^2}{4\hbar}$. The optical response of graphene arising from this transition is nearly constant and covers a broad wavelength range from near-ultraviolet to mid-infrared. Mak et al. demonstrated that the absorbance of graphene in this wavelength range is independent from the microscopic parameters of graphene and verified that it is indeed equal to $\pi\alpha$ for photon energies between 0.5 and 1.2 eV [17, 18] at a finite temperature and a finite doping level.

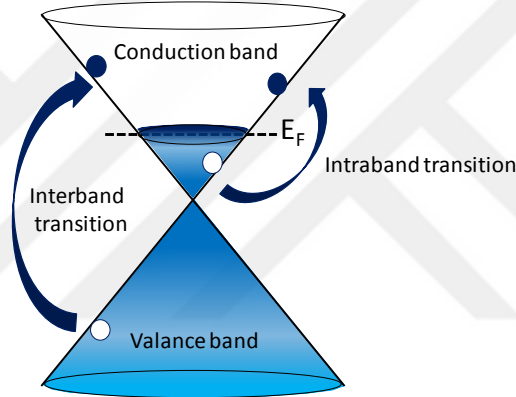


Figure 1.1.5. Schematic of the interband and the intraband transitions of a monolayer graphene.

Optical transitions that occur in this wavelength range have nearly zero sensitivity to the carrier density, however, they can be controlled by shifting the Fermi level and hence, the desired absorption can be prohibited due to Pauli exclusion principle.

At low photon energies (i.e. wavelengths greater than the mid-infrared), the intraband transitions are responsible for the optical response of graphene. As can be seen from Fig.1.1.5, direct absorption of a photon during an intraband transition violates the momentum conservation and hence, additional phonon transitions are required to conserve the momentum. Furthermore, the optical sheet conductivity of graphene [16] becomes frequency-dependent in the case of the intraband transitions. The optical sheet conductivity (i.e. absorbance) of graphene varies significantly with the carrier density [16] at low photon

energies (≤ 0.5 eV) and contribution of the intraband transitions to the absorbance decreases with the increasing photon energy.

Since the unique absorption of graphene stems from the characteristics of the Dirac fermions, it only appears for energies close to the Dirac point. For photon energies, which are greater than 2 eV, the nearest-neighbor hopping may occur and the Dirac fermion approximation may fail. Furthermore, an effect known as the triangular warping occurs for the photon energies near 5 eV [15], where the shape of the band structure deviates from a perfect cone and hence, the linear dispersion relation cannot be assumed for the carriers. Therefore, near such photon energies, the optical response of graphene is not simply explained by the models that are described above.

1.2 Optical Characterization Methods for Graphene

Different optical characterization tools have been used to investigate the optical properties of graphene. Spectrophotometry [18], time-resolved spectroscopy [16], and Raman spectroscopy [19, 20] were used to investigate the optical characteristics of graphene that was used in our mode locking experiments. In Section 1.2, these methods will be discussed in detail.

Spectrophotometry covers the measurement techniques which are utilized to investigate the linear optical properties of different materials. It gives information about the transmittance and absorbance of a given material as a function the wavelength by using a broadband light source and a monochromator. In a spectrophotometer, there is a compartment in which a sample is placed at the path of the measurement beam. The other sample holder, which is also located in the same compartment, is used as the reference for the measurements. The sample and the reference holder are illuminated by a broadband light source and intensity of the light beam is measured with respect to the reference after passing through the sample.

The number of graphene layers and the absorption amount per layer can be measured by using spectrophotometers. As expected from Eq. (1.1.10), the optical absorption of graphene is proportional to the number of layers and it increases with the increasing number of layers. Figure 1.2.1 shows, the measured linear transmission of the monolayer graphene on quartz sample, which was used in our experiments.

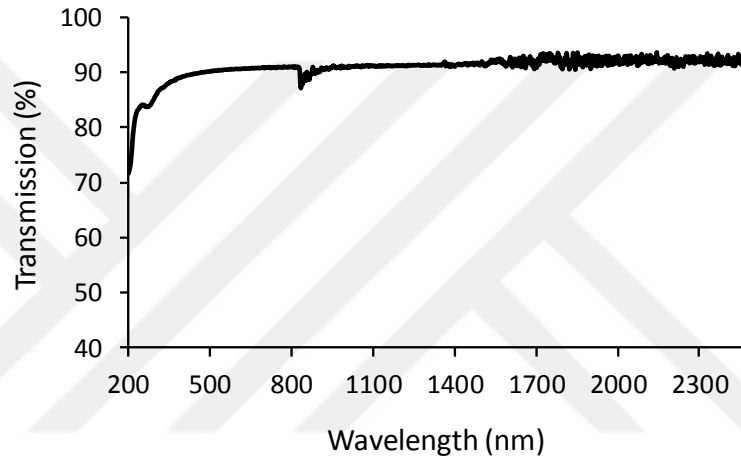


Figure 1.2.1. Optical transmission spectrum of our monolayer graphene grown on a quartz substrate.

As can be seen from Fig. 1.2.1, optical response of graphene, due to the interband transitions, is nearly constant from near-ultraviolet to mid-infrared. The measured transmission was not exactly 97.7%, since the optical loss arising from the substrate is not subtracted and the sample was placed at normal incidence. The glitch around 800 nm was due to the mechanical noise of the spectrophotometer. The characteristic optical response of graphene, due to the interaction of graphene with the high-energy photons in the ultraviolet region, can be further seen from Fig. 1.2.1.

Spectrophotometers provide useful information about the basic characteristics of a given material, however, it does not give the time-resolved details of the optical properties. On the other hand, transient absorption measurement tools are based on the use of a high peak-

power ultrafast laser source and provide the time- and intensity-dependent nonlinear optical properties of a material.

Time-resolved spectroscopy has been used as an effective tool to measure the ultrafast carrier dynamics of graphene. In this technique, graphene sample is excited with an ultrafast laser source and then, its absorbance is measured with respect to the time delay between pump and probe pulses. In 2007, Dawlaty et al. measured the ultrafast relaxation times of the carriers in graphene by using an ultrafast pump-probe setup [21]. Their pump-probe source was a 85-fs Ti^{3+} :sapphire laser and their sample was a graphene on SiC substrate. The carriers of graphene were excited with the energetic pump pulses and their relaxation time was monitored by using the weak-energy probe pulses. Their measurements demonstrated that, the photo-excited carriers come back to an equilibrium state (i.e. Fermi-Dirac like distribution state) through a fast carrier-carrier scattering process among themselves and then, they recombine back (i.e. electron-hole recombination) on a slower time scale near the Dirac point. Dawlaty et al. performed a bi-exponential fit to find the time scales of the both processes and hence, the time scale for the fast and slow decays were found in the range of 70-120 fs and 0.4-1.7 ps respectively [21].

In another study, Heinz et al. extensively characterized the dependence of the interband/intraband transition rates to the incident light fluence by using a similar pump-probe setup [16]. The probe source was a 100-fs Ti^{3+} :sapphire laser operating at 800 nm and the pump source was at 400 nm, which was obtained from the frequency-doubled pump laser. They measured the optical conductivity as a function of the delay between the pump and the probe sources and concluded that since the carriers in graphene are described as the Fermi-Dirac system, the intra and interband transition rates have an electronic temperature (i.e. incident laser fluence) dependence. According to their study, which assumed non-interacting electrons, the optical sheet conductivity of graphene can be written as [16]

$$\sigma_{\text{intra}} = \frac{e^2 8 \ln 2}{2h} \frac{\Gamma k_B T}{(\hbar\omega)^2 + \Gamma^2} \quad (1.2.1)$$

and

$$\sigma_{\text{inter}} = \frac{\pi e^2}{2h} \tanh\left(\frac{\hbar\omega}{4k_B T}\right) \quad (1.2.2)$$

for the intraband and interband transitions. Here, Γ is the scattering rate of the carriers, k_B is the Boltzmann constant, T is the electronic temperature (induced by the pump laser), and $\hbar\omega$ is the energy of the probe beam. For Eq. (1.2.1), the intraband contribution to the optical response of graphene is expected to have a positive transient sign and it dominates at low pump fluence levels (i.e. low electronic temperature). The intraband transition further enhanced the optical conductivity due to the additional free carriers which were formed after the optical excitation. In the case of Eq. (1.2.2), the interband contribution gives a negative transient sign due to the bleaching of the absorption. In their experimental/model results [16], if the temperature of the system is increased (i.e. higher laser fluences), the interband transition start to dominate for the same photon energy and at low fluence levels the intraband transition dominates the optical conductivity of graphene (i.e. positive transient sign). However, the contribution coming from the interband transition forces the transient to change its sign (e.g. negative) at high fluence levels (i.e. high electronic temperatures) for the same photon energy [16]. Hence, the transient response of the graphene changes with the incident fluence level of the pump-probe system.

The carrier dynamics of graphene offers rich physical phenomena and it has been extensively investigated by different groups. Since our aim was to use graphene and graphene-based devices as modulators for generating femtosecond pulses, it is sufficient to focus on the carrier recombination time and the saturation characteristics of graphene. Other studies, which further investigate the carrier dynamics of the fast and slow relaxation processes in detail, can be found in Refs. [22, 23].

Figure 1.2.2 shows a typical transient absorption measurement data, which gives information about the fractional transmission change as a function of the time delay between the pump and the probe pulses. As can be seen, the fractional change in the transmission increases rapidly upon excitation and then, the carriers decay back to their original state through carrier-carrier scattering and recombination processes as described above. The use of graphene for femtosecond pulse generation purposes considers the slow decay time (τ) of the interband transitions, which is also called as the recovery time, and it should be smaller than the cavity round-trip time to work as an effective fast optical modulator. As can be seen from Fig.1.2.2, our measurements yielded 1.5 ps for the slow component of the carrier relaxation time, which agrees with the literature values given above [21], and indicated that graphene is suitable for femtosecond pulse generation.

Apart from the time-dependent nonlinear optical characterization of graphene, it is also important to explore the behavior of graphene with respect to the incident fluence level. For a monolayer graphene, the linear absorption due to the interband transition is nearly wavelength-independent and around 2.3%. It is known that the transmission of graphene increases with the increasing incident fluence and saturates at a certain level, which is called as the saturation fluence (J_{sat}).

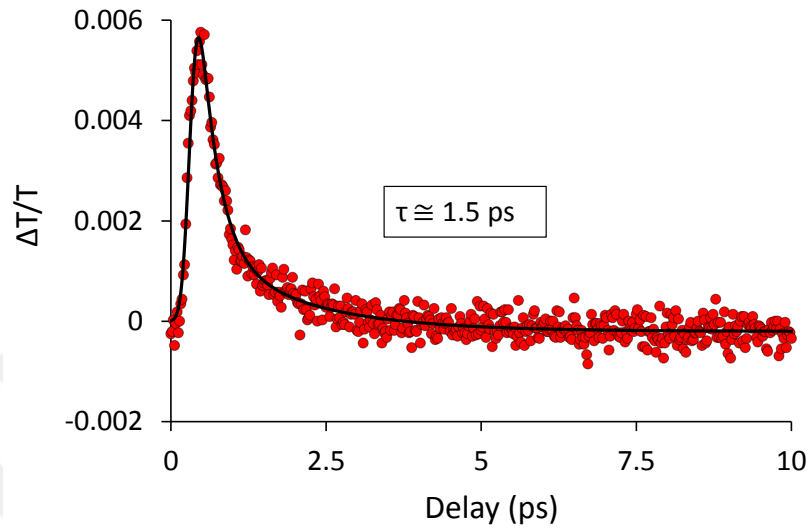


Figure 1.2.2. The measured fractional change in the transmission of graphene as a function of the time delay. The measurement was performed by using the pump-probe setup at Koç University Surface Science and Technology Center (KUYTAM). (Adapted with permission from [24], (The Optical Society)).

Furthermore, the difference between the saturated transmission value and the linear transmission value is called as the modulation depth (Mod. depth) and gives the percentage of the absorption amount that can be saturated to increase the optical transmission. To investigate the fluence-dependent response of graphene, z-scan technique can be used [25]. However, it can be also explored by using a pump-probe setup. Figure 1.2.3 shows, the saturation curve that was obtained for our graphene on quartz sample by using the pump-probe setup at Koç University Surface Science and Technology Center (KUYTAM). As can be seen, the transmission of graphene increases with the increasing incident fluence and saturates at high incident fluence levels. Typical values for the saturation fluence of a monolayer graphene is of the order of 15-30 $\mu\text{J}/\text{cm}^2$ [26-28] and up to 1% of modulation depth can be achieved for a monolayer graphene [26-28]. As can be seen from Fig. 1.2.3,

our measurement also yielded the saturation fluence (J_{sat}) and the modulation depth (Mod. depth) values which agree with the literature.

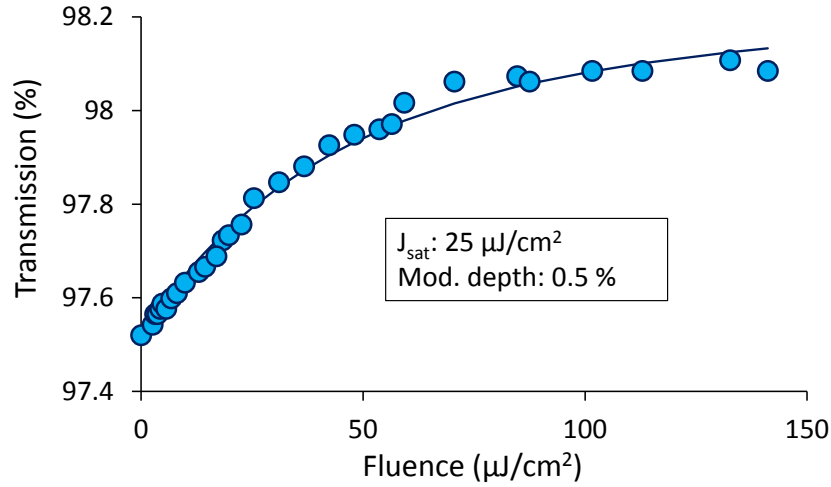


Figure 1.2.3. The measured saturation fluence and the modulation depth of our monolayer graphene on quartz sample by using the femtosecond transient spectroscopy system at Koç University Surface Science and Technology Center (KUYTAM). (Adapted with permission from [24], (The Optical Society)).

To find the modulation depth value of the graphene sample, the fit equation

$$\Delta A = -\frac{q_0}{T_0 \ln 10} \left(1 - \frac{J_{sat}}{J} \left(1 - e^{\left(-\frac{J}{J_{sat}} \right)} \right) \right) \quad (1.2.3)$$

was used. Here, ΔA is the difference between the absorbance amount obtained from the pumped (i.e. pump laser is on) graphene and from the unpumped graphene (i.e. pump laser is off), T_0 is the steady-state transmission of graphene ($\sim 97.7\%$), q_0 is the modulation depth, J is an arbitrary fluence level, and J_{sat} is the saturation fluence. Equation (1.2.3)

was used to determine the modulation depth and then, the corresponding saturation fluence is found by using

$$\Delta A = -\frac{q_0}{T_0 \ln 10} \frac{1}{e} = -\frac{\Delta A_{\max}}{e} \quad (1.2.4)$$

Since ΔA reaches its maximum value $\Delta A_{\max}$ at $J = J_{\text{sat}}$.

The detailed information about the saturable absorber parameters for femtosecond pulse generation, such as saturation fluence, modulation depth, and recovery time will be given for a general saturable absorber and a graphene saturable absorber in Section 2.3.1. The measurement setup used for the pump-probe and the saturation experiments will also be described in Chapter 4.

Another important tool, which has been utilized to characterize graphene, is the Raman spectroscopy. The Raman shift of the Stokes and the anti-Stokes processes are direct indicators of the vibrational energy states of graphene. The number of transferred graphene layers and their optical quality can be roughly estimated by simply measuring its transmission spectrum and looking at the graphene flake formations with an optical microscope. Furthermore, in 2006, Ferrari et al. proposed a more precise method to realize the features of graphene by using Raman spectroscopy [19, 20]. In graphene, a strong phonon energy shift occurs under a laser excitation and hence, a large amount of information, such as number of layers, defects, optical quality, and doping level can be extracted by using the Raman spectroscopy. In a typical Raman spectroscopy, the sample is illuminated by a monochromatic laser beam (usually 532 nm) which interacts with the molecular vibrational modes of the sample. The radiation resulted from the inelastic scattering (i.e. Raman scattering) is collected and sent to a monochromator. The inelastic scattering can be Stokes, creation of a phonon, or anti-Stokes, annihilation of a phonon, depending on the thermodynamic equilibrium population of the energy states of a material. If the atoms or molecules are populated in the ground state and excited to an upper level,

the scattered photon has less energy than the incident photon and hence, the process is called as the Stokes scattering. On the other hand, if the atoms or molecules are populated at an excited level and they lose energy after the excitation, the process is called as the anti-Stokes and the resulted photon has a less energy than the incident one. Since most of the materials have higher ground level populations in the thermodynamic equilibrium, the Stokes peaks are stronger than the anti-Stokes peaks in general.

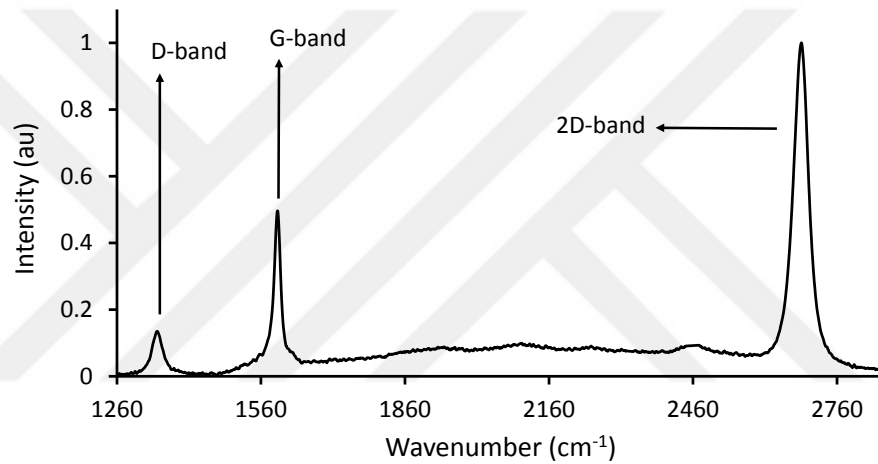


Figure 1.2.4. The Raman spectrum of a monolayer graphene on a quartz substrate. (Adapted with permission from [24], (The Optical Society)).

Figure 1.2.4 shows a typical Raman spectrum of a monolayer graphene measured at Koç University Surface Science and Technology Center (KUYTAM). In the Raman spectrum of graphene (Fig. 1.2.4), there are three main characteristic peaks (D, G, and 2D), which occur due to the different phonon transfer processes. The first band near 1350 cm⁻¹ is not visible in a pristine graphene because D-band stems from the crystal symmetries and the disordered structures in graphene. At first, a charge carrier in graphene is excited via incident photon and then, it is inelastically scattered by a phonon. If a second elastic scattering occurs due to a defect, the D-peak occurs in the spectrum [19, 20] and hence, a spectrum with a low intensity D-peak gives the purity of a graphene sample. The G-peak

arises due to the in-plane and the out-of-plane stretching of the carbon-carbon bonds in the graphene lattice [19, 20]. If the incident photon interacts with the stretching phonon vibrations, one phonon is created and hence, this one phonon process is responsible for the observation of the G-peak near 1500 cm^{-1} . The last band shown in Fig.1.2.4 is the 2D-band. It is the overtone of the D-peak and located near 2500 cm^{-1} , however, it is not related with the defects in graphene and it is always present in the Raman spectrum of graphene. The 2D-band originates from a two-phonon scattering process, where the momentum conservation is satisfied by the two phonons with opposite wave-vectors [19, 20]. The D/G and G/2D ratios, and FWHM of the 2D-peak are used to characterize the graphene sample. The D/G ratio provides information about the crystal quality of graphene and the G/2D ratio gives the number of graphene layers [19, 20]. FWHM of the 2D-peak also provides information about the number of layers and it becomes larger going from graphene to graphite. Although these peaks are the fingerprints of graphene and provides a large amount of information about the number of transferred graphene layers, in some cases, bilayer graphene acts as an isolated single layer and can exhibit similar peak ratios. Therefore, together with the Raman spectroscopy, one should also perform a steady-state optical transmission measurement to obtain an accurate information about the number of layers of a graphene sample.

1.3 Novel Graphene-Based Modulators with Voltage Reconfigurable Absorption Levels

In recent years, due to its nearly constant and broadband absorption, saturation, and fast recovery time, monolayer graphene has been used as an effective passive modulator to generate ultrashort pulses from solid-state or fiber lasers operating in a wide wavelength range [19, 20, 24, 27-39]. Our group, together with C. Kocabas's group from Bilkent University have been also contributing to the field of ultrashort pulse generation by using graphene as a passive modulator. To the best of our knowledge, we demonstrated, the

highest peak power obtained from a graphene mode-locked solid-state laser, which will be also presented in Chapter 4 [24, 40], femtosecond pulse generation from a Cr:LiSAF laser with graphene for the first time [39], and the shortest pulse ever obtained from a graphene mode-locked laser [41]. In addition, in collaboration with F. Rotermund's group from Ajou University, we demonstrated the use of a graphene as a passive modulator up to as high a wavelength as possible (2500 nm) for the first time to our knowledge [38]. Despite the unique optical properties of graphene, one potential drawback arises due to its broadband absorption of 2.3%. This nearly constant absorption can lead to an excessive round-trip optical insertion loss of 5% and such a loss level may not be tolerable for lasers with low gains or lasers operated at low optical pumping levels. Therefore, it may not be possible to use graphene as a modulator for lasers, in which the net optical amplification is comparable to this loss level. To overcome this limitation, it is important to have a control over the absorption of graphene while maintaining its saturable absorber properties. Since reducing the thickness of an atomic layer graphene is not physically possible, different approaches have been proposed to control the absorption in graphene. In Section 1.3, these methods will be discussed and the operation principles for our graphene-based devices with superior designs, which enable the modification of the absorption amount in graphene will be presented.

Due to the interband transitions of the carriers from the valance to the conduction band in graphene, a nearly constant absorption of 2.3% can be achieved from near-ultraviolet to mid-infrared. As illustrated in Fig. 1.3.1 (a), if we neglect the unintentional doping (it also shifts the Fermi level), the Fermi level lies at the Dirac point and hence, absorption occurs for all wavelengths readily. If the final state is occupied with the carriers, the transition is not allowed due to Pauli exclusion principle. To block the absorption of a desired wavelength, one possible remedy is to shift the Fermi level up from the Dirac point to occupy the final state with the carriers. As can be seen from Fig.1.3.1 (b), if the incident

photon energy E_p is less than the Fermi level shift, no absorption occurs and hence, graphene becomes transparent for the wavelengths with such photon energies.

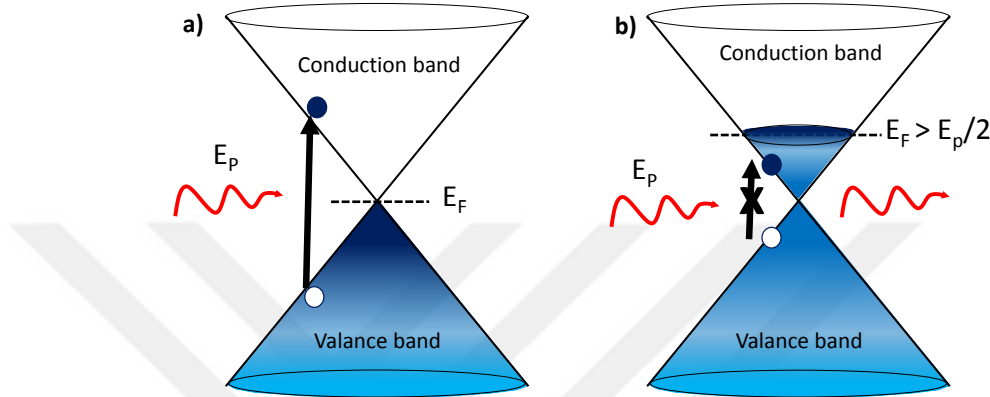


Figure 1.3.1. (a) Sketch of the absorption in graphene when the Fermi level is at the Dirac point and (b) the Fermi level position is shifted up.

Going from the absorbing state to the transparent state in graphene does not occur sharply at the room temperature due to the nature of the Fermi-Dirac distribution (Figure 1.3.2)

$$f(E)_{FD} = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)} \quad (1.3.1)$$

which gives the probability that a particle will have an energy E for a given temperature T . Therefore, it is possible to block the transitions not only for a certain photon energy E_p but also for wavelengths with energies near E_p .

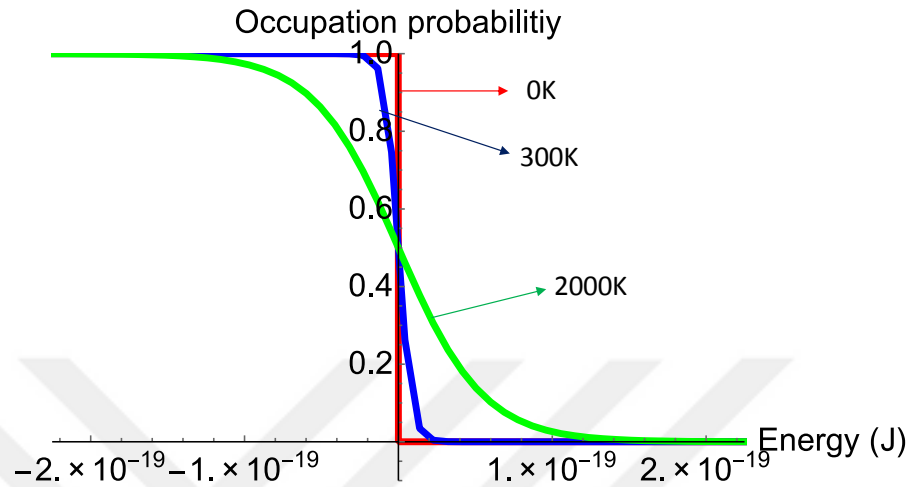


Figure 1.3.2. Illustration of the Fermi-Dirac distribution at different temperatures.

Different methods have been proposed to block the desired transitions of monolayer graphene by shifting the Fermi level position from the Dirac point via chemical or electrostatic doping. In the case of the chemical doping, a fixed amount of shift in the Fermi level position can be achieved by n- or p-type doping (Figure 1.3.3). Several groups have been proposed graphene structures with shifted Fermi levels by using the chemical doping method [42]. However, chemical doping of graphene is not a suitable approach to control the loss level inside a laser resonator, since it leads to an irreversible change in the absorption and the insertion loss cannot be dynamically controlled. Alternatively, adjustable control of absorption can be achieved by using capacitor structures, which shift the Fermi level via electrostatic gating. However, graphene-based solid-state capacitors operate over a limited wavelength range due to the requirement of high applied voltages to shift the Fermi level for visible and near-infrared region with a risk of dielectric breakdown [43, 44]. On the other hand, graphene-based supercapacitors, which will be described next, have the advantage of the dynamic control of the absorption over a broad wavelength range from visible to near-infrared [45-48].

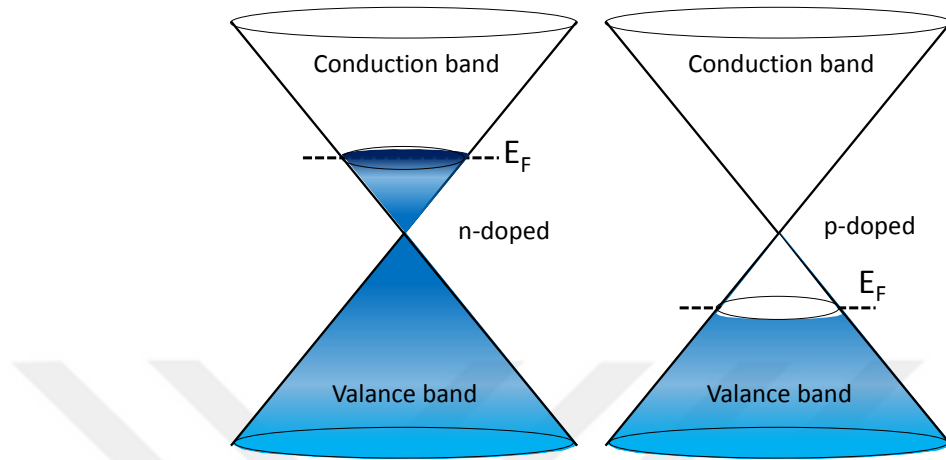


Figure 1.3.3. Energy-band diagram for n-doped (left) and p-doped (right) graphene.

A capacitor is simply used as an energy storage device with two conducting plates (i.e. electrodes) separated by an insulating medium. In the case of a solid-state capacitor, a solid insulating medium is commonly used between the plates. For supercapacitors, the electrodes of the capacitor are separated by a high-dielectric-constant ionic electrolyte, which can be organic or inorganic [49]. Application of a voltage bias between the electrodes of the supercapacitor polarizes the high-dielectric-constant electrolyte and hence, leads to the formation of an ultrathin electrical double layer (EDL) [50-52]. As shown in Fig.1.3.4, positively charged ions inside the electrolyte are attracted by the negatively charged plate and then, these positive ions further attract the negative ions of the electrolyte and vice versa. Thus, several EDLs, which act as separate supercapacitors connected in series with few nanometer thicknesses, are formed inside the electrolyte and hence, large electric fields are produced within the EDLs even with low applied voltages.

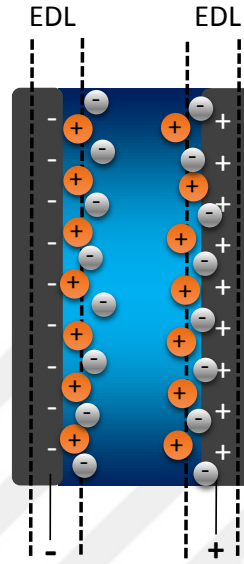


Figure 1.3.4. Schematic of the electrical double layer formation inside a supercapacitor.

In the case of a graphene-based supercapacitor, the supercapacitor architecture is formed by the graphene-graphene or the graphene-metal electrodes, which are separated by a high-dielectric-constant ionic electrolyte. The fabrication and the optical characterization details of the supercapacitor structures used in our experiments will be discussed in detail in Chapters 5 and 6.

In this electrostatic gating scheme, which uses an electrolyte, ultrathin EDLs with very large electrical fields are formed near the graphene surface and hence, the Fermi level of graphene can be dynamically shifted from the Dirac point into the conduction band or the valance band depending on the polarity of the applied voltage. It is not possible to obtain a high level of Fermi level shift in graphene layers via solid-state capacitor structures as opposed to the supercapacitors, since the voltage drops linearly through the dielectric layer within a solid-state capacitor. The amount of Fermi level shift ΔE_F in graphene electrode can be expressed as [45]

$$\Delta E_F = \hbar v_F \sqrt{\pi n} \quad (1.3.2)$$

where $\hbar$ is the Planck's constant, v_F is the Fermi velocity, and n is the carrier density given by

$$n = \int f(E)g(E)dE \quad (1.3.3)$$

Here, $f(E)$ is the Fermi-Dirac distribution function given in Eq. (1.3.1) and $g(E)$ is the density of states for graphene given by

$$g(E) = \frac{2|E|}{\pi \hbar^2 v_F^2} \quad (1.3.4)$$

The Fermi level shift, which is around 2.3 eV, is obtained at low operating voltages (-3.5-5V) in graphene by our collaborator C. Kocabas's group. 2.3 eV of Fermi level shift enables the operation of this device from visible to near-infrared as an effective modulator without dielectric breakdown [45] as opposed to the graphene-based solid-state capacitors, which require high voltages to achieve the same amount of shift.

In this optical modulator, which is based on ionic gating, graphene electrodes can be modelled as variable resistors and capacitors with quantum capacitances C_Q given by [45]

$$C_Q = \frac{2e^2}{\hbar v_F} \sqrt{\frac{n}{\pi}} \quad (1.3.5)$$

Capacitance of the graphene electrode is minimum near the Dirac point and it increases with the increasing voltage. In our architecture, since the capacitance of the EDL-based supercapacitors are much larger than the quantum capacitance of the graphene electrodes, the equivalent capacitance of the device is defined by the total capacitance of the EDL-based ultrathin supercapacitors. The resulting electronic properties of the supercapacitor can be found in Ref. [45].

Graphene-based supercapacitors have been demonstrated for different photonic and electronic applications by several groups [50, 52, 53]. However, their use as an effective passive modulator with a voltage configurable absorption level was demonstrated for the first time by our groups [54-56] and will be discussed in Chapters 5, 6, and 7.



Chapter 2

ULTRASHORT LASER PULSES

Ultrashort laser pulses have been widely used in different applications, such as ultrafast spectroscopy [57-60], optical coherence tomography [61-63], multi-photon microscopy [64-66], and high-harmonic generation [67-69], which require high temporal and spatial resolutions with a sufficient laser intensity. Hence, it is important to explore different lasers in the mode-locked regime and to investigate new technologies to generate ultrashort pulses from lasers. In Chapter 2, characteristic features of ultrashort pulses, propagation of such pulses in nonlinear media, and dispersion control methods to generate solitary ultrashort pulses will be discussed.

2.1 Characteristics of Ultrashort Laser Pulses

An ultrashort pulse refers to an electromagnetic wave packet that is described by the temporal and spectral components of the electric field. Duration of an ultrashort pulse is of the order of picosecond or less, which is significantly shorter than the cavity round-trip time of a typical solid-state laser.

In a laser resonator, infinitely many longitudinal modes oscillate at discrete, equally spaced resonant frequencies and the net electric field due to such modes also randomly oscillates over time and hence, the laser produces approximately constant output power as a function of time. If these modes are forced to oscillate with a fixed phase relation among themselves, the laser operates in the pulsed regime. Hence, it is possible to generate train of periodic pulses with short temporal durations. In this case, output power of the laser is distributed among the multiple longitudinal modes oscillating with a fixed phase inside the resonator and output power becomes time-dependent.

Typical characteristics of an ultrashort pulse are its duration, repetition rate, energy, and peak power. Repetition rate f_{rep} of a pulse is equal to the free spectral range (i.e. the difference between the two adjacent longitudinal modes, ν_{FSR}) and written as [70]

$$f_{rep} = \frac{c}{2L} \quad (2.1.1)$$

where c is the speed of light in vacuum and L is the optical path length of the laser resonator. Furthermore,

$$T_R = \frac{1}{f_{rep}} \quad (2.1.2)$$

is the cavity round-trip time of the laser resonator. In the pulsed regime, output power (P_{out}) of the laser is distributed among the locked modes and provides the pulse energy as,

$$E_p = \frac{P_{out}}{f_{rep}} \quad (2.1.3)$$

Peak power of the pulse is defined as

$$P_{peak} = \frac{E_p}{\tau_p} \quad (2.1.4)$$

and it increases as the pulse duration (τ_p) decreases. Spectral bandwidth of the gain medium is defined as $\Delta\nu$. Since temporal and spatial characteristics of the electric field are related to each other through Fourier transform, they cannot vary independently. Hence, if all the modes of the spectral gain bandwidth are locked with a fixed phase, the pulse width becomes

$$\tau_p \approx \frac{1}{\Delta\nu} \quad (2.1.5)$$

Pulse width τ_p of an ultrashort pulse can be defined as the time difference between the pulse peak and the first zero. Such pulses are called as transform-limited pulses and satisfy a minimum duration-bandwidth product given by [71]

$$\tau \Delta \nu = K \quad (2.1.6)$$

Here, τ is the FWHM (full-width-half-maximum) of the pulse and K is a constant, which depends on the actual pulse shape (e.g. for a sech-shaped pulse, $K = 0.315$). Value of the K determines how close is the duration of the pulse to the shortest possible duration for a given spectral width.

A common femtosecond laser requires a spectral bandwidth, which can sustain over 100,000 locked modes corresponding to a 10 THz bandwidth. For example, a solid-state laser with 100 MHz pulse repetition rate and 100 mW of output power will have a pulse energy of 1 nJ and with a 10 THz spectral bandwidth, it can generate 30-fs transform-limited ($K=0.315$), sech-shaped pulses. In this example, the peak power of the pulses for the same laser will be around 0.033 MW.

2.2 Pulse Propagation in Nonlinear Media

In general, the polarizability of a medium depends on the intensity of the interacting electric field. Since the intensity of a femtosecond light source is sufficiently high, it induces an intensity-dependent polarization with a linear and a nonlinear response inside a material. The effects such as high harmonic generation, Raman, and Kerr effect stem from the nonlinear part and the classical effects such as reflection and refraction arise from the linear response of the material. In this Section, effect of the material dispersion on an ultrashort laser pulse, nonlinear effects, such as self-focusing and self-phase modulation will be discussed. Furthermore, a specific type of a pulse with a balanced nonlinearity (i.e. solitary pulse) and the methods to compensate the given nonlinear effects inside the resonator will be presented.

2.2.1 Effects of Dispersion on Ultrashort Pulses

In a dispersive medium, where the refractive index is a function of the frequency, each frequency component of the pulse will undergo different time delays and hence, an ultrashort pulse will experience a broadening due to the frequency-dependent refractive index. Hence, the generated pulses are no longer transform-limited due to this varying phase difference. The dispersion of a given material can be described by either the frequency or the wavelength-dependent refractive index as [71]

$$\frac{dk}{d\omega} = \frac{1}{c} \left(n - \lambda \frac{dn}{d\lambda} \right) \quad (2.2.1)$$

$$\frac{d^2k}{d\omega^2} = \frac{\lambda^3}{2\pi c^2} \left(\frac{d^2n}{d\lambda^2} \right) \quad (2.2.2)$$

and

$$\frac{d^3k}{d\omega^3} = - \left(\frac{\lambda}{2\pi c} \right)^2 \frac{1}{c} \left(3\lambda^2 \frac{d^2n}{d\lambda^2} + \lambda^3 \frac{d^3n}{d\lambda^3} \right) \quad (2.2.3)$$

Here, k is the wave vector, ω is the frequency of the light, and n is the wavelength-dependent refractive index, which can be determined by using the Sellmeier equation for a given material. Equations (2.2.1), (2.2.2), and (2.2.3) stand for the inverse of the group velocity of the pulse at which the pulse envelope propagates, the second-order group velocity dispersion (GVD), and the third-order group velocity dispersion respectively.

Furthermore, $\frac{\omega}{k}$ gives the phase velocity of the pulse at which any fixed phase point of the

electric field cycle is displaced. If $\frac{d^2k}{d\omega^2} > 0$, the group velocity dispersion introduced by the material to the pulse is positive and the low frequency components of the pulse travel faster

than the higher ones. If $\frac{d^2k}{d\omega^2} < 0$, the high frequency components travel faster than the lower ones. If the refractive index of the material decreases with the wavelength, the blue components refracts more than the red ones (i.e. normal dispersion) and vice versa for the increasing refractive index (i.e. anomalous dispersion). In general, it is sufficient to consider the second-order dispersion to estimate the broadening of an ultrashort pulse. However, for the lasers with broad spectral widths, higher-order terms should also be considered to describe the pulse evolution while propagating in the dispersive medium. The final duration of a pulse after it passes through a medium with a second-order dispersion (D), can be calculated from [70]

$$\tau_{final} = \tau_{initial} \sqrt{1 + \left(\frac{4 \ln 2 D}{\tau_{initial}^2} \right)^2} \quad (2.2.4)$$

where τ_{final} and $\tau_{initial}$ are final and initial pulse durations respectively.

2.2.2 Self-Focusing and Self-Phase Modulation of Ultrashort Laser Pulses

Lasers, which generate ultrashort pulses, have sufficiently high intensities to bring out nonlinear processes, such as Kerr effect, high-harmonic generation, and Raman effect depending on the order of the nonlinearity. If the intensity of the laser pulse is high enough to create an intensity-dependent refractive index change inside the medium, Kerr effect takes place, which shapes the pulse in the time and the space domain. The resulting intensity-dependent refractive index becomes [70]

$$n = n_0 + n_2 I \quad (2.2.5)$$

In Equation (2.2.5), n_0 is the ordinary refractive index and n_2 is the nonlinear refractive index, which depends on the intensity.

Typical laser beam has a Gaussian intensity distribution, where the beam has a higher intensity on the beam axis and a lower intensity at the edges of the Gaussian profile. Due to the Gaussian-shaped intensity distribution, if a beam with sufficiently high intensity passes through a medium, it will undergo a self-focusing process in the space domain as shown in Fig. 2.2.1.

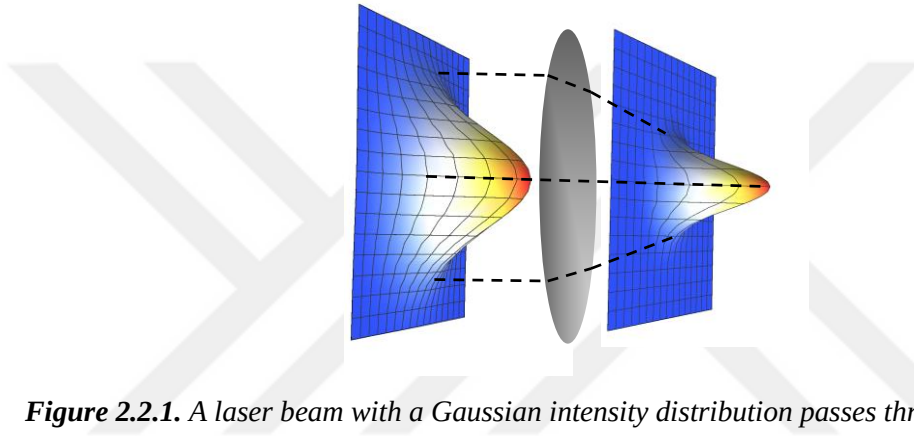


Figure 2.2.1. A laser beam with a Gaussian intensity distribution passes through a medium and gets focused due to the Kerr effect.

Due to this intensity-induced refractive index change, the medium acts as an artificial positive lens and hence, in every pass through the medium, the beam will be more focused and the optical intensities become even higher until it causes instabilities in the pulsed regime or optical damage inside the medium. Such effects occur when the intracavity pulse peak power exceeds the critical power [72]

$$P_{cr} = \frac{\alpha \lambda^2}{8\pi n_0 n_2} \quad (2.2.6)$$

which gives an upper limit to the peak power of the pulse that can be achieved during single-pulse mode-locked operation. In Eq. (2.2.5), α is a dimensionless correction factor, which varies between 3.77-6.4, and λ is the central wavelength of the pulsed laser. If the Kerr nonlinearity coefficient (γ), the length l_m of the medium, and the effective area of

(A_{eff}) the beam inside the Kerr medium are known, the nonlinear refractive index (n_2) can be determined from

$$n_2 = \frac{1}{2\pi} \frac{\gamma \lambda A_{eff}}{2l_m} \quad (2.2.7)$$

and Eq. (2.2.7) can be used to estimate the critical power for a given medium. Self-focusing of the pulse due to the Kerr effect is advantageous in some cases. For example, a commonly used mode locking technique, which is called as Kerr-lens mode locking (KLM), relies on the self-focusing of the laser beam inside the laser gain medium due to the Kerr effect as explained in Section 2.3.2.

In the temporal domain, intensity-induced refractive index change leads to a time varying phase across the pulse. This phase variation is called as the self-phase modulation (SPM) [73] and occurs when the intensity of the pulse is sufficient to modulate its own phase. When more than one ultrashort laser pulses interact inside the Kerr medium, the same process is called as the cross-phase modulation (XPM). Since the intensity of the pulse has the highest value at the center of the pulse as shown in Fig. 2.2.1, the phase change is maximum at the center and hence, the pulse gets broadened as it passes through the Kerr medium.

Effect of the self-phase modulation on an ultrashort pulse can be described by following the analysis of Ref [70]. If the second-order dispersion is neglected, the evolution of the pulse envelope function ($a(z, T)$) due to the Kerr effect can be written as

$$\frac{\partial a}{\partial z} = -i\gamma a(z, T)|a(z, T)|^2 \quad (2.2.8)$$

In Eq. (2.2.8), T is the measured time in the reference frame, where the pulse propagates at the group velocity (u_g), and equals to $t - \frac{z}{u_g}$. As can be seen from Eq. (2.2.8), the

evolution of the pulse envelope depends on the amount of the Kerr nonlinearity (γ) inside the medium. If we consider that the power $|a(z, T)|^2$ remains constant with an initial value $P(0, T)$, the pulse envelope function becomes [70]

$$a(z, T) \cong a(0, T) \exp(-i\gamma P(0, T)z) \quad (2.2.9)$$

with a nonlinear phase shift ϕ_{NL} equals to

$$\phi_{NL}(z, T) = -\gamma P(0, T)z \quad (2.2.10)$$

Self-phase modulation leads to a phase shift on the pulse envelope in the time domain, and it acts as a second-order positive dispersion source, where the dynamic frequency of the pulse is downshifted at the leading edge. Figure 2.2.2 shows the temporal intensity profile (a) and the electric field (b) of a Gaussian pulse propagating in a medium without dispersion. As can be seen, in the presence of the second-order positive dispersion (c) and the self-phase modulation (d), the frequency components of the leading edge of the pulse are downshifted and hence, the pulse gets broadened in the time domain with a downshifted dynamic frequency at the leading edge. Furthermore, at the center of the pulse, the frequency shift is approximately linear as shown in Fig. 2.2.2 (d). In this case, addition of the second-order negative dispersion can compensate the pulse broadening due to the self-phase modulation and hence, the pulse propagates through the medium with a constant spatial and a temporal shape. Such pulses are called as the solitary optical pulses and will be discussed in the following section.

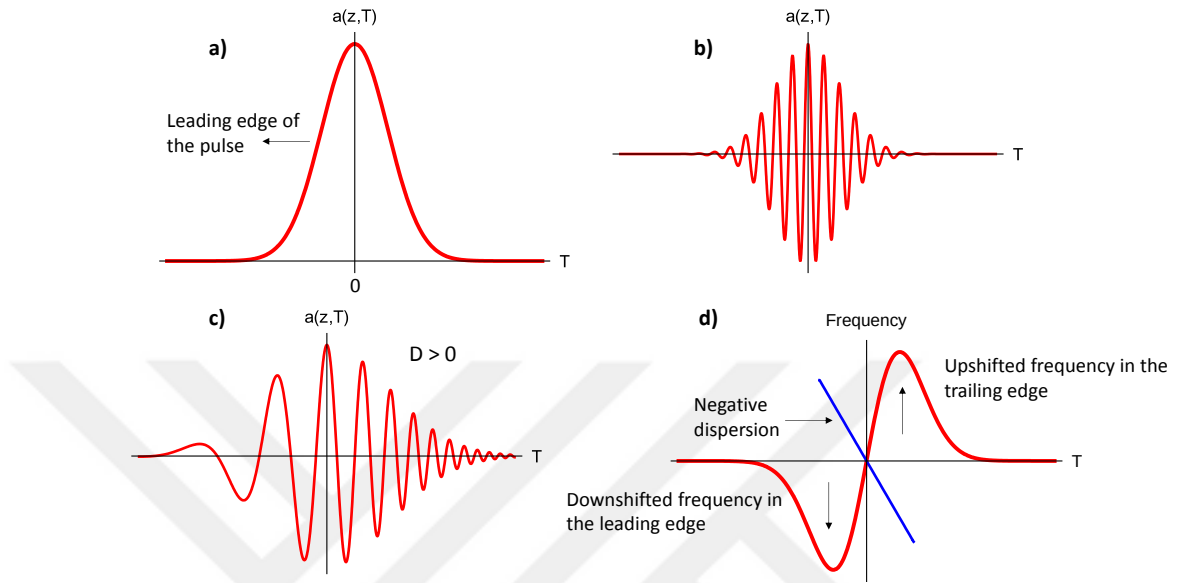


Figure 2.2.2. (a) The temporal envelope and (b) the electric field distribution of an incident Gaussian pulse. (c) The evolution of the electric field in the presence of the second-order positive dispersion. (d) A phase shift occurs in the pulse due to the self-phase modulation and it can be balanced by introducing negative second-order dispersion.

2.2.3 Optical Solitons and Methods to Control Nonlinear Effects During Pulse Propagation in Nonlinear Media

An optical soliton is a specific type of pulse that propagates without distortion in time and space domain. They can be obtained by cancelling the self-phase modulation and the second-order dispersion effects due to the medium in which the pulse propagates. Evolution of the pulse envelope function under the self-phase modulation is given in Eq. (2.2.8). If the second-order dispersion and the self-phase modulation exist at the same time, the pulse envelope function can be written as [74]

$$\frac{\partial a}{\partial z} = iD \frac{\partial^2 a}{\partial T^2} - i\gamma a(z,T)|a(z,T)|^2 \quad (2.2.11)$$

where D is the second-order dispersion term. Equation (2.2.11) is called as the Nonlinear Schrödinger Equation because the potential energy term is a nonlinear order of the wave function itself. The analytical solution of Eq. (2.2.11) can be found in Ref. [74] and given by

$$a(z, T) = a_0 \operatorname{sech} \left(\frac{T}{\tau_0} \right) e^{-i\varphi/2} \quad (2.2.12)$$

Here, φ is the nonlinear phase shift of the soliton, which is equal to $\frac{\gamma a_0^2 z}{2}$, T is the time at which the pulse envelope propagates, and $1.76 \tau_0$ gives the duration τ_p of the sech-shaped pulses [71]. Furthermore, the nonlinear phase shift is also given by [74]

$$\varphi = \frac{|D|}{\tau_0^2} \quad (2.2.13)$$

The energy of the soliton (W) can be found by integrating the power with respect to the time as

$$W = \int_{-\infty}^{+\infty} |a(z, T)|^2 dT = a_0^2 \int_{-\infty}^{+\infty} \operatorname{sech}^2 \left(\frac{T}{\tau_0} \right) dT = 2\tau_0 a_0^2 \quad (2.2.14)$$

From Eq. (2.2.13) and Eq. (2.2.14), the energy required to propagate the fundamental soliton without distortion can be obtained as [74]

$$W = \frac{4|D|}{\gamma \tau_0} \quad (2.2.15)$$

Equation (2.2.15) is known as the soliton-area theorem, which connects the intracavity energy of the resonator (W) to the duration of the sech-shaped pulses for a fixed amount of resonator dispersion (D), and nonlinearity (γ). As described in Fig. 2.2.2 (d), addition of the sufficient negative second-order dispersion balances the self-phase modulation effects.

Hence, the amount of the negative dispersion needed to compensate the self-phase modulation (and the second-order positive dispersion) and to generate solitary optical pulses can be determined by using Eq. (2.2.15). As an example, consider a 20-mm Cr^{4+} :forsterite crystal with a nonlinear refractive index of $6 \pm 4 \times 10^{-20} \text{ m}^2/\text{W}$ [75], which provides a Kerr nonlinearity coefficient (γ) of approximately $5 \times 10^{-6} \text{ 1/W}$ when the laser beam at a wavelength of 1250 nm is focused to an effective area of nearly $5 \times 10^{-10} \text{ m}^2$ (By using Eq. (2.2.7)). If the intracavity energy (w) of the resonator is 100 nJ, nearly -7100 fs^2 dispersion (D) is required inside the resonator to obtain solitary pulses with 100-fs pulse durations.

In the remainder of Chapter 2, optical elements (e.g. specially designed mirrors, diffraction gratings, substrates, and prism pairs) which are used to compensate the positive second-order dispersion and the self-phase modulation effects on ultrashort pulses will be discussed.

Typical laser mirrors provide reflectivity at a specific wavelength and they are composed of alternating high-low index quarter wavelength dielectric layers with a strong Bragg-reflection. The reflectivity bandwidth ($\Delta\lambda$) of a standard Bragg mirror is determined by [76]

$$\frac{\Delta\lambda}{\lambda_0} = \frac{4}{\pi} \arcsin\left(\frac{n_H - n_L}{n_H + n_L}\right) \quad (2.2.16)$$

Here λ_0 is the central wavelength, n_H and n_L are the high and low index materials used for the mirror fabrication respectively. For a broadband mirror fabrication, Silicon Dioxide ($n=1.48$) and Titanium Dioxide ($n=2.4$) materials are commonly used and for a central wavelength of 800 nm, nearly 250 nm reflectivity bandwidth can be achieved. However, in some cases, the reflectivity bandwidth of a standard Bragg mirror is not sufficient to cover the spectral bandwidth of a mode-locked laser and the variation of the phase is not

controlled over such a broad bandwidth. To overcome these problems, Szipoecs and Krausz [77] proposed to use chirped mirrors, in which the layer stacks of the mirrors have different depths for a given wavelength. Therefore, each wavelength component of the pulse penetrates different depths inside the mirror and hence, each wavelength component of the pulse acquires a different phase delay over a much broader reflectivity range. However, one drawback arises because of the impedance mismatch between the ambient medium and the mirror layers, and the mismatch within the layers of the mirrors. These mismatches cause variations in the phases of each wavelength component and result in strong oscillations in the group delay dispersion of the mirror. Therefore, it becomes difficult to use such mirrors as robust pulse compression elements for the ultrashort pulse generation. This difficulty was solved with the design of the double-chirped mirrors (DCMs), which was introduced by Kaertner et al. [78]. In the DCM design, matching sections inside the mirror stack and an anti-reflection coating for the ambient impedance match were used to avoid the undesired group delay dispersion oscillations due to the mismatches.

Another dispersive mirror design that has been used for dispersion control is the Gires-Tournois interferometer (GTI) mirror, which works similarly to a Fabry-Pérot interferometer. The GTI mirror was introduced by Gires-Tournois et al. [79] as an alternative method for pulse compression. It is a special type of a Fabry-Pérot interferometer with one of the mirrors having a reflectivity of nearly 100%. Due to this high reflectivity, a GTI mirror practically does not change the power of the pulse while tuning its phase. Furthermore, the interferometer structure enables the phase variation between the different frequency components of the pulse and hence, the broadened parts of the pulse are compensated by bouncing the beam from the GTI mirror. The negative dispersion obtained from the GTI mirror can be adjusted by changing the angle of incidence of the beam or by adjusting the mirror separation of the interferometer structure,

similar to a Fabry-Pérot interferometer. However, for the femtosecond pulse generation applications, the mirror separation should be order of few microns and it is not practical for obvious reasons. An improved design, which consists of again an interferometer structure, but with multilayer and alternating index dielectric coatings on the mirrors was introduced by Happner and Kuhl [80] to overcome the practical problems. By using this improved design, the negative dispersion coming from the GTI mirror can also be controlled for the pulses with femtosecond durations. Nevertheless, interferometer structure of the GTI mirror limits the operation bandwidth of such mirrors and hence, the pulse duration should be above the round-trip time of the GTI to use it as an effective dispersion compensation element.

Another alternative optical component that has been used to compress the pulse duration is a diffraction grating. A reflective diffraction grating consists of a reflective layer and a repeating groove pattern engraved on its surface. When the groove pattern dimensions are wider than the wavelength of the incident light, the diffraction grating splits the incident light into its spectral components. Hence, it acts as a dispersive element and has been widely used in monochromators, spectrometers, and wavelength-tuning experiments, which require spectral spreading of the incident light. Figure 2.2.3 shows schematic of the diffraction from a reflective diffraction grating (a) and photograph of the reflective diffraction grating that has been used to tune the output wavelength of a solid-state laser in our laboratory at Koç University (b).

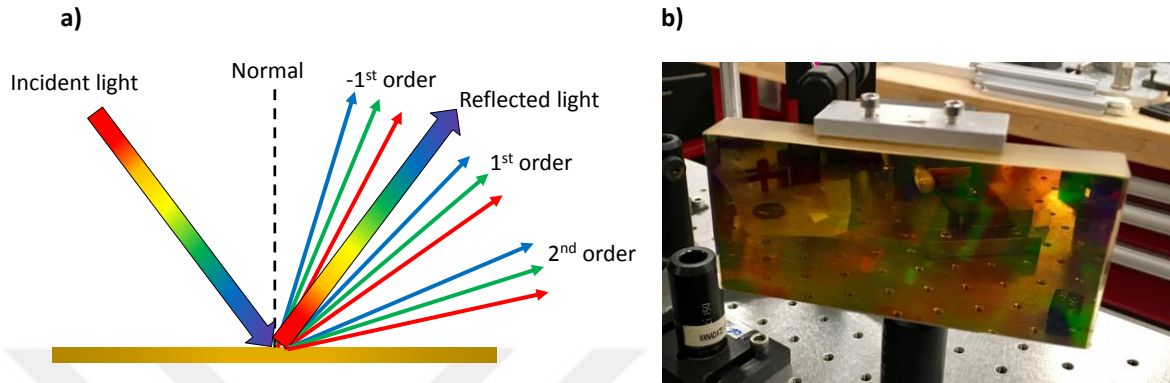


Figure 2.2.3. (a) Schematic description of the diffraction from a reflective grating. (b) Photograph of the reflective diffraction grating that is used in our laboratory.

As shown in Fig. 2.2.3, if the incident light falls on the grating with an angle of θ , the zeroth-order reflection (i.e. the ordinary reflection without diffraction) will also have an angle of reflection θ on the other side of the grating normal. Depending on the groove spacing d there can be additional in-plane diffracted components with different order numbers (m). If the first-order diffraction has an angle θ' with respect to the grating normal, the grating equation can be written as [81]

$$\sin \theta' - \sin \theta = \frac{m\lambda}{d} \quad (2.2.17)$$

since the incident and diffracted beams are on opposite sides of the grating normal.

Diffraction gratings have been also utilized as dispersive elements since the frequency components of the pulse acquire different phase delays due to the engraved groove patterns. Diffraction grating pairs can be used for both stretching and compressing of the pulses externally or inside a resonator. For the experiments, which require short pulse durations and high peak powers at the same time, high optical intensities may cause undesired pulse distortions or destruction of the gain medium because of the nonlinear effects described before. As a possible remedy, the chirped-pulse amplification method has been widely used [82]. In this method, the pulse is broadened (i.e. stretched) with an extra

chirp using a strong dispersive element (e.g. diffraction grating) without decreasing its peak power before passing through the amplifier medium, and then it is compressed back to nearly its initial duration after the amplifier medium with the help of another dispersive element having the opposite chirp. Hence, short pulses with high peak powers can be obtained without pulse distortions or any other destructive effects. In 1968, Treacy et al. demonstrated for the first time that a pair of diffraction gratings can be used to compress the pulse duration [81]. The second-order dispersion equation for a pair of parallel diffraction gratings, which is shown in Fig.2.2.4, can be obtained by tracing the frequency-dependent ray path. The phase delay equation for the first-order diffraction ($m=1$) can be written as [71, 81]

$$\varphi(\omega) = \frac{\omega}{c} \overline{ACP}(\omega) + 2\pi \frac{b}{d} \tan(\theta') \quad (2.2.18)$$

for the configuration shown in Fig. 2.2.4. Here, $\varphi(\omega)$ is the phase delay, ω is the angular frequency of the light, d is the groove spacing, and b is the distance between the gratings. In Eq. (2.2.18), the second term is obtained by recalling that there is a 2π relative phase shift at each groove of the grating. Therefore, by using the groove density ($N = 1/d$) for the distance $\overline{BC}$, Eq. (2.2.18), which gives the total phase shift on $\overline{ACP}$, can be obtained. The group delay can be further obtained by taking the first derivative and by using Eq. (2.2.17) as [71, 81]

$$\frac{d\varphi(\omega)}{d\omega} = \left(\frac{b}{c}\right) \frac{1 + \cos(\theta + \theta')}{\cos(\theta')} \quad (2.2.19)$$

Equation (2.2.19) shows that the group delay is equal to the total path length divided by the speed of light in vacuum and hence, it is simply equal to the phase delay. The second-order derivative further gives the second-order group delay dispersion as [71, 81]

$$\frac{d^2\varphi(\omega)}{d\omega^2} = D = -\frac{\lambda^3}{2\pi c^2} \frac{N^2 b}{\cos^3(\theta')} \quad (2.2.20)$$

where the angular frequency is written in terms of the central wavelength.

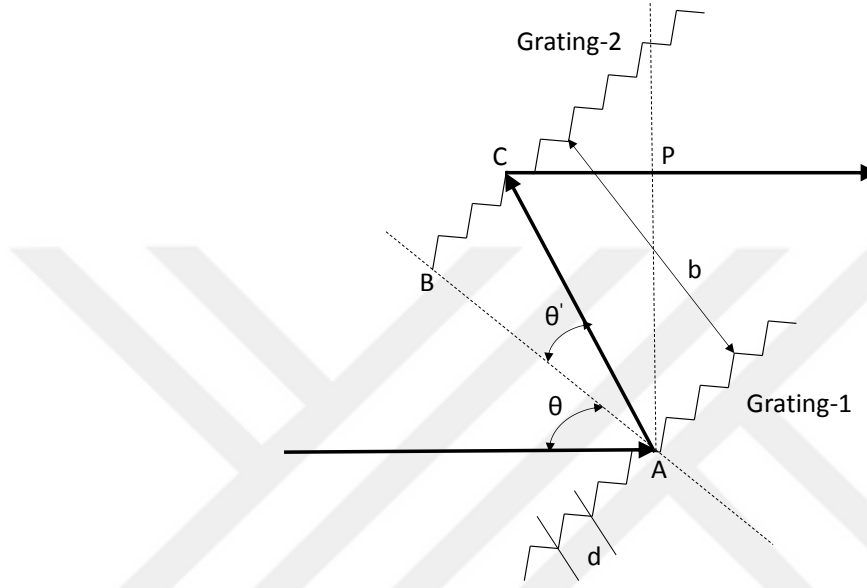


Figure 2.2.4. Schematic diagram for a pair of parallel diffraction gratings.

Since the spectral resolution of the grating increases with the increased spot area illuminated by the incident light on the diffraction grating, the groove density of a diffraction grating is an important parameter for spectroscopic applications, which require high spectral resolution.

Apart from the diffraction configuration given by Eq. (2.2.17) and Fig. 2.2.3 (a), there is another type of configuration, in which the diffracted beam is going back along the direction of the incident beam. In other words, the angle of the incidence and the diffraction are the same. This configuration is called as the Littrow configuration, which satisfies the following condition

$$2 \sin \theta = m \frac{\lambda}{d} \quad (2.2.21)$$

It is usually preferred when the reflective diffraction grating is one of the end mirrors of the wavelength-tunable laser. In our mode locking experiments, diffraction gratings were not used for dispersion control due to their high optical insertion losses.

In 1984, Fork et al. demonstrated that the dispersion control to generate solitary optical pulses can also be achieved by using another well-known optical element with lower optical insertion loss, a pair of prisms [83]. Figure 2.2.5 shows the polychromatic light dispersion and schematic illustration of the optical path of the beam after passing through a prism pair. In a typical laser resonator, a prism pair is placed in the high reflector arm and the refracted wavelength components are reflected back by using an end mirror as shown in Fig.2.2.5. Such prisms are fabricated based on a material with a positive (or negative) dispersion at a given wavelength and they are generally cut at a specific apex angle (α), which is equal to the Brewster's angle (θ_B) to minimize the reflection losses of the p-polarized light (i.e. the electric field of the light is along the plane of incidence).

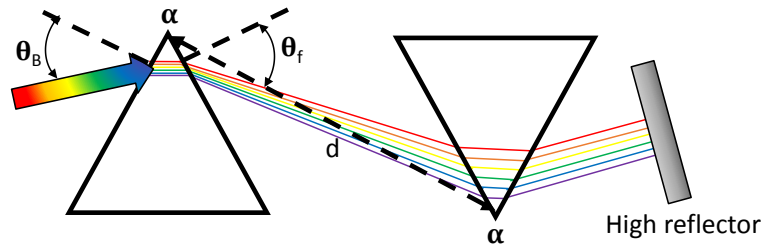


Figure 2.2.5. Propagation of the light through a pair of prism.

The group delay dispersion due to a slab material and the Brewster's angle formula are given by [71, 84]

$$\frac{d^2\phi(\omega)}{d\omega^2} = D = \frac{\lambda^3 L}{2\pi c^2} \frac{d^2 n}{d\lambda^2} \quad (2.2.22)$$

and

$$\theta_B = \arctan\left(\frac{n_2}{n_1}\right) \quad (2.2.23)$$

respectively. In Eq. (2.2.22), L is the length and n is the wavelength-dependent refractive index of the slab material. In Eq. (2.2.23), n_1 and n_2 are the refractive indices of the initial and the final medium respectively.

For an incident light with an angle of incidence θ_B , the accumulated phase of the light for a single pass through a prism pair can be written as [83]

$$\varphi(\omega) = \frac{\omega}{c} l \cos(\theta_B) \omega \quad (2.2.24)$$

where l is the separation distance between the prism apices and ω is the frequency of the refracted light. By following the analysis done by Fork et al., the optical path ($P(\omega)$) of the light which goes through a pair of prisms can be written as [83]

$$P(\omega) = l \cos(\theta_B) \omega \quad (2.2.25)$$

By using the second-order derivative of the optical path in terms of the wavelength of the refracted light [83]

$$\frac{d^2 P(\lambda)}{d\lambda^2} = 2 \left(\frac{d^2 n(\lambda)}{d\lambda^2} + \left(2n - \frac{1}{n^3} \right) \left(\frac{dn}{d\lambda} \right)^2 \right) l \sin(\theta_B) - 4 \left(\frac{dn}{d\lambda} \right)^2 l \cos(\theta_B) \quad (2.2.26)$$

the second-order dispersion can be expressed as [83]

$$\frac{d^2 \varphi(\omega)}{d\omega^2} = D = \frac{\lambda^3}{2\pi c^2} \frac{d^2 P(\lambda)}{d\lambda^2} \quad (2.2.27)$$

In Eq. (2.2.27), d is the tip-to-tip prism separation. The wavelength-dependent refractive index of a given prism material for Eq. (2.2.26) can be estimated by using the Sellmeier equation, which relates the refractive index to the wavelength. If a second prism pair is added to the same arm, the second-order dispersion can be obtained by using an optical path length of [83]

$$P(\omega) = 2l \cos(\theta_B) \omega \quad (2.2.28)$$

Since the refractive index of a material is wavelength dependent as shown in Eq. (2.2.22), sometimes it is sufficient to use a slab material to adjust the dispersion inside a resonator. On the other hand, if a pair of prism is required for the dispersion compensation, its material should be chosen carefully and the light should be incident on the prism at the Brewster's angle to avoid the undesired positive (or negative) dispersion due to the propagation inside a material and to minimize the reflection losses respectively. Figure 2.2.6 (a) shows typical material dispersions per mm for common materials, such as sapphire, fused silica, and CaF_2 . The second-order negative dispersion amount obtained from a fused silica prism pair at different tip-to-tip separation distances are further shown in Fig. 2.2.6 (b).

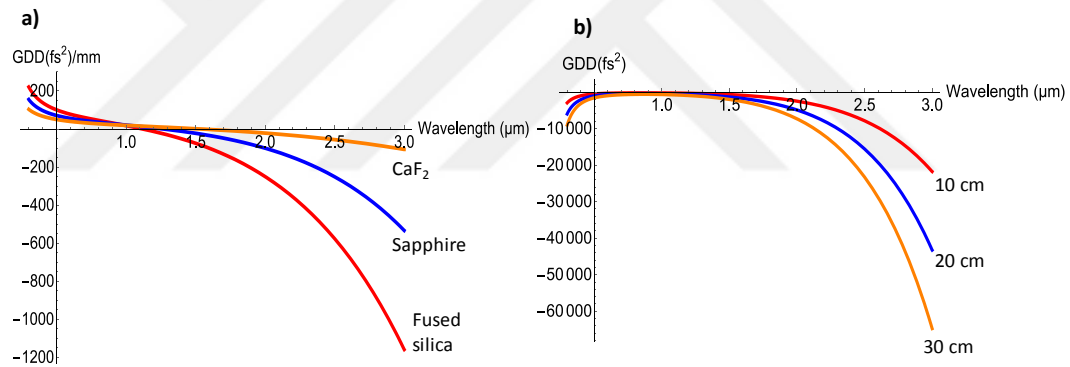


Figure 2.2.6. (a) The second-order negative group delay dispersion (GDD) introduced by different slab materials. (b) The resulting GDD obtained from a fused silica prism pair at different prism separations.

2.3 Femtosecond Pulse Generation

Ultrashort laser pulses with durations much shorter than the cavity round-trip time can be generated by a special technique, which is called as mode locking. Mode locking is a method that distributes the output energy of a laser among the modes of the resonator and enables the generation of ultrashort pulses with a broad bandwidth. The first investigation on the mode-locked operation of lasers was done by Gürs on ruby lasers [85] and by Statz

and Tang on He-Ne laser [86]. The first papers explaining the mechanism behind the mode-locked operation were presented by DiDomenico [87], Hargrove et al. [88], and Yariv [89].

Depending on the physical mechanism behind the mode locking, pulsed operation can be achieved actively or passively. In the active mode locking [90, 91], ultrashort pulses are obtained by modulating the cavity with an externally driven loss or modulating the round-trip phase change by using an acousto- or electro-optic modulator. If the modulator frequency is synchronized with the cavity round-trip time, short pulses can be obtained from such resonators. In the case of the passive mode locking, there is no need for an external mechanism to change the loss amount inside the resonator and mode-locked operation can be initiated due to an intensity-dependent periodic loss.

Shortest optical pulses that ever generated directly from a resonator are around 5 fs [92], which corresponds to an optical cycle of nearly 2 around 800 nm and hence, such laser pulses are called as few-cycle optical pulses. One can also start with a longer pulse duration and use external pulse compression techniques to achieve pulses with femtosecond durations. It is also possible to obtain even shorter pulses with attosecond (10^{-18} s) durations indirectly from a resonator. Such techniques rely on the high harmonic generation via noble gases or combination of the two phase-locked femtosecond pulses in the optical region [93]. Such an ultrashort pulse roughly travels 0.3 nm in one attosecond, which nearly corresponds to the spacing between the atoms in a solid and hence, attosecond pulses enable researchers to investigate different types of interesting phenomena and extremely nonlinear optical interactions. Since direct or indirect ultrashort pulse generation techniques rely on the mode-locked operation of the lasers, exploring new devices for ultrashort pulse generation applications is substantial in many aspects and hence, in this thesis novel graphene-based modulators were explored to initiate mode-locked operation of solid-state lasers. In our experiments, ultrashort pulses were generated by using a passive modulator

and in the following sections of Chapter 2, two main passive mode locking methods will be emphasized.

2.3.1 Saturable Absorber Mode Locking

Saturable absorber mode locking is based on the use of a material, in which the optical transmission increases with the increasing light intensity. A saturable absorber has a certain level of optical insertion loss due to its steady-state absorption at a specific wavelength, but when it is exposed to a high intensity light, the ions (or charge carriers) are depleted from the ground state and hence, the transmission increases leading to a reduction amount in the optical insertion loss of the absorbing material. The time required for the ions (or charge carriers) to go back to their initial states is called as the recovery time of the material. Depending on the duration of the recovery time, a saturable absorber can be classified as a fast or a slow in comparison with the cavity round-trip time. Our experiments presented in this thesis were conducted by using two solid-state lasers with nearly 5 and 130 MHz repetition rates, which give cavity round-trip times of the order of 200 ns and 7 ns respectively. Hence, the graphene-based saturable absorbers that were used in our experiments are fast saturable absorbers due to their recovery times (~ 1.5 ps), and fast saturable absorber analysis will be emphasized at this point.

Herman A. Haus provides an analysis in the article [74] to investigate the pulse characteristics of the fast saturable absorber mode-locked lasers. The fast saturable absorber analysis, which is investigated in the time domain will be summarized here to demonstrate the basic characteristics of the generated pulses from a passively mode-locked laser.

The transmission ($s(t)$) of the saturable absorber when it is exposed to a time-dependent laser intensity ($I(t)$) is given by [74]

$$s(t) = \frac{s_0}{1 + \frac{I(t)}{I_{sat}}} \quad (2.3.1)$$

Here, s_0 is the unsaturated loss, which is smaller than one, and I_{sat} is the saturation intensity of the absorber. For a weak saturation, this equation can be written as

$$s(t) = s_0 - \frac{s_0 I(t)}{I_{sat}} \quad (2.3.2)$$

Since the intensity multiplied by the effective area (A_{eff}) gives the power carried by the beam, the beam amplitude ($a(t)$) can be normalized so that $|a(t)|^2$ gives the power and Eq. (2.3.2) becomes [74]

$$s(t) = s_0 - \frac{s_0 |a(t)|^2}{I_{sat} A_{eff}} \equiv s_0 - \gamma |a(t)|^2 \quad (2.3.3)$$

where γ is the Kerr nonlinearity coefficient, which gives rise to the self-phase modulation and self-focusing as described in the previous sections. If the self-amplitude (i.e. the self-phase) modulation term is treated as constant in the fast saturable absorber analysis, the master equation for the pulse evolution (Equation (2.2.10) with constant SPM) can be written as

$$\frac{1}{T_R} \frac{\partial}{\partial T} a = (g - l)a + \frac{g}{\Omega_g^2} \frac{\partial^2}{\partial t^2} a + \gamma |a|^2 a \quad (2.3.4)$$

Here, $|a|^2$ is the instantaneous power, Ω_g is the gain bandwidth, T_R is the cavity round-trip time, T and t are the long-term and the short-term time scales respectively. Since the recovery time of the saturable absorber is shorter than the cavity round-trip time for this analysis, the net gain (g) of the laser medium is assumed to be constant and the loss is written as l . The solution of Eq. (2.3.4) for the pulse evolution of the fast saturable absorber mode-locked laser has a sech-shaped temporal profile as expected from the previous analysis (without the nonlinear phase shift introduced by SPM) [74]

$$a(t) = A_0 \operatorname{sech}\left(\frac{t}{\tau}\right) \quad (2.3.5)$$

where A_0 is the pulse amplitude and τ is the pulse duration. Therefore, fast saturable absorber mode-locked lasers produce pulses with sech-shaped temporal profiles.

In this thesis, graphene and graphene-based devices are used as fast saturable absorbers. Hence it is important to realize the behavior of graphene saturable absorbers, based on their energy level structures. The absorption (α) for the interband transitions of graphene can be written in terms of the quasi-Fermi levels [94, 95]

$$\alpha = \alpha_0 (f_v - f_c) = \frac{e^2}{4\hbar} \left(f_v \left(-\frac{\hbar\omega}{2} \right) - f_c \left(\frac{\hbar\omega}{2} \right) \right) \quad (2.3.6)$$

where α_0 gives the steady-state absorption coefficient (i.e. initial states are filled and final states are empty), f_v is the Fermi-Dirac occupation probability for the valance band and f_c is for the conduction band respectively. The occupation probabilities can be written as [94, 95]

$$f_i = \frac{1}{1 + \exp\left(\frac{E_i - F_i}{k_B T}\right)} \quad (2.3.7)$$

for $i=1,2$. Here, F_i is the quasi-Fermi level and E_i is the energy of the initial and final state which differ by the photon energy $\hbar\omega$. When the light intensity on graphene increases, more carrier pairs are generated as expected and the quasi-Fermi level approaches to the E_i and hence, f_i approaches to 1/2. Therefore, the absorption coefficient approaches to zero and the graphene becomes transparent (i.e. absorption is bleached). A simple saturation model similar to Eq. (2.3.1) can be written in terms of the carrier density (N) as [94, 95]

$$\alpha(N) = \frac{\alpha_s}{1 + \frac{N}{N_s}} + \alpha_{ns} \quad (2.3.8)$$

where α_s and α_{ns} are the saturable and the non-saturable absorption, N is the carrier density, and N_s is the carrier density obtained at the saturation point. The change in the absorption with respect to the carrier density can be defined as [94, 95]

$$\Delta\alpha(N) = \alpha(N) - \alpha(0) = -\alpha_s \frac{N/N_s}{1 + N/N_s} \quad (2.3.9)$$

The time rate of change in the photo-induced carrier density can be written by using a rate equation as [94, 95]

$$\frac{\partial N}{\partial t} = \frac{I\alpha}{\hbar\omega} - \frac{N}{\tau} - D\nabla^2 N \quad (2.3.10)$$

In Eq. (2.3.10), I is the incident light intensity, τ is the electron-hole recombination time for graphene, and the last term represents the electron-hole recombination that occurs out of the excitation region. For the long pulse illumination (i.e. the pulse duration of the incident light is longer than the recombination time), the left-hand side of Eq. (2.3.10) is equal to zero and hence, N is equal to

$$N = \frac{I\alpha\tau}{\hbar\omega} \quad (2.3.11)$$

where the out of region electron-hole recombination is omitted. If Eq. (2.3.11) is substituted by using Eq. (2.3.8), the intensity-dependent absorption can be written as

$$\alpha(I) = \frac{\alpha_s}{1 + \frac{I}{I_s}} + \alpha_{ns} \quad (2.3.12)$$

which is similar to Eq. (2.3.1) with a non-saturable term.

If the pulse duration of the incident light is shorter than the recombination time and the pulse has a Gaussian spatial profile, the photo-induced carrier density will also have a Gaussian profile and can be written as [94, 95]

$$N(r, t) = N_0 \exp\left[-\frac{4 \ln 2 r^2}{w_0^2}\right] \exp\left(-\frac{t^2}{\tau_0^2}\right) \quad (2.3.13)$$

In Eq. (2.3.13), N_0 is the peak carrier density, w_0 is the radius of the incident light spot, and τ_0 is the duration of the incident pulse. Hence, the time rate of change in the photo-induced carrier density can be written as

$$\frac{\partial N}{\partial t} = -\frac{2t}{\tau_0^2} N_0 \exp\left[-\frac{4 \ln 2 r^2}{w_0^2}\right] \exp\left(-\frac{t^2}{\tau_0^2}\right) \quad (2.3.14)$$

where the negative sign indicates that the carrier density is reduced. Equation (2.3.14) can be further put into Eq. (2.3.10) to estimate the intensity-dependent absorption.

Saturable absorbers have intrinsic features, such as modulation depth, recovery time, saturation fluence, non-saturable loss amount, and damage threshold. The modulation depth of a saturable absorber gives the maximum intensity-dependent change in the absorption due to a high intensity light exposure and it can be estimated from the difference between the saturated absorption value and the steady-state absorption value, which are given in above equations. As previously discussed in Chapter 1, recovery time gives the time scale, in which the excited carriers go back to their original states and defined as τ in above equations. The pulse fluence that reduces the saturable loss of an absorber to its 1/e value is equal to the saturation fluence of the saturable absorber (i.e. saturation intensity (I_s)). Furthermore, the non-saturable loss (α_{ns}) is the intrinsic absorption amount of the saturable absorber which cannot be saturated. The damage threshold of the saturable absorber gives the fluence level at which an optical damage is observed on the saturable absorber. It is also a crucial parameter since pulsed lasers with high energies are often needed in a wide range of applications.

Different materials have been widely used as effective saturable absorbers. These include semiconductor saturable absorber mirrors (SESAMs), single-walled carbon nanotubes (SWCNT), graphene, topological insulators, and black phosphorous. Semiconductor saturable absorber mirrors consist of a highly reflective Bragg mirror and a saturable absorber quantum-well layer [96]. They are fabricated by using III-V group semiconductors and their band-gaps are engineered so that the device can operate at a specific wavelength. SESAMs have been commonly used to generate short pulses from various lasers, but they require complex and costly fabrication facilities and their operation wavelength is limited by the band-gap of the semiconductor material. Recently emerging alternatives are SWCNTs, black phosphorous, topological insulators, and graphene. SWCNTs are discovered by Sumio Iijima in 1991 [97]. They are formed by rolled-up graphene sheets and possess favorable saturable absorber characteristics (e.g. fast recovery time and sufficient modulation depth [36, 98, 99]). In addition, they do not require complex fabrication schemes and hence, they have been used as passive modulators for femtosecond pulse generation in a broader wavelength range in comparison with SESAMs. However, their operation at longer wavelengths ($>2\ \mu\text{m}$) is limited due to the infrared absorption of the polymer host (PMMA), in which the nanotubes are placed. Furthermore, diameters of typical carbon nanotubes, which play a crucial role in the type of their band structure, are usually around 1-3 nm and makes them more suitable for near-infrared lasers. Topological insulators and black phosphorous materials are also good candidates as fast saturable absorbers and their applications as passive optical modulators can be found in Ref. [100-106]. The last alternative material, which is graphene, is superior to any other saturable absorber in terms of the fabrication scheme and electromagnetic spectrum coverage. It is a zero band-gap material with a nearly constant, broadband absorption, and fast recovery time. The physical structure and the favorable optical characteristics of graphene, as a saturable absorber, were discussed in detail in Chapter 1. Graphene saturable absorber

mode-locked Cr^{4+} :forsterite laser will be presented in Chapter 4. Furthermore, dynamic control of the absorption in graphene has been demonstrated by our groups recently and novel graphene-based broadband supercapacitors with adjustable absorption levels have been used for the first time to generate femtosecond pulses. In Chapters 5, 6, and 7, the experimental setups and the results conducted with such graphene-based devices will be presented in detail.

2.3.2 Kerr-Lens Mode Locking

Kerr-lens mode locking has been widely employed as an effective technique to generate ultrashort pulses from different lasers [107-111] and it was demonstrated for the first time by Spence et al. to generate femtosecond pulses from a Ti^{3+} :sapphire laser [112]. Kerr-lens mode locking (KLM) relies on the Kerr nonlinearity coefficient of a medium. Due to the nonlinear Kerr effect, the shape of the pulse changes in the temporal and spatial domain as discussed before. The temporal broadening of the pulse (i.e. self-phase modulation) was previously presented in detail. Here, Kerr-induced self-focusing effect will be revisited to further explain the Kerr-lens mode locking. To exploit the Kerr nonlinearity of a gain medium to initiate the mode-locked operation, volumes of the pump and the laser beams are adjusted so that the pump is more focused inside the gain medium as shown in Fig. 2.3.1. When the laser beam with a sufficient intensity passes through the gain medium, it will also be focused as shown in Fig. 2.3.1 due to the self-focusing.

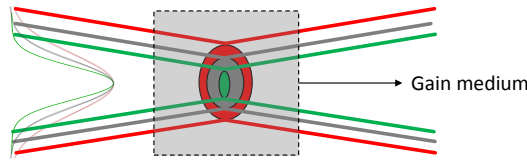


Figure 2.3.1. The high intensity laser beam (grey) gets more focused than the low intensity one (red) and overlaps better with the pump beam (green) inside the gain medium.

This process repeats itself and when the laser beam achieves the best overlap with the pump beam, the intense laser beam experiences higher optical gain. Hence, this forces the laser to favor the higher intensity beam and enables the mode-locked operation. Here, the Kerr medium acts as an artificial saturable absorber, which provides the survival of the high intensity pulses rather than the low intensity ones. In the previous section, where the saturable absorber mode locking was discussed, the temporal profiles of the obtained pulses were given as sech. Since the intensity-dependent Kerr effect is assumed to act as an artificial fast saturable absorber, the master equation solution for the Kerr-lens mode locking is same with the saturable absorber mode locking and hence, the ultrashort pulses generated via Kerr-lens mode locking (KLM) have also a temporal profile of a sech.

Chapter 3

SOLID-STATE LASERS: OPERATION PARAMETERS and DESIGN PRINCIPLES

In 1917, Albert Einstein established the fundamental theory of the stimulated emission for the first time and then, Arthur Leonard Schawlow, Charles Hard Townes, Nikolay Basov, and Alexander Prokhorov were among the several scientists who investigated the first operational laser. Based on the previous research, the first operating laser was demonstrated by Theodore Maiman in 1960. Due to their remarkable characteristics, such as monochromaticity, coherence, high spectral brightness, and directionality, lasers not only have found widespread applications in medicine [61], biology [66], chemistry [57], physics [113, 114], industry [115-117], and even in archeology [118], but also they have been used as essential tools in many other cutting-edge technologies and in everyday life [119]. Therefore, lasers and laser-based technologies have attracted a great deal of research interest in recent years.

In Chapter 3, general characteristics and operation principles, such as oscillation condition, threshold pump power, output power, and slope efficiency of lasers will be given. This will be followed by description of the design principles of the solid-state laser resonators. In the remainder of Chapter 3, two different solid-state gain media, Ti^{3+} :sapphire and Cr^{4+} :forsterite, which were used in our mode locking experiments, will be discussed.

3.1 Operation Parameters of Solid-State Lasers

In its simplest form, lasers consist of an amplification medium for the optical gain and two highly reflecting mirrors for positive feedback. The amplification medium operates at the optical frequencies and can be classified according to the physical state of the medium (e.g. gaseous, liquid, and solid). Since our experiments, presented in this thesis, were performed

by using solid-state lasers, the forthcoming discussions about the lasers will consider only the solid-state gain medium.

Gain medium of the solid-state lasers consists of discrete energy levels. Ti^{3+} :sapphire and Cr^{4+} :forsterite gain media are four-level atomic systems, which is illustrated in Fig. 3.1.1. In the four-level atomic system, the pump photons at the wavelength of λ_p are absorbed by the gain medium and they excite the ground level (g) ions to an upper-state (3). From level (3) to level (2), a rapid non-radiative decay occurs and this is followed by the both spontaneous and stimulated emission from level (2) to level (1) at the wavelength of λ_L . Then, another rapid non-radiative decay occurs between level (1) and the ground state (g) for the remaining ions. Both non-radiative decays are fast compared to the radiative transition and their population densities can be neglected. Since the spontaneously emitted photons during the transition between level (2) and (1) do not share the same direction or phase as opposed to the stimulated emission, they will only add noise to the laser beam and hence, their contribution can be further neglected.

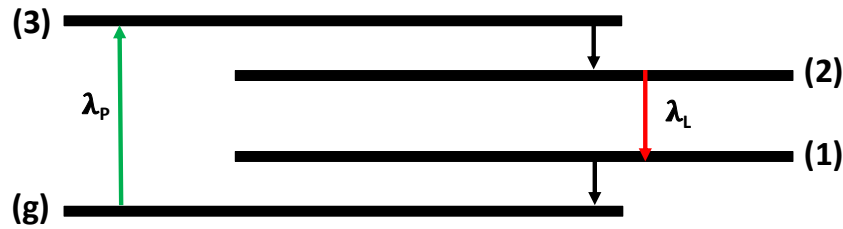


Figure 3.1.1. Description of the energy levels of the four-level solid-state gain media.

Therefore, the rate equation, which considers the time rate of change of the population of the level (2) can be written as [70]

$$\frac{dN_2}{dt} = W_p N_g - \frac{N_2}{\tau_f} - \frac{\sigma I}{h\nu} N_2 \quad (3.1.1)$$

Here, $\sigma_a = \sigma_e = \sigma$ are the absorption and emission cross-sections respectively, I is the intensity, and ν is the frequency of the electromagnetic wave, which is equal to $E_2 - E_1 / h$ and τ_f is the fluorescence lifetime. If the total atomic density is defined as

$$N_t = N_2 + N_g \quad (3.1.2)$$

and the pumping rate per atom is given by

$$W_p = \frac{\sigma_a I_p}{h \nu_p} \quad (3.1.3)$$

The population inversion can be shown as [70]

$$\Delta N = \frac{\Delta N_0}{1 + \frac{I}{I_s}} \quad (3.1.4)$$

In Eq. (3.1.4), the small-signal inversion (ΔN_0) and the saturation intensity (I_s) are defined as follows [70]

$$\Delta N_0 = \frac{N_t W_p \tau_f}{1 + W_p \tau_f} \quad (3.1.5)$$

and

$$I_s = \frac{h \nu}{\sigma \tau_f} (1 + W_p \tau_f) \quad (3.1.6)$$

The above analysis demonstrates that if there is an optical pumping, an ideal four-level atomic system will always have the population inversion. The population inversion states that the atomic system is deviated from its thermal equilibrium, in which the upper level population exceeds the lower one. Furthermore, the differential gain coefficient of a medium can be written in terms of the stimulated emission cross-section and the population inversion as [70]

$$g = \sigma_e \Delta N = \frac{g_0}{1 + \frac{I}{I_s}} \quad (3.1.7)$$

In Eq. (3.17), g_0 is the small-signal differential gain coefficient and it is equal to $\sigma_e \Delta N_0$. The threshold value of the $(g_0)_{th}$ depends on the total resonator losses (L) and the reflectivities of the laser mirrors (R_1, R_2). When $g_0 > (g_0)_{th}$ is achieved, lasing starts and hence, intensity of the circulating light increases exponentially until it becomes comparable to the saturation intensity (I_s). The threshold condition for the light oscillation inside the resonator can be written as [70]

$$\exp(2gl_m) = \exp(2l_m L) \left(\frac{1}{R_1 R_2} \right) \quad (3.1.8)$$

where l_m is the length of the gain medium. To achieve the lasing condition, the laser should be pumped with a sufficient input pump power so that the threshold value for the population inversion can be obtained. For our laser resonators, which consist of spherical end mirrors, the circulating beam inside the cavity has a Gaussian-shaped spatial profile. The threshold pump power that is required to start lasing is given by [120]

$$(P_p)_{th} = \frac{\pi \hbar \nu_p (w_L^2 + w_p^2) (L + T)}{4 \eta_a \sigma_e \tau_f} \quad (3.1.19)$$

for a four-level gain medium with a Gaussian-shaped beam profile. In Eq. (3.1.19), $h\nu_p$ is the energy of the pump photons, L is the total resonator loss, T is the total transmissions of the resonator mirrors (e.g. output coupler), σ_e is the stimulated emission cross-section, η_a is the fraction of the pump power absorbed by the gain medium, τ_f is the fluorescence lifetime of the gain medium, and w_L and w_p are the laser and pump spot-sizes inside the gain medium respectively. As can be seen from Eq. (3.1.19), the threshold pump power required to achieve lasing can be determined by using the parameters of the gain medium

and the resonator given above. If the other parameters are constant, product of the fluorescence lifetime and the stimulated emission cross-section ($\sigma_e \tau_f$) of a gain medium further provides an estimate for the threshold pump power such that; if the product is high, the required threshold pump power is low (e.g. for $\text{Cr}^{3+}:\text{LiSAF}$ $320 \mu\text{s} \times 10^{-20} \text{cm}^2$ [121]) and if the product is low (e.g. for $\text{Ti}^{3+}:\text{sapphire}$ $131 \mu\text{s} \times 10^{-20} \text{cm}^2$ [122] and for $\text{Cr}^{4+}:\text{forsterite}$ $\sim 0.45 \mu\text{s} \times 10^{-20} \text{cm}^2$ [123]), the threshold pump power will be high. In addition, solid-state lasers such as $\text{Cr}^{4+}:\text{forsterite}$ and $\text{Cr}^{4+}:\text{YAG}$ have temperature-dependent lifetimes [123] due to the phonon-assisted non-radiative relaxations and hence, they require cooling systems for efficient laser operation.

For the input pump powers, greater than the threshold pump power, laser produces a finite output power, which is given by

$$P_{out} = \eta(P_{in} - (P_p)_{th}), \quad (3.1.20)$$

where η is the slope efficiency of the laser. As can be seen from Fig. 3.1.2, when the threshold pump power $(P_p)_{th}$ is reached, the output power of the laser increases with respect to the per unit increase in the input pump power. Therefore, efficiency of a laser can be estimated from the slope of this curve.

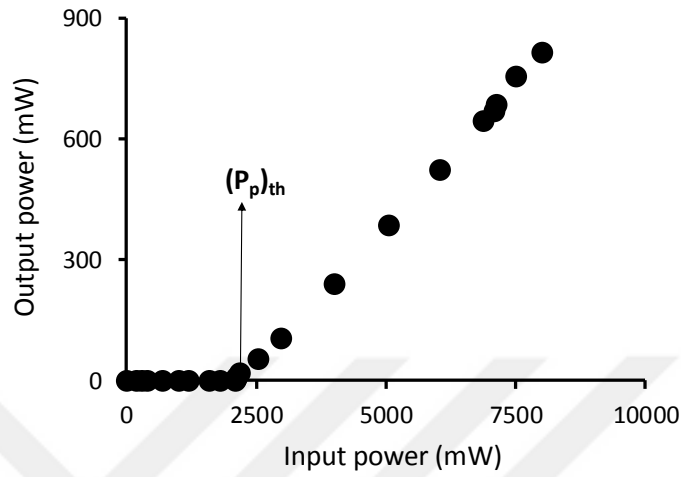


Figure 3.1.2. Efficiency curve of a solid-state laser.

The slope efficiency (η) of a laser gives how much change occurs in the output power per unit increase in the input pump power and the formula is given by [70]

$$\eta = \frac{\lambda_p}{\lambda_L} \frac{T}{T + L} \eta_a \quad (3.1.21)$$

where λ_p and λ_L are the pump and the laser wavelengths respectively. As can be seen from Eqs. (3.1.20) and (3.1.21), the maximum slope efficiency is obtained when the resonator losses are minimized. If this is the case, efficiency of a laser can be given by $\frac{\lambda_p}{\lambda_L}$. This is known as the quantum efficiency and gives the maximum possible efficiency for a laser.

To estimate the passive losses of the resonator or any other intracavity element, the threshold pump power, measured with different cavity configurations, can be used. Since the other laser parameters are fixed for a given laser resonator, the threshold pump power can also be written as [70]

$$(P_p)_{th} = A(L + T) \quad (3.1.22)$$

If the transmission of the output coupler (T) is fixed and the total loss of the original resonator (L_1) is known, the optical insertion loss (L_2), introduced by an optical element, can be estimated by measuring the threshold pump power with $(P_p)_{th2}$ and without $(P_p)_{th1}$ the optical element and it is given by

$$L_2 = \frac{(P_p)_{th2}}{(P_p)_{th1}} (L_1 + T) - T \quad (3.1.23)$$

Equation (3.1.23) is obtained by dividing the threshold pump power formula for the first (without the optical element) resonator configuration with the second (with the optical element) one.

3.2 Design Principles for Solid-State Lasers with Multipass-Cavity Extensions

In Section 3.2, a brief description of the ray model, which only considers the ray aspect of light, will be given without introducing the wave properties of light. In this discussion, the optical rays propagate in the paraxial regime, in which they remain close to the optical axis. After introducing the ABCD matrix formalism for the ray propagation through an optical system, properties of a TEM₀₀ Gaussian beam will be presented and design principles for the multipass-cavity extensions will be given.

Any optical system can be considered as a black box which modifies the parameters of the initial ray after passing through the system. The optical rays can be described by its height (r_i) and the angle (θ_i) it makes with respect to the optical axis. The effect of the optical system on the beam can be calculated by using the ABCD matrix equation [70]

$$\begin{bmatrix} r_f \\ \theta_f \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} r_i \\ \theta_i \end{bmatrix} \quad (3.2.1)$$

Here, r_f and θ_f are the final ray height and the angle respectively. Therefore, the effect of any optical system on an initial ray can be described by using the following equation

$$r_f = M_T r_i \quad (3.2.2)$$

where M_T is the ray transfer matrix. There are three basic rules about the ABCD matrix formalism: 1) The ray transfer matrix for a cascaded optical system can be written as the multiplication of each transfer matrices. 2) Any paraxial optical system can be described as the composition of displacement and thin lens matrices, which are given by [70]

$$\text{Displacement: } \begin{bmatrix} 1 & d \\ 0 & 1 \end{bmatrix} \quad (3.2.3)$$

and

$$\text{Lens: } \begin{bmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{bmatrix} \quad (3.2.4)$$

Here, d is the amount of the displacement and f is the focal length of the thin lens. 3) The stability of a laser resonator is given by the following inequality

$$\left| \frac{A+D}{2} \right| \leq 1 \quad (3.2.5)$$

The above inequality guarantees that the resonator is stable, in other words, the ray height is confined inside the resonator.

The laser resonator, which is built by using spherical end mirrors, support confined TEM₀₀ Gaussian beams. The radius of curvature $R(z)$ and the spot size $w(z)$ information of the beam at a given location on the optical axis is provided by the q-parameter $q(z)$ [70],

$$\frac{1}{q(z)} = \frac{1}{R(z)} - i \frac{\lambda}{n_0 \pi w^2(z)} \quad (3.2.6)$$

In Eq. (3.2.6), n_0 is the refractive index of the medium, in which the beam propagates, and λ is the wavelength. The radius of curvature and the spot size functions are given by [70]

$$R(z) = (z - z_f) \left(1 + \left(\frac{z_0}{z - z_f} \right)^2 \right) \quad (3.2.7)$$

and

$$w(z) = w_0 \sqrt{1 + \left(\frac{z - z_f}{z_0} \right)^2} \quad (3.2.8)$$

In Eq. (3.2.7) and Eq. (3.2.8), z is the propagation direction, w_0 is the beam waist, where the beam radius has a minimum, z_f is the location of the beam waist, and z_0 is a very important parameter, which is known as the Rayleigh range of the beam and given by [70]

$$z_0 = \frac{n\pi w_0^2}{M^2 \lambda} \quad (3.2.9)$$

The Rayleigh range gives the distance at which the beam radius is increased by a factor of square root of 2. In Eq. (3.2.9), M^2 is the M-square parameter of the beam and gives the amount of the beam deviation from an ideal Gaussian. For an ideal Gaussian beam, $M^2 = 1$.

For a q-preserving resonator extension (e.g. q-preserving multipass-cavity), the initial and the final q-parameters of the Gaussian beam are equal at a given location as described in Fig. 3.2.1.

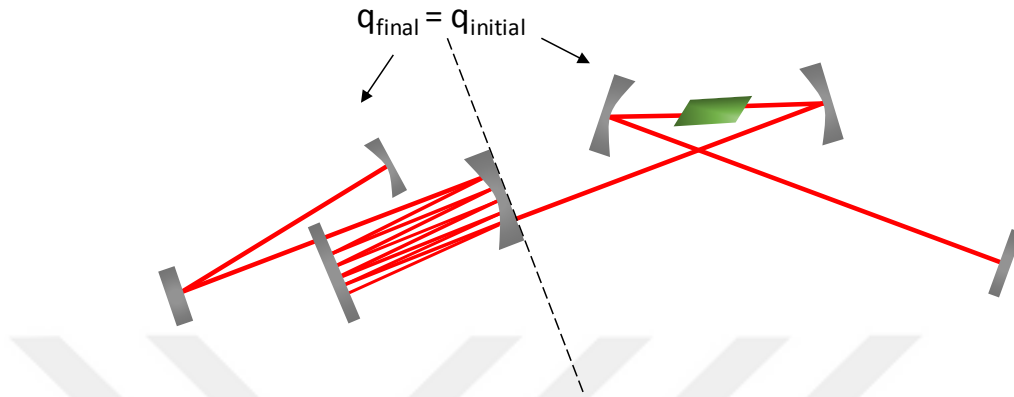


Figure 3.2.1. The initial and the final q -parameters of the beam are equal after passing through a q -preserving cavity extension. Therefore, the extension has no effect on the q -parameter of the original resonator.

Preservation of the q -parameter provides that the beam parameters, such as the radius of curvature and the spot size remain invariant after n number of round-trips inside the resonator extension.

Based on the previous discussion, the design principles for the multi-pass cavity (MPC) extensions will be described here. Multipass-cavities were first introduced by Herriot et al. [124] and have been used as practical methods to increase the effective optical path length with a compact mirror configuration. As discussed in Chapter 2, the pulse repetition rate of a laser resonator is determined by the effective optical path length (L) of the cavity as $f_{\text{rep}} = c/2L$. Hence, as the cavity length increases, the pulse repetition rate, f_{rep} decreases and the laser produces fewer pulses per second. Increasing the cavity length is important for biomedical applications, since the interaction of the low repetition rate laser with the tissue generates less heat on the sample. Furthermore, in sensing applications, the increased path length increases the interaction amount between the laser in use and the material that is under investigation. The multipass-cavity extensions can also be used to scale up the

pulse energy of a laser without increasing the input pump power since the pulse energy is inversely proportional to the pulse repetition rate. The MPC consists of two highly reflecting mirrors each with a notch to inject and extract the beam. In order not to perturb the mode-matching condition of the original resonator, the MPC design should satisfy the q-preserving condition. The ray transfer matrix for the MPC extension can be written as [70]

$$M_T^n = \begin{bmatrix} \frac{A-D}{2} \frac{\sin(n\varphi)}{\sin(\varphi)} + \cos(n\varphi) & B \frac{\sin(n\varphi)}{\sin(\varphi)} \\ C \frac{\sin(n\varphi)}{\sin(\varphi)} & \frac{D-A}{2} \frac{\sin(n\varphi)}{\sin(\varphi)} + \cos(n\varphi) \end{bmatrix} \quad (3.2.10)$$

Here, n is the number of bounces of the beam inside the MPC, φ is the angular advance of the spot pattern after each round-trip, and given by [70]

$$\cos(\varphi) = \frac{A+D}{2} \quad (3.2.11)$$

If the q-preserving condition is satisfied, the ray transfer matrix for the MPC will have no effect on the q-parameter of an initial beam and it is given by

$$M_T^n = (-1)^m I \quad (3.2.12)$$

when the angular advance (φ) is equal to $(m\pi/n)$. In Eq. (3.2.12), I is the identity matrix, m and n are both integers, which stand for the number of round-trips and the number of semicircular paths that the spot pattern on the MPC completes before exiting the system respectively. In our experiments, we used a flat-curved MPC extension. If the radius of curvature of the curved mirror is equal to R_2 , separation between the MPC mirrors (d), can be written as [70]

$$d = \frac{R_2}{2} \left(1 - \cos\left(\frac{m\pi}{n}\right) \right) \quad (3.2.13)$$

to satisfy the q-preserving condition [125]. Figure 3.2.2 shows the photograph of the spot distribution on the flat MPC mirror of our Cr^{4+} :forsterite laser, which was used in the mode locking experiments, and photograph of the bouncing beam between the flat-curved MPC mirrors. Another MPC laser with the Ti^{3+} :sapphire gain medium is further shown in the right-hand side of Fig. 3.2.2. The MPC Ti^{3+} :sapphire laser was also built in our laboratory at Koç University and the short-cavity version of this laser (without MPC) was used in our mode locking experiments.

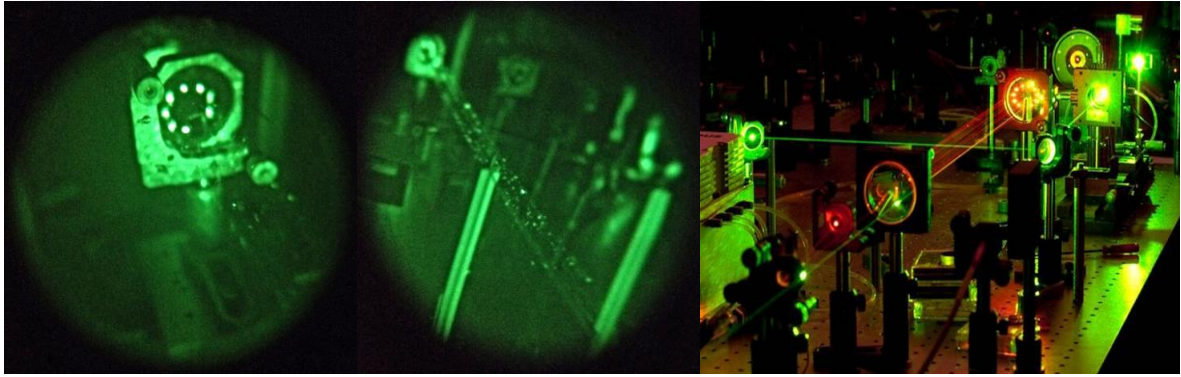


Figure 3.2.2. Photographs of the spot distribution on the flat MPC mirror of our Cr^{4+} :forsterite laser (left) and the bouncing beams between the MPC mirrors (middle). These photographs were taken by using an infrared viewer and a camera. The MPC Ti^{3+} :sapphire laser (right) (Photograph by Aref Mostafazadeh).

3.3 Cr^{4+} :forsterite and Ti^{3+} :sapphire Lasers

A solid-state host material is used as an optical amplifier in a solid-state laser when it is doped with laser-active ions. These hosts are selected due to their robustness, thermal conductivity, optical transparency, and stability under ambient conditions. Furthermore, the laser active ions inside the solid-state host media can be a transition metal (e.g. Cr, Ti, Fe, Co) or a rare-earth (e.g. Tm, Nd, Er, Ho) ion. Each ion has its own unique feature and has been widely used in the field of solid-state laser development. Our experiments were conducted with two different solid-state lasers, in which the transition metal ions were used

as the laser active ions. Hence, the main characteristics of such laser ions will be shortly described here and then, our laser systems will be presented in the remaining parts of this section.

The laser-active media with a broad gain bandwidth are important for generating ultrashort laser pulses with tunable wavelengths. The transition metal ion doped solid-state hosts provide broad absorption and emission transitions due to the electron-phonon coupling, which results from the interaction of the laser-active ions with the surrounding vibrating lattice. In the case of a rare-earth ion doped medium, the optical transitions have narrower bandwidths, since the 4f shell electrons are involved, and they are shielded from the host lattice. Hence, the availability of the electron-phonon coupling in the gain media provide ultrashort pulses, which are tunable over a broad wavelength range [126].

One of the most commonly used transition metal ion doped solid-state host is the forsterite (Mg_2SiO_4), which is a semi-precious gemstone from the olivine family and has an orthorhombic crystal structure. Due to its optical transparency in the infrared region and its stability under ambient conditions, it has been used as an effective solid-state laser material. The first lasing from a Cr^{4+} doped forsterite host was first demonstrated by Petrievic et al. in 1988 [127] and the first mode-locked operation was introduced by A. Seas et al. in 1991 [128]. The Cr^{4+} :forsterite gain media are pumped by 1064 nm light sources and its emission wavelength is around 1.3 μm . The emission of the Cr^{4+} :forsterite laser covers an important range. Since the absorption of water becomes stronger for the wavelengths greater than 1.4 μm [84], and the strong wavelength dependence of the Rayleigh scattering ($\sim \lambda^{-4}$) decreases the effective penetration depth of a shorter wavelength light source in tissues, which contain a large amount of water. Therefore, operation wavelength of the Cr^{4+} :forsterite crystal makes it a very suitable coherent light source for biomedical applications, where the water absorption and the Rayleigh scattering are important issues for the deep-tissue imaging. Hence, Cr^{4+} :forsterite lasers have been used

as reliable light sources in the optical coherence tomography [62]. One practical problem about the Cr^{4+} :forsterite lasers stems from the temperature-dependent upper-state lifetime of the Cr^{4+} :forsterite crystal. The phonon assisted non-radiative decay generates heat inside the gain media and reduces the efficiency of the laser and hence, higher pumping levels may not yield higher output powers due to the thermal loading inside the crystal. Cryogenic cooling mechanisms have been used as a remedy, but the efficient room temperature operation was demonstrated by A. Sennaroglu [129] and it does not create a practical limitation for our laser at Koç University. There are also other studies, which involve Cr^{4+} :forsterite lasers, done by our group for the first time. Such as; the highest pulse energy (81nJ) directly obtained from a mode-locked Cr^{4+} :forsterite laser at room temperature [130], the highest peak powers generated from the single-walled carbon nanotube [131] and the graphene mode-locked solid-state laser [24], the first demonstration of a graphene-based supercapacitor mode-locked laser [54], and the first demonstration of a graphene-gold-based supercapacitor mode-locked laser [55]. The last three studies, performed by using this laser, will be presented in Chapters 4,5, and 6 respectively.

The other commonly used transition metal ion doped solid-state gain media is the Ti^{3+} :sapphire. Sapphire (Al_2O_3) is a well-known gemstone and has a trigonal crystal system. Ti^{3+} doped sapphire supports a large gain bandwidth and enables ultrashort pulse generation up to a duration as short as 5 fs [92]. It was first introduced by P. F. Moulton et al. in 1986 [132], and become a widespread solid-state laser due to its good thermal conductivity, robustness, and excellent tunability (650-1100 nm). Furthermore, the first Kerr-lens mode-locked operation was demonstrated by D. E. Spence et al. in 1991 [112]. Ti^{3+} :sapphire gain media are usually pumped by another optical source with a wavelength of 532 nm. The frequency-doubled Nd:YAG, Nd:Vanadate, Nd:YLF lasers have been commonly used as pump sources. Furthermore, the recent advancements in the diode technology also enable direct diode pumping by using 520 nm laser diodes [133, 134]. The

operation wavelength range (650-1100 nm) of the Ti^{3+} :sapphire laser and the availability of ultrashort pulse generation, makes it a remarkable coherent light source for applications, such as multi-photon microscopy [135], frequency metrology [136], multicolor ultrafast spectroscopy [137], micromachining [138], terawatt and petawatt physics research [139]. Furthermore, the nonlinear frequency conversion can also be used to extend the wavelength range of the Ti^{3+} :sapphire lasers [140]. Our group has been also contributing to the research and the development of the Ti^{3+} :sapphire lasers with the multi-pass cavity extensions [141]. Furthermore, the first demonstration of a graphene-based supercapacitor saturable absorber mode-locked Ti^{3+} :sapphire laser [56] will be presented in detail in Chapter 7. Figure 3.3.1 further shows, photographs of the two different gain media that were introduced above and used in our mode locking experiments.

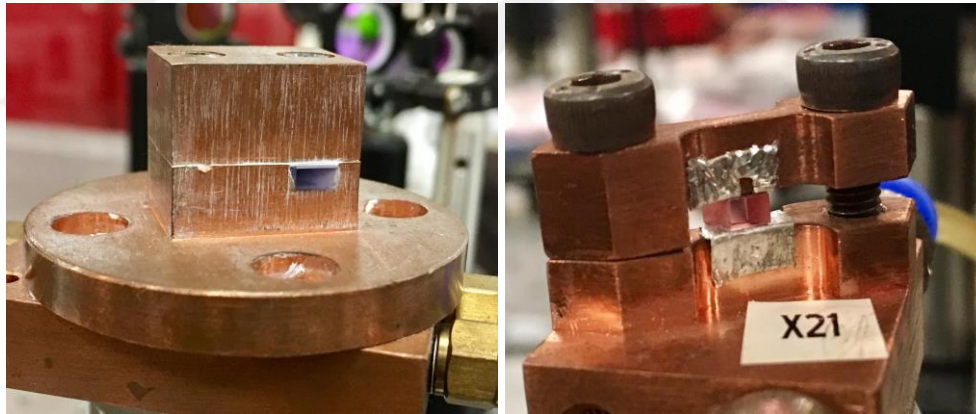


Figure 3.3.1. In our mode locking experiments, the Cr^{4+} :forsterite (left) and the Ti^{3+} :sapphire (right) gain media were used.

Chapter 4

GRAPHENE SATURABLE ABSORBER MODE-LOCKED MULTIPASS-CAVITY Cr⁴⁺:FORSTERITE LASER

In this Chapter, use of a graphene saturable absorber (GSA) on a quartz and on a YAG substrate to generate femtosecond pulses from a multipass-cavity (MPC) Cr⁴⁺:forsterite laser will be presented. To the best of our knowledge, this was the first demonstration of the use of a GSA in an energy-scaled femtosecond laser. In the first part of Chapter 4, the fabrication stages and the optical characterization results of graphene saturable absorbers will be given. This will be followed by the description of our multipass-cavity (MPC) Cr⁴⁺:forsterite laser setup and the continuous-wave operation results. The results obtained from the GSA mode-locked MPC Cr⁴⁺:forsterite laser will be presented in the last part of Chapter 4.

4.1 Fabrication and Optical Characterization of Graphene Saturable Absorbers

Our mode locking experiments were conducted by using two different graphene saturable absorbers (GSAs) which were fabricated by C. Kocabas's group at Bilkent University. The chemical vapor deposition method (CVD) was used to synthesize the monolayer graphene. The copper foils with high purities were placed in a quartz chamber and the synthesis furnace was heated to 1000 °C and kept at 300 mTorr under the flow of hydrogen and argon. A mixture of methane was chosen as the carbon source for graphene. After monolayer graphene was obtained on the copper substrate, it was spin-coated by using a photoresist. Then, the copper was etched by using 1 M iron chloride solution. When the etching process was finished, graphene with the photoresist was pasted to a polymer (polydimethylsiloxane, PDMS) and then, monolayer graphene was transfer-printed onto an optically polished 1-mm thick quartz substrate (and 2-mm thick YAG (yttrium aluminum

garnet, Y₃Al₅O₁₂) substrate). At the end of the fabrication process, the photoresist was removed by using acetone. The details of the fabrication process can be found in Ref. [142]. Quartz and YAG were chosen as substrates for the monolayer graphene, since their transparency is high in a broad wavelength range, which also covers the operation wavelength of our laser. Hence, the graphene saturable absorber on quartz (GSA-quartz) and the GSA-YAG were operated as effective saturable absorbers with minimum optical insertion losses.

To evaluate the merit of the graphene samples, Raman spectroscopy and steady-state transmission measurements were performed. Figure 4.1.1 shows the Raman spectrum of the GSA-quartz sample. The sample was illuminated by using a 532 nm light source and the characteristic peaks, which were described in Chapter 1, were investigated. The defect amount on the sample was calculated from the D/G ratio and it was 0.135. Furthermore, the FWHM of the 2D peak was measured to be 38 cm⁻¹ providing that our graphene was indeed a monolayer sample [24]. Figure. 4.1.2 demonstrates, the Raman spectra of the GSA-YAG (a) and the bare YAG (b). In this case, the D/G ratio was calculated to be 0.151 and the FWHM of the 2D peak was around 34 cm⁻¹ [40]. The additional peaks in the Raman spectrum were due to the YAG substrate, which is shown in Fig. 4.1.2 (b). The steady-state transmission spectrum for the GSA-quartz sample was measured by using UV-Shimadzu spectrophotometer. The measured transmission was not exactly 97.7% since the loss arising from the substrate is not subtracted and the sample was placed at the normal incidence. The glitch around 800 nm was due to the mechanical noise of the spectrophotometer. The transmission spectrum shown in Fig. 4.1.3 clearly shows that the GSA-quartz has a nearly constant, broadband absorption over a broad wavelength range.

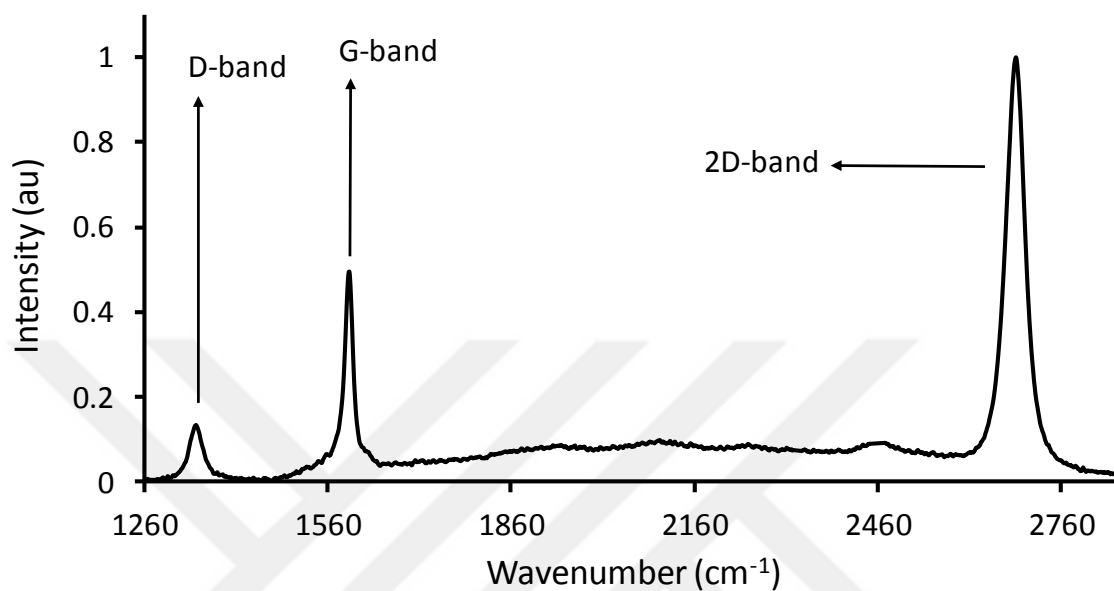


Figure 4.1.1. Measured Raman spectrum of the graphene on quartz substrate. (Adapted with permission from [24], (The Optical Society)).

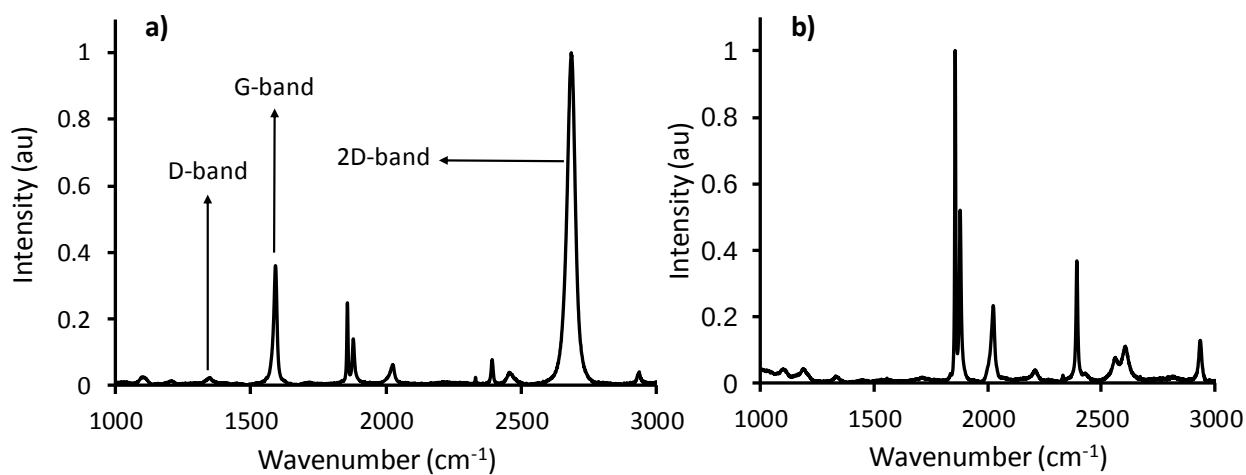


Figure 4.1.2. (a) Measured Raman spectra of graphene on YAG substrate and (b) the bare YAG.

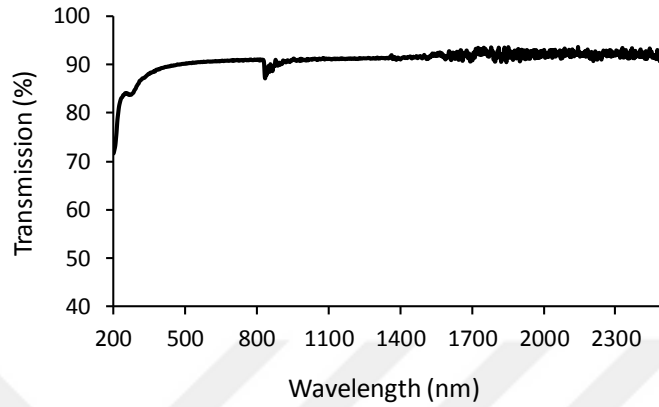


Figure 4.1.3. The steady-state transmission spectrum of the graphene on quartz sample.

To investigate the saturable absorber properties of our samples, we also performed nonlinear optical characterization experiments by using a commercial ultrafast pump-probe spectrometer (HELIOS, Ultrafast Systems) at Koç University Surface Science and Technology Center (KUYTAM). For the pump-probe experiments, which characterizes the ultrafast relaxation dynamics of the carriers, a tunable optical parametric amplifier (TOPAS, Spectra Physics) was used as a pump source and the probe was chosen to be a broadband near-infrared continuum, spanning from 900-1600 nm. The pump source was seeded with 2 mJ, 100 fs, 1 kHz pulses from a commercial Ti³⁺:sapphire chirped-pulse amplifier (Spitfire ACE, Newport-Spectra Physics) and set at 400 nm. The time-resolved carrier relaxation response of the graphene on quartz and YAG samples are shown in Fig. 4.1.4. By fitting a decaying biexponential function to the data, the carrier recovery times (τ) for both samples were determined as can be seen from Fig. 4.1.4 [24, 40]. The other two important saturable absorber parameters, the saturation fluence and the modulation depth, were also measured at 1250 nm (operation wavelength of the Cr⁴⁺:forsterite laser) by using the same pump-probe setup. As Fig. 4.1.5 demonstrates, the measured transmissions of both samples increased with an increasing incident fluence as expected from a saturable absorber. The saturation fluence for the GSA-quartz (GSA-YAG) was determined to be 25

$\mu\text{J}/\text{cm}^2$ ($70 \mu\text{J}/\text{cm}^2$) and the modulation depth of the sample was determined to be 0.5% (0.77%) [24, 40] by using the saturable absorber analysis, which was presented in Chapter 2.

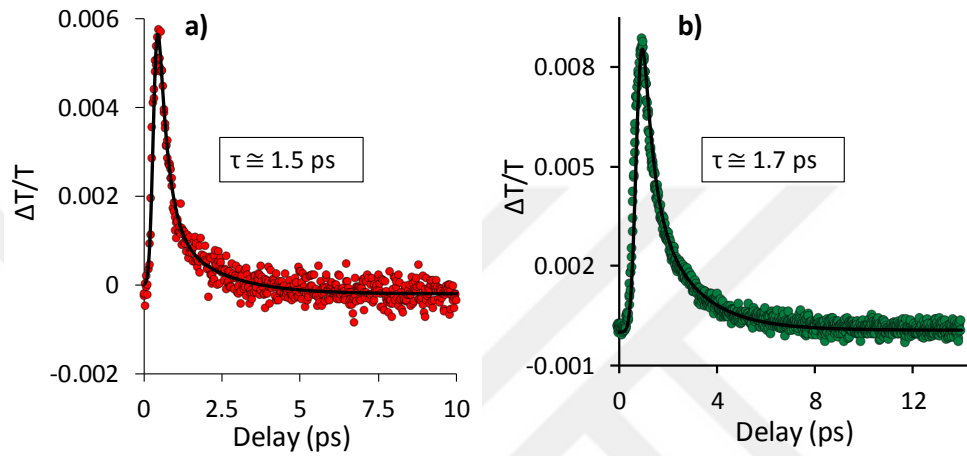


Figure 4.1.4. (a) The measured variation of the fractional transmission change at 1250 nm as a function the delay for the graphene on quartz and (b) the graphene on YAG samples. (Adapted with permission from [24], (The Optical Society)).

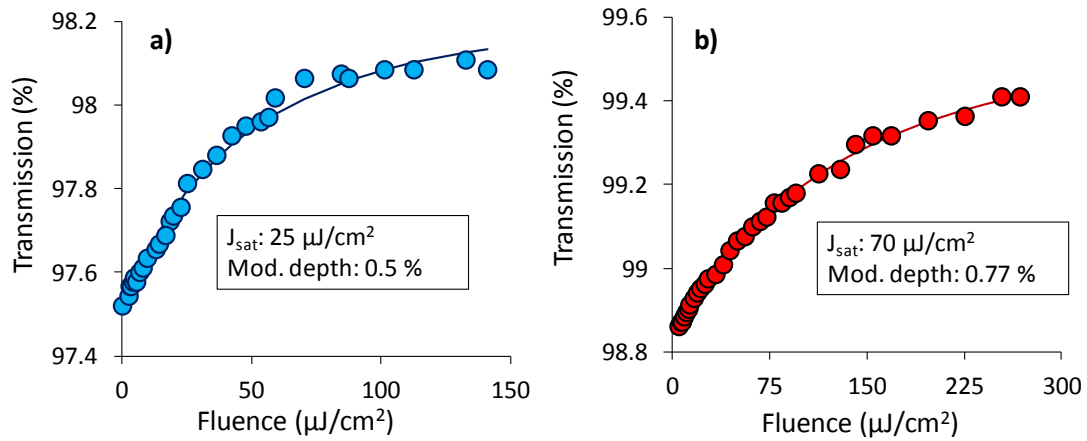


Figure 4.1.5. (a) Measured change in the transmission of the graphene on quartz and (b) the graphene on YAG saturable absorbers at 1250 nm. (Adapted with permission from [24], (The Optical Society)).

4.2 Experimental Setup

In order to explore the saturable absorber performance of the graphene on quartz (GSA-quartz) and the graphene on YAG (GSA-YAG) samples, we used a multipass-cavity (MPC) Cr⁴⁺:forsterite laser operating near 1250 nm. Figure 4.2.1 shows the three stages of the final resonator architecture. In our experiments, we started with an x-cavity Cr⁴⁺:forsterite laser as shown in Fig.4.2.1 (a). A continuous-wave Yb:fiber laser at 1064 nm was used to end-pump a 20-mm long, Brewster-cut Cr⁴⁺:forsterite crystal. The Cr⁴⁺:forsterite crystal had a 70% absorption at the pump wavelength and it was mounted in a copper holder and kept at 20 °C by water cooling. Two curved and highly reflecting double-chirped mirrors (DCMs), each with 10 cm radius of curvature (M1 and M2), a high reflector (HR), and an output coupler (OC) with 2.4% (and 4.7%) transmission at the laser wavelength were used to build the x-cavity. A focusing lens (L1) with a 20-cm focal length was used to focus the pump beam inside the crystal. By using the ABCD matrix formalism, which was discussed in Chapter 3, the pump waist was estimated to be 30 μm by inside the crystal.

To increase the optical path length and to reduce the pulse repetition rate of the laser, a multipass-cavity (MPC) extension was introduced to the short x-cavity by removing the HR mirror as shown in Fig. 4.2.1 (b). To adjust the inclination angle of the beam entering to the MPC, two flat DCM mirrors (M3 and M4) were introduced to the original resonator. The MPC consisted of a flat (M5) and a curved (M6) (with a 4-m radius of curvature) two high reflector mirrors with notches for the beam injection and extraction. The laser beam completed $n=9$ round-trips inside this extension and m value was equal to 4. The separation between the MPC mirrors was 165 cm and for this separation, the angular advance of the circular spot pattern was 80°. As can be seen from Fig. 4.2.1 (b), the 9th beam passed through the notch of the M6 and retro-reflected by using a second curved mirror (M8) with radius of curvature 2 m. This mirror was located at 165 cm from the M5 to maintain the q-

preserving condition, which was discussed in Chapter 3. The MPC introduced an additional effective optical path length of 59.4 m to the original resonator without perturbing the q-parameter of the short x-cavity.

To create a waist and to obtain sufficient incident fluence on the graphene samples, a second x-cavity was built as shown in Fig. 4.2.1 (c). This extension was further used to balance the cavity nonlinearities due to the self-phase modulation effects, which were described in Chapter 2. Hence, the flat high reflector mirrors were chosen as DCM and GTI (Gires-Tournois interferometer) mirrors which introduced second-order negative group delay dispersion (GDD) to the resonator. Four of the mirrors were GTIs (M9, M10 and M15, M16) each with -250 fs^2 GDD and the four of them were DCMs (M7, M10, M11, and M16) each with -150 fs^2 GDD at the laser wavelength of 1250 nm. To further increase the negative GDD of the mirrors, the circulating beam reflected off four times from the GTI mirrors and two times from the three of the DCMs in each round-trip. Together with the positive GDD coming from the cavity components (MPC, $+360 \text{ fs}^2$, crystal $+800 \text{ fs}^2$, air $+794 \text{ fs}^2$, and substrates $\sim +7 \text{ fs}^2$ for quartz and YAG) and the total negative GDD due to the DCM and GTI mirrors, the net intracavity dispersion of the resonator was estimated to be around -4440 fs^2 . The other two curved high reflectors (M13 and M14) each with a radius of curvature of 50 cm were further used to create a waist and to saturate the samples. For this configuration, the estimated waist on the graphene samples was $97 \text{ }\mu\text{m}$. With the addition of the second x-cavity, the total effective optical path length increased to 66.5 m.

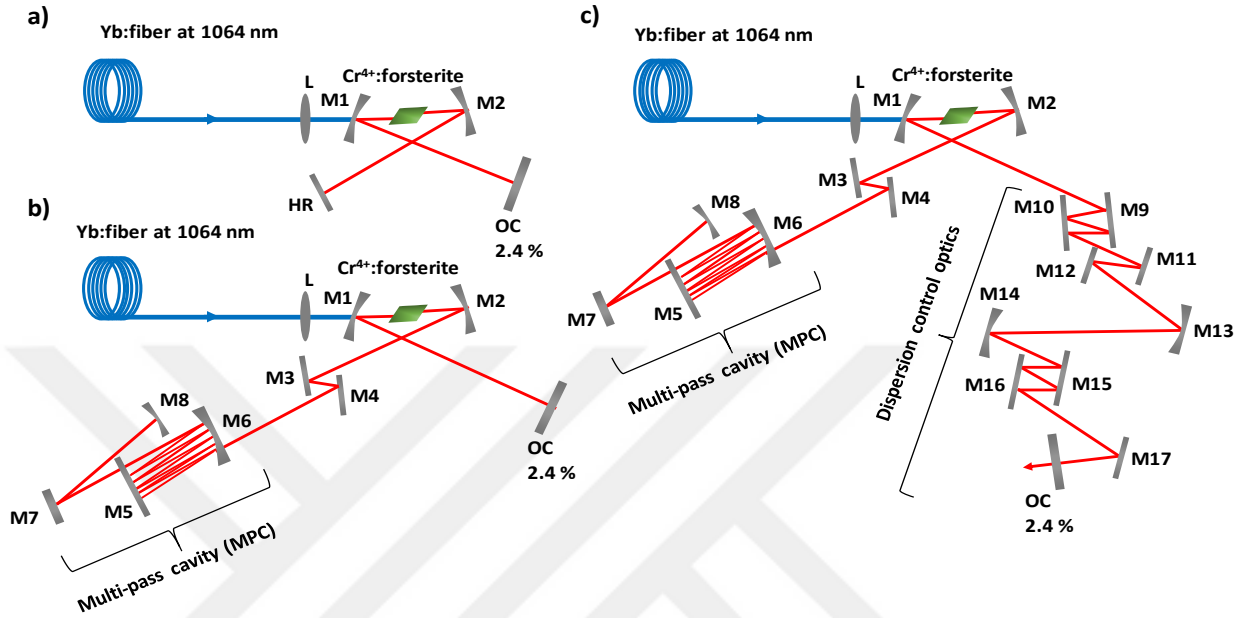


Figure 4.2.1. (a) Experimental setup of the x-cavity and (b) the multipass-cavity Cr⁴⁺:forsterite laser. (c) The final resonator architecture consisted of the MPC and dispersion control optics.

4.3 Continuous-Wave Operation Results

For the x-cavity architecture shown in Fig. 4.2.1 (a), 670 mW of output power was obtained with 7 W of input pump power with a slope efficiency of 13.4%. The threshold input pump power for the x-cavity laser was measured to be 2.1 W. After the addition of the MPC (Fig.4.2.1 (b)), the threshold value for the input pump power increased to 2.6 W and the slope efficiency reduced to 12%. At the highest input power of 7 W, 550 mW of output power was obtained from this configuration. For the final laser architecture, which consisted of the MPC and dispersion control optics (Fig.4.2.1 (c)), the highest output power was 480 mW for 7 W of input pump power. The measured threshold pump power was 2.7 W and the slope efficiency was 11%. These values were measured with the 4.7% output coupler. For the output coupler with 2.4% transmission, 298 mW of output power was obtained with 7 W of input pump power with a slope efficiency of 6.4%. Furthermore, the

threshold pump power with this output coupler was measured to be 2.4 W. The graphene on quartz (YAG) sample was placed at Brewster's incidence between the two curved mirrors (M13 and M14) to minimize the reflection losses and to avoid etalon effects. After introducing the GSA-quartz (GSA-YAG), the threshold pump power increased to 5.2 W (5 W) for the 4.7% output coupler and 4.12 W (4.15 W) for the 2.4% output coupler and hence, the slope efficiency of the laser reduced to 4.3% (5.6%) for the 4.7% and 2.3% (3.4 %) for the 2.4% output coupler respectively. Figure 4.3.1 shows the power efficiency curves of the short x-cavity and the MPC Cr⁴⁺:forsterite laser operated with the 4.7% output coupler. The power efficiency curves of the laser in the final resonator configuration with and without the GSA-quartz (GSA-YAG) for two different output couplers are further shown in Fig. 4.3.2.

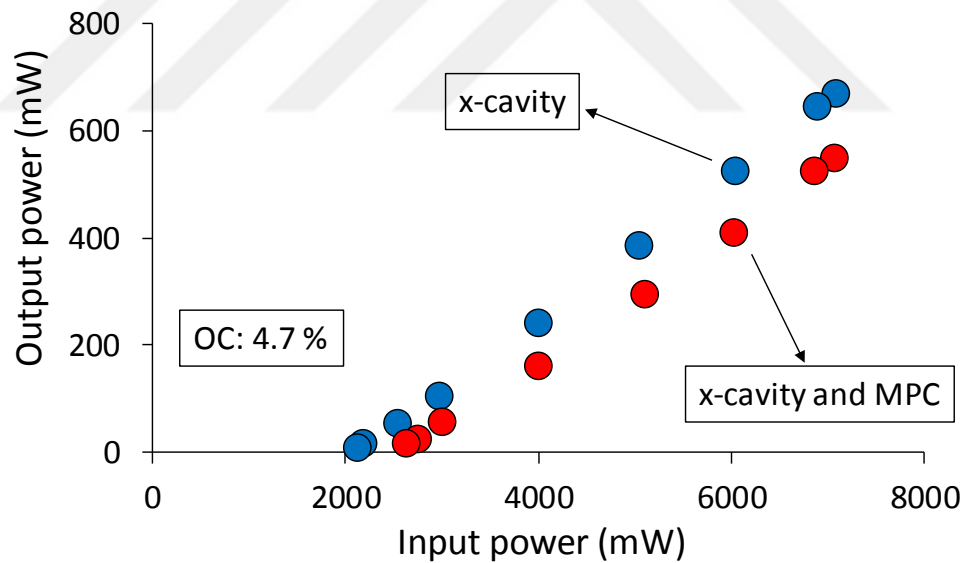


Figure 4.3.1. Power efficiency curves for the short x-cavity and the MPC Cr⁴⁺:forsterite laser with the 4.7% output coupler.

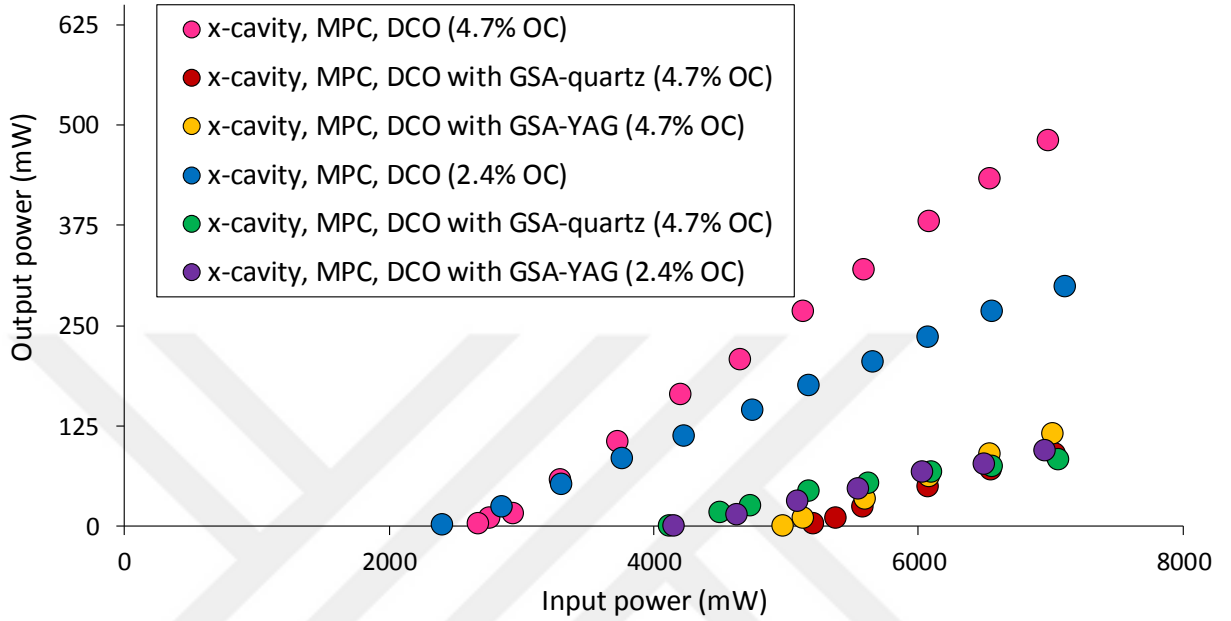


Figure 4.3.2. Power efficiency curves for the laser resonator with GSA samples on different substrates and with different output couplers (DCO: dispersion control optics, MPC: multipass-cavity). (Adapted with permission from [24], (The Optical Society)).

By using the threshold pump power analysis, introduced in Chapter 3, $(P_p)_{th} = A(L + T)$, the additional round-trip optical insertion loss (L) of the MPC was estimated to be 1.72%. The MPC extension introduced nearly 60 m additional optical path length to the original resonator and hence, the total round-trip resonator length (d) was 66.5 m corresponding to a 4.51 MHz pulse repetition rate, $f_{rep} = \frac{c}{2d}$. Although the output power of the laser decreased and the threshold pump power increased, since the pulse repetition rate of the laser was decreased from nearly 150 MHz to 4.51 MHz, an approximately 30 times increase in the pulse energy was obtained at the same input power level due to the compact MPC extension design. The single-pass insertion losses of the GSA-quartz and the GSA-YAG samples were also estimated to be 3.15% and 4% by using the same threshold pump

power analysis. The loss difference between the two samples was probably due to the use of different substrates with different optical lengths.

4.4 Mode-Locked Operation Results

When the GSA-quartz (or GSA-YAG) sample was placed inside the resonator, mode-locked operation was initiated by translating the output coupler. Figure 4.4.1 shows, photograph of the GSA-quartz mode-locked MPC Cr⁴⁺:forsterite laser. The GSA-quartz mode-locked MPC Cr⁴⁺:forsterite laser (with 2.4% OC) produced nearly transform-limited (assuming a sech² temporal profile) 94-fs pulses with a time-bandwidth product of 0.32. The corresponding spectral bandwidth was 18 nm at the central wavelength of 1252 nm [24]. With the 4.7% output coupler, the measured mode-locked spectral width was 17.6 nm and the corresponding transform limited pulses were 100 fs with a time-bandwidth product of 0.33. At the maximum input power level, the mode-locked resonator with 4.7% (2.4%) output coupler produced an output power of 24 mW (11 mW). Further increase in the output power resulted in temporal and spectral instabilities, such as multi-pulsing and generation of a continuous-wave peak in the mode-locked spectrum.

The mode-locked laser resonator was characterized by using a collinear autocorrelation setup, an optical spectrum analyzer, and an RF (radio-frequency) spectrum analyzer. Figure 4.4.2 shows the measured autocorrelation trace of the femtosecond pulses, which were generated from the GSA-quartz mode-locked MPC Cr⁴⁺:forsterite laser. The measured mode-locked spectra are shown in Fig. 4.4.3 and the RF spectrum measurement results are further demonstrated in Fig. 4.4.4.

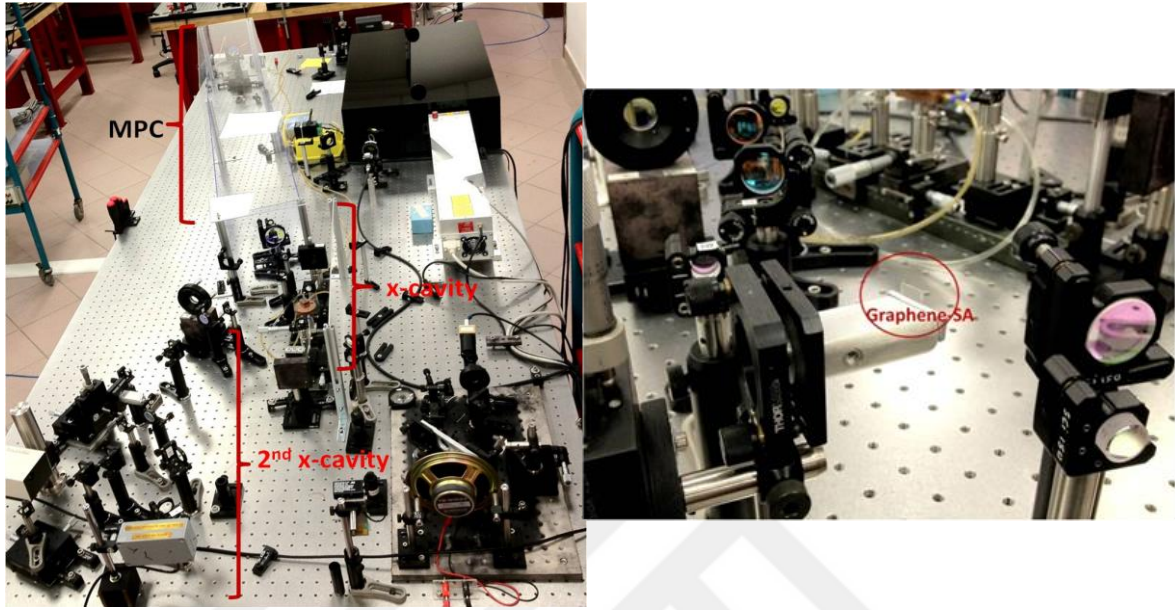


Figure 4.4.1. Photograph of the MPC Cr^{4+} :forsterite laser (left) and the GSA-quartz sample, which was placed between the two curved mirrors (right).

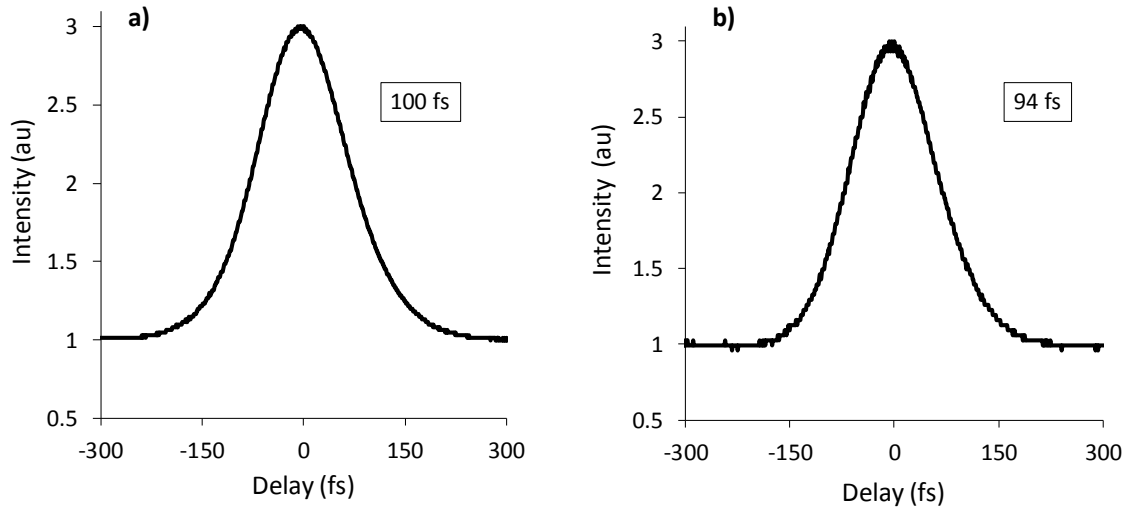


Figure 4.4.2. (a) Collinear autocorrelation data for the GSA-quartz mode-locked Cr^{4+} :forsterite laser with the 4.7 % and (b) 2.4 % output coupler. (Adapted with permission from [24], (The Optical Society)).

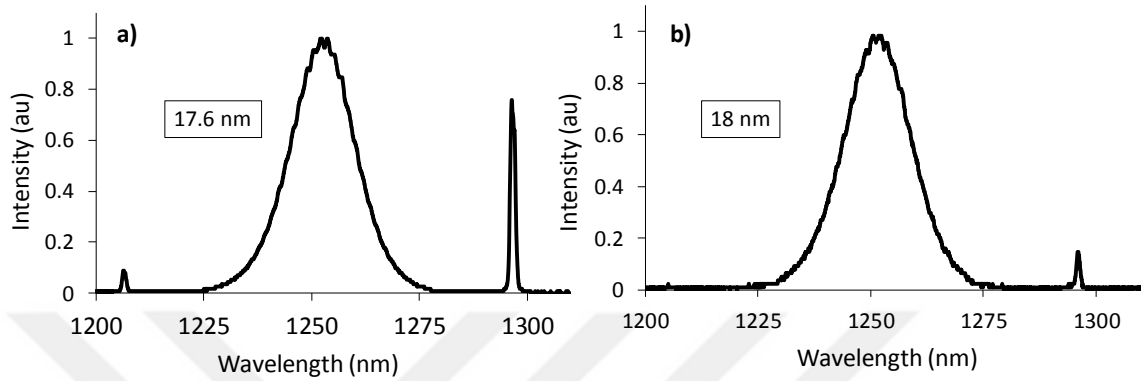


Figure 4.4.3. (a) Measured mode-locked spectra of the femtosecond MPC Cr⁴⁺:forsterite laser for the 4.7 % and (b) for the 2.4 % output coupler. In each case, Kelly sidebands [143] were observed on both sides of the spectra. (Adapted with permission from [24], (The Optical Society)).

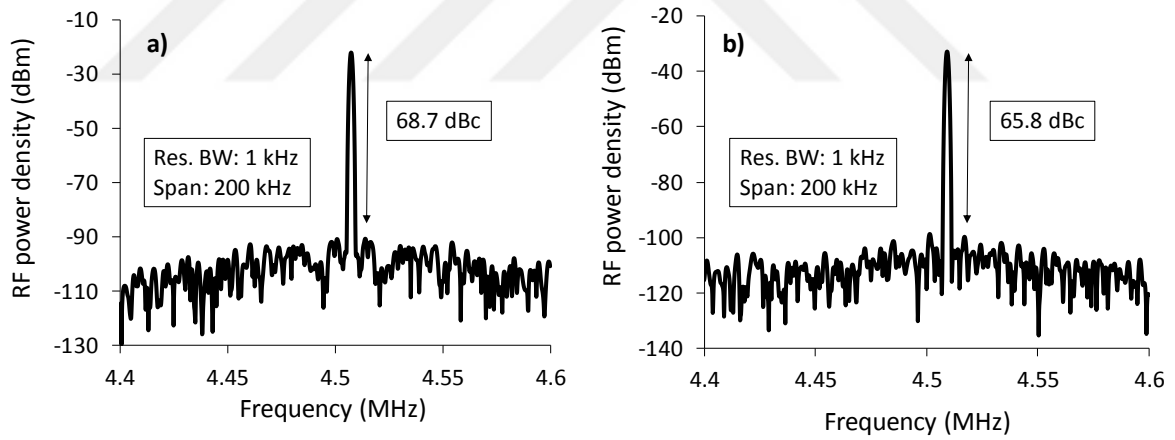


Figure 4.4.4. (a) RF spectra of the GSA-quartz mode-locked MPC Cr⁴⁺:forsterite laser. The sideband noise level was determined to be 68.7 dBc for the 4.7% output coupler and (b) 65.8 dBc for the 2.4% output coupler indicating stable mode-locked operation. (Adapted with permission from [24], (The Optical Society)).

The mode-locked laser parameters such as pulse energy (E_p), pulse peak power (P_{peak}), spectral width ($\Delta\lambda$), pulse duration (τ_p), and time-bandwidth product ($\Delta\nu \cdot \tau_p$) which were introduced in Chapter 2, are summarized in Table 4.4.1 for the GSA-quartz mode-locked MPC Cr⁴⁺:forsterite laser.

Table 4.4.1. Summary of the femtosecond laser parameters for the GSA-quartz mode-locked multipass-cavity Cr⁴⁺:forsterite laser.

Output coupler (%)	Mode-locked output power (mW)	Pulse energy (nJ)	Pulse peak power (kW)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
2.4	11	2.4	25	1252	18	94	0.32
4.7	24	5.3	53	1252	17.6	100	0.33

As can be seen from Table 4.4.1, femtosecond pulse characteristics were nearly the same for both output couplers. However, with 4.7% output coupler, higher output powers were obtained and hence, the laser produced pulses with higher peak powers. To the best of our knowledge, 53 kW of peak power was the highest peak power obtained from a graphene mode-locked solid-state laser. For the single pulse mode-locked operation output power of 24 mW and the estimated waist of 90 μm , the incident fluence on the GSA-quartz was estimated to be 382 $\mu\text{J}/\text{cm}^2$ and no damage was observed on the graphene up to this fluence level.

In the case of the GSA-YAG mode-locked MPC Cr⁴⁺:forsterite laser, the resonator produced transform-limited pulses as short as 92 fs (112 fs) with a time-bandwidth product of 0.33 (0.36) with the 4.7% (2.4%) output coupler [40]. Similarly, further increase in the energy of the pulses resulted in the mode locking instabilities due to the cavity nonlinearities. For the GSA-YAG mode-locked resonator, the pulse duration, the mode-

locked spectrum, and the RF spectrum were shown in Fig.4.4.5 (a), (b), and (c) respectively for the 4.7% OC.

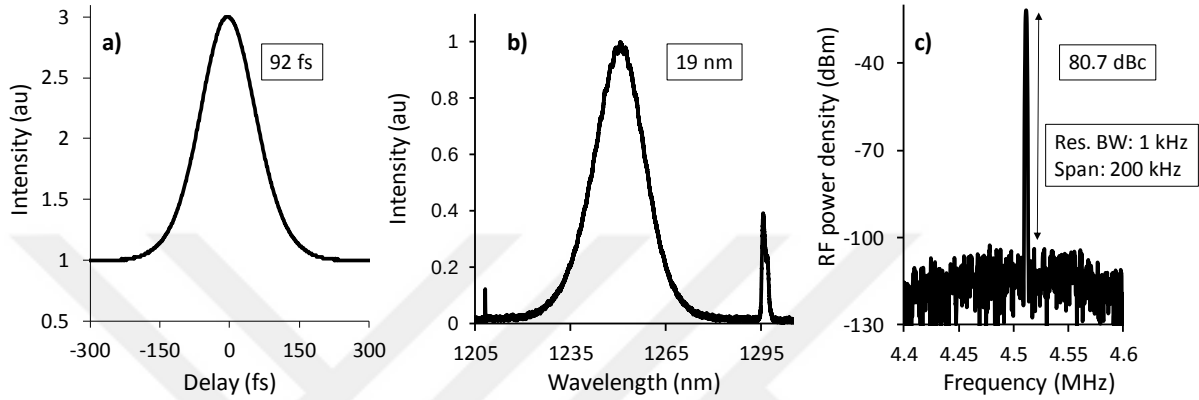


Figure 4.4.5. (a) Autocorrelation trace, (b) mode-locked spectrum, and (c) RF spectrum of the GSA-YAG mode-locked Cr⁴⁺:forsterite laser with the 4.7% output coupler. (Adapted with permission from [40], (The Optical Society)).

Table 4.4.2. GSA-YAG mode-locked multipass-cavity Cr⁴⁺:forsterite laser.

Output coupler (%)	Mode-locked output power (mW)	Pulse energy (nJ)	Pulse peak power (kW)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
2.4	14	3.1	27	1258	17	112	0.36
4.7	22	4.9	53	1250	19	92	0.33

Table 4.4.2 summarizes the mode locking results obtained from the GSA-YAG mode-locked MPC Cr⁴⁺:forsterite laser. As can be seen, use of the YAG substrate did not affect the femtosecond pulse characteristics. Similar to the GSA-quartz sample, the incident fluence on the GSA-YAG was estimated to be 351 $\mu\text{J}/\text{cm}^2$ and no damage was observed up to this level. As described before, any further increase in the pulse energy resulted in the mode locking instabilities for both GSAs. This was mainly due to the insufficient amount of the fixed negative group delay dispersion ($\text{GDD} \sim 4440 \text{ fs}^2$) inside the resonator, which

was unable to balance the cavity nonlinearities. The main source of the cavity nonlinearity was the Cr⁴⁺:forsterite gain medium. Hence, by using the soliton-area theorem ($W\tau = \frac{4|D|}{\gamma}$), introduced in Chapter 2, the nonlinear refractive index (n_2) of the Cr⁴⁺:forsterite medium was estimated from the nonlinearity coefficient (γ), the resonator dispersion (D), the pulse duration (τ 1.76), and the intracavity energy (W). For the GSA-quartz mode-locked laser, the nonlinear refractive index (n_2) was estimated to be $11.83 \pm 0.2 \times 10^{-20}$ m²/W and for the GSA-YAG mode-locked resonator, it was estimated to be $11.1 \pm 0.2 \times 10^{-20}$ m²/W respectively [24, 40]. Both of the values were in agreement with the previously reported nonlinear refractive index values for the Cr⁴⁺:forsterite gain medium [75]. Furthermore, by using the estimated nonlinear refractive index values, the limiting factor for further power scaling, the critical power ($P_{cr} = \frac{\alpha\lambda^2}{8\pi n_0 n_2}$), was also estimated for both GSAs. The results are summarized in Table 4.4.3.

Table 4.4.3. Measured maximum intracavity peak powers and the estimated critical powers for the GSA-quartz and the GSA-YAG mode-locked MPC Cr⁴⁺:forsterite laser.

Saturable absorber	Maximum intracavity peak power (MW)	Critical power (MW)
GSA-quartz	1.13	1.21
GSA-YAG	1.13	1.29

The critical power provides an order-of-magnitude estimate for the maximum intracavity peak power that can be attained before the mode locking instabilities occur due to the cavity nonlinearities. As can be seen from Table 4.4.3, the estimated critical powers for the self-focusing were in good agreement with the measured values, which indicates that the self-focusing in the Cr⁴⁺:forsterite gain medium was the major factor that limits further energy scaling.

CHAPTER 5

MODE-LOCKED OPERATION OF A FEMTOSECOND Cr⁴⁺:FORSTERITE LASER BY USING VOLTAGE-CONTROLLED GRAPHENE SATURABLE ABSORBER

Graphene saturable absorbers have been successfully employed as effective saturable absorbers to generate femtosecond pulses from different lasers operating in the near and mid-infrared [28, 36, 38]. However, due to its small-signal round-trip insertion of nearly 5%, it is challenging to operate low gain lasers with graphene saturable absorbers. Hence, one possible remedy involves using graphene-based supercapacitor structures, in which the absorption amount of graphene can be dynamically controlled with low operating voltages (0-3V). In Chapter 5, the use of a graphene-based voltage-controlled saturable absorber (VCG-SA) to generate femtosecond pulses from a multipass-cavity (MPC) Cr⁴⁺:forsterite laser will be presented. To the best of our knowledge, this was the first demonstration of a graphene-based supercapacitor mode-locked laser. In the first part of Chapter 5, the fabrication stages and the optical characterization results of the voltage-controlled graphene saturable absorber (VCG-SA) will be given. This will be followed by the voltage-dependent continuous-wave and mode-locked operation results.

5.1 Fabrication and Optical Characterization of Voltage-Controlled Graphene Saturable Absorber

Voltage-controlled graphene supercapacitor saturable absorber (VCG-SA) consisted of an electrolyte with a dielectric constant of 14, which was sandwiched between the two graphene electrodes. The VCG-SA, shown in Fig.5.1.1 (a), was fabricated by C. Kocabas's group at Bilkent University. Graphene electrodes of the supercapacitor were synthesized by using chemical vapor deposition (CVD) method and transfer-printed onto a 1-mm thick, 1-in. diameter quartz substrate as shown in Fig.5.1.1 (a). The 100 μ m spacing between the

graphene electrodes was filled with an electrolyte (Diethymethyl (2-methoxyethyl) ammonium bis (trifluoro- methylsulfony) imide [DEME][TFSI]), which had a relative dielectric constant of 14 ($\epsilon_r = 14$). The electrical connections to the graphene electrodes were made by using carbon tapes. Fabrication details of the VCG-SA can be found in Ref. [45].

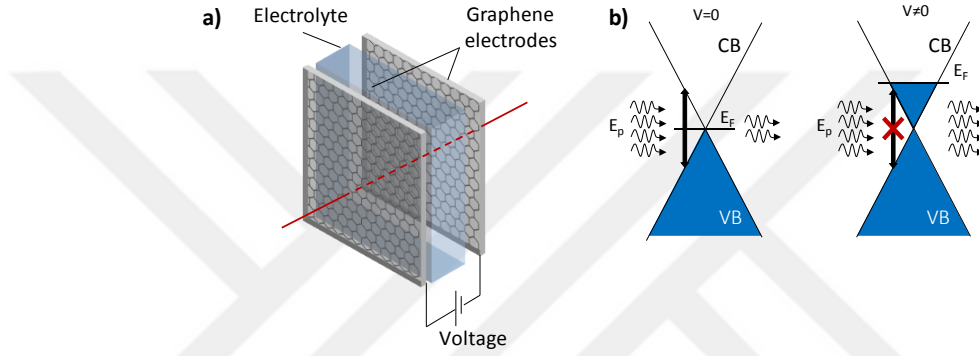


Figure 5.1.1. (a) Schematic of the graphene-based supercapacitor architecture. (b) The energy-band structure of graphene for the unbiased and the biased case. E_p and E_F are the photon and the Fermi energies, VB and CB are the valance and the conduction bands respectively. (Adapted with permission from [54], (The Optical Society)).

In Chapter 1, the electrostatic shifting of the Fermi level of graphene by using supercapacitor architectures were discussed. In summary, the application of a voltage bias to the graphene electrodes polarizes the electrolyte, which enables the formation of the ultrathin electrical double layers (EDLs). As can be seen from Fig.5.1.1 (b), the Fermi level shift completely supresses the absorption of the VCG-SA for wavelengths with photon energy below $2|E_F|$.

Prior to the mode locking experiments, the voltage-dependent optical response of the VCG-SA was explored by using a spectrophotometer. Further characterization of the device, which includes the electronic characteristics, can be found in Ref. [45]. Since the aim of the supercapacitor architecture was to reduce the optical insertion loss of graphene, the

electrolyte was chosen to be transparent in the operation wavelength of the Cr⁴⁺:forsterite laser. Figure 5.1.2 shows, the measured transmission spectrum of the electrolyte (Diethymethyl (2-methoxyethyl) ammonium bis (trifluoro- methylsulfony) imide [DEME][TFSI]). Note that the absorption losses near 1250 nm (Cr⁴⁺:forsterite) were minimal for this specific electrolyte. In Chapter 7, another graphene-based supercapacitor design, which consisted the same electrolyte, will be presented. Hence, the optical transmission of the electrolyte near the operation wavelength of the Ti³⁺:sapphire laser (800 nm) was also pointed out in Fig.5.1.2. The voltage-dependent change in the steady-state optical transmission of the VCG-SA is further shown in Fig.5.1.3, where $(\Delta T/T_0)$ is the normalized change in the steady-state transmission with respect to the transmission of the unbiased VCG-SA. As can be seen from Fig.5.1.3, the steady-state transmission of the device could be changed from 600 nm up to the near-infrared wavelengths by applying few volts only (0-3V) as opposed to the graphene-based solid-state capacitor structures, which was described in Chapter 1. Furthermore, 3% of maximum fractional change in the transmission was obtained near the operation wavelength of our laser (1250 nm).

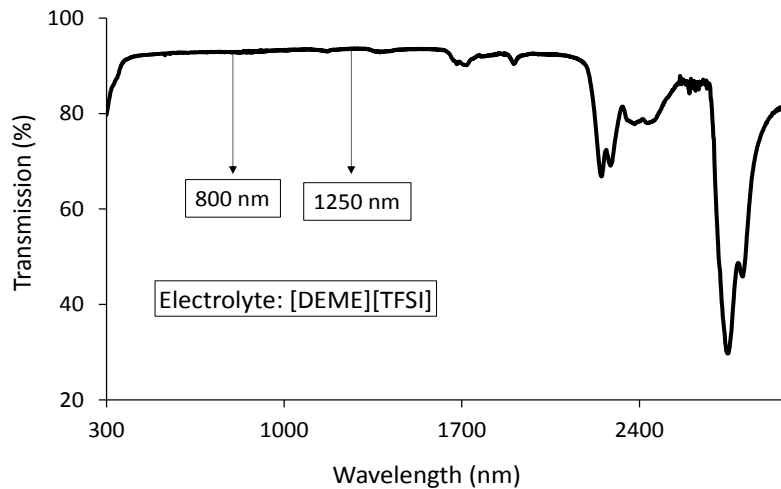


Figure 5.1.2. Measured transmission spectrum of the electrolyte.

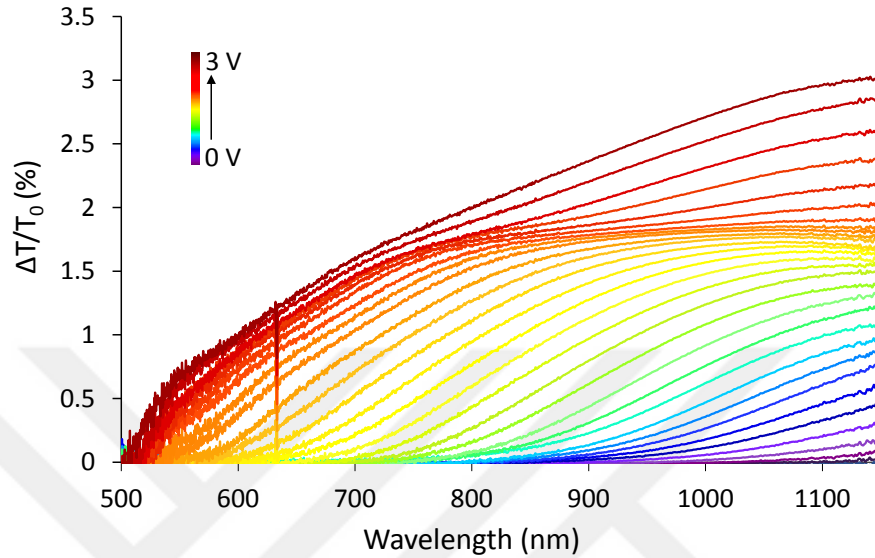


Figure 5.1.3. Normalized change in the transmission of the voltage-controlled graphene saturable absorber as a function of the wavelength at different applied voltages. (Adapted with permission from [54], (The Optical Society)).

Figure 5.1.4 (a) further shows the variation of the normalized transmission of the device at three selected wavelengths, 950, 1064, and 1200 nm. As can be seen, transmission of the VCG-SA could be increased by applying a bias voltage. The two-step behavior in Fig. 5.1.4 (a) was due to the use of two graphene electrodes. As the bias voltage increased, one of the graphene electrodes becomes transparent before the other one and at high voltages, the VCG-SA becomes completely transparent. Figure 5.1.4 (b) shows the variation of the Fermi level shift of the VCG-SA as a function of the applied voltage. The linear change in the Fermi level shift indicated that higher bias voltages were required to completely block the absorption at shorter wavelengths (i.e. higher photon energies) as expected. For example, at 2V of applied bias, the change in the transmission starts for nearly 600 nm, whereas, nearly 1.2V was sufficient to change the transmission at 800 nm. This clearly demonstrated the low-voltage modulation capability of the VCG-SA at high photon energies without reaching the dielectric breakdown limit.

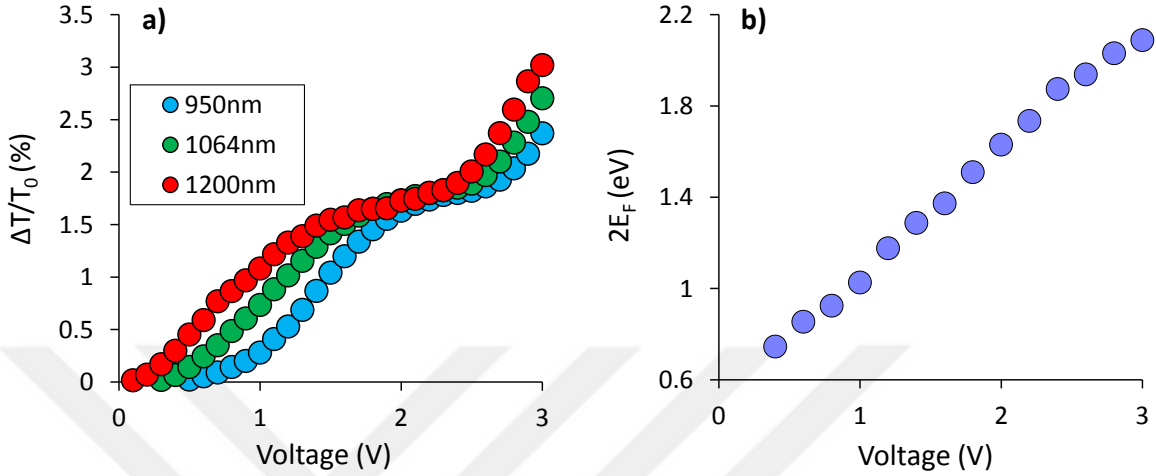


Figure 5.1.4. (a) Measured fractional change in the transmission spectrum of the VCG-SA as a function of the bias voltage at three selected wavelengths. (b) The Fermi level shift of the VCG-SA as a function of the bias. (Adapted with permission from [54], (The Optical Society)).

To evaluate the fast saturable absorber characteristics of the VCG-SA, a transient absorption measurement was performed by using the pump-probe setup, which was described in Chapter 4. As a pump source, the output of our tunable optical parametric amplifier was used and set to 700 nm. The probe source was chosen to be the laser wavelength of the Cr⁴⁺:forsterite gain medium, 1250 nm. Figure 5.1.5 demonstrates, the normalized change in the transmission with respect to the delay between the pump and the probe beam at five selected bias voltages. As can be seen, the typical ultrafast responses for graphene were obtained for bias voltages less than 1V. For these voltages, the recovery time (τ) of graphene was measured to be around 1.9 ps. For voltages beyond 1V, the VCG-SA had more complicated decay dynamics as can be seen from Fig.5.1.5. This was possibly due to the mixed response of the intraband and the interband transitions of graphene at 1250 nm as discussed in Chapter 1 [54].

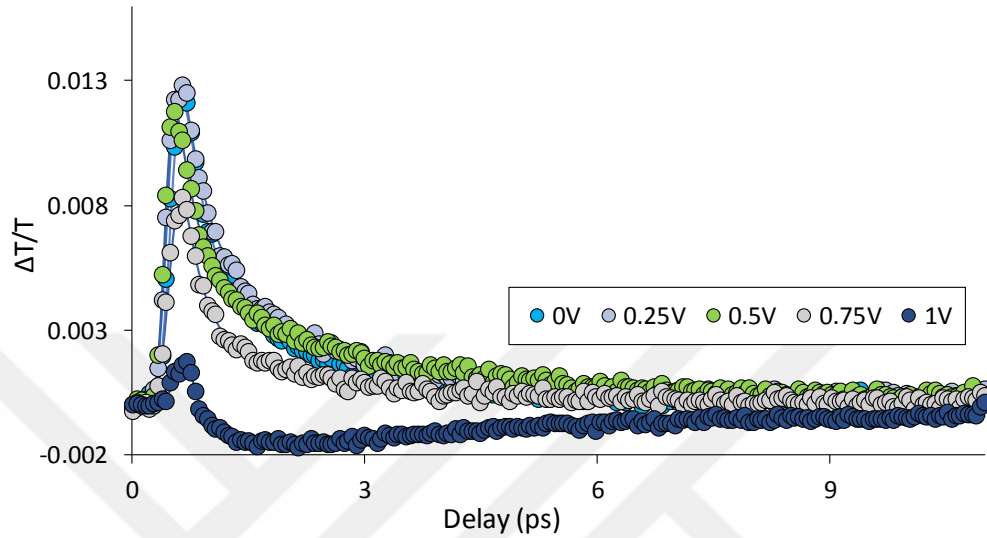


Figure 5.1.5. Measured ultrafast response of the VCG-SA at the probe wavelength of 1250 nm for different bias voltages. (Adapted with permission from [54], (The Optical Society)).

Saturation measurements were also performed to investigate the saturation fluence and the modulation depth of the graphene-based supercapacitor with respect to the applied bias voltages. By using the same pump-probe setup, saturation dynamics of the VCG-SA were explored at 1250 nm. Figure 5.1.6 (a) shows, the measured change in the transmission of the VCG-SA as a function of the incident fluence at different bias voltages. The saturation fluence of the VCG-SA monotonically increased from 137 $\mu\text{J}/\text{cm}^2$ (0V) to 456 $\mu\text{J}/\text{cm}^2$ (1V), whereas, the modulation depth decreased from 1.09% (0V) to 0.69% (1V) [54] with respect to the bias voltage as can be seen from Fig. 5.1.6 (b). Absorption of the graphene electrodes was completely blocked for voltages beyond 1V (near 1 eV photon energy for 1250 nm) due to Pauli blocking and hence, the VCG-SA could not be used as a fast saturable absorber in the mode locking experiments for voltages greater than 1V.

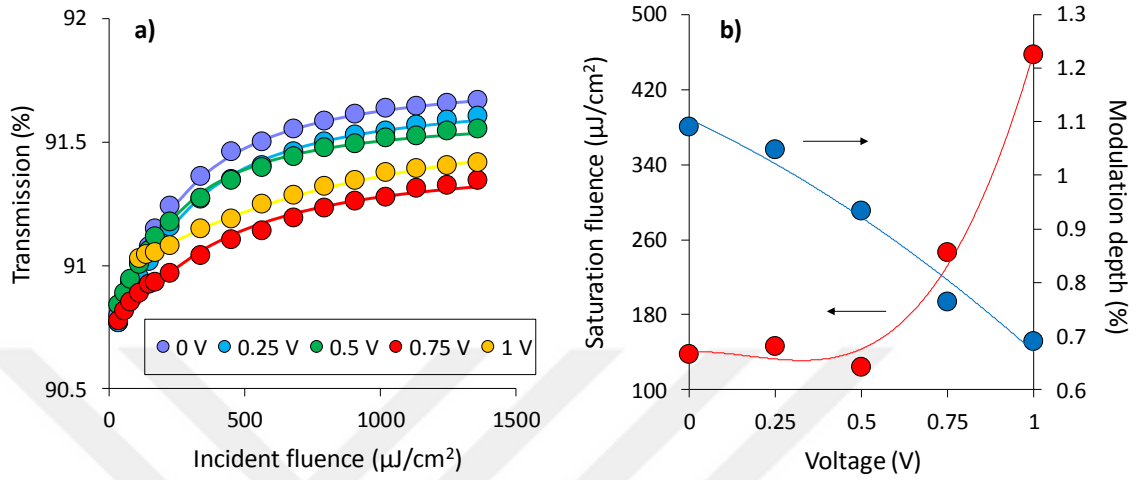


Figure 5.1.6. (a) Measured change in the transmission of the VCG-SA as a function of the incident fluence at 700 nm. **(b)** Measured variation in the modulation depth and the saturation fluence as a function of the applied bias. (Adapted with permission from [54], (The Optical Society)).

5.2 Experimental Setup and Voltage-Dependent Continuous-Wave Operation Results

Mode locking performance of the voltage-controlled graphene-based supercapacitor saturable absorber (VCG-SA) was explored in the multipass-cavity (MPC) Cr⁴⁺:forsterite laser, which was described in detail in Chapter 4. The VCG-SA was placed inside the resonator between the two curved high reflectors as shown in Fig. 5.2.1.

Without the saturable absorber, the resonator produced 350 mW of output power at an 8 W of input power with the 2.4% output coupler. After the insertion of the VCG-SA at 0V of bias, the output power of the laser decreased to 13 mW and the threshold pump power increased from 2.7 W to 6 W. However, application of the bias voltage led to an increase in the output power and decrease in the threshold pump power due to the suppression of the absorption in the graphene electrodes.

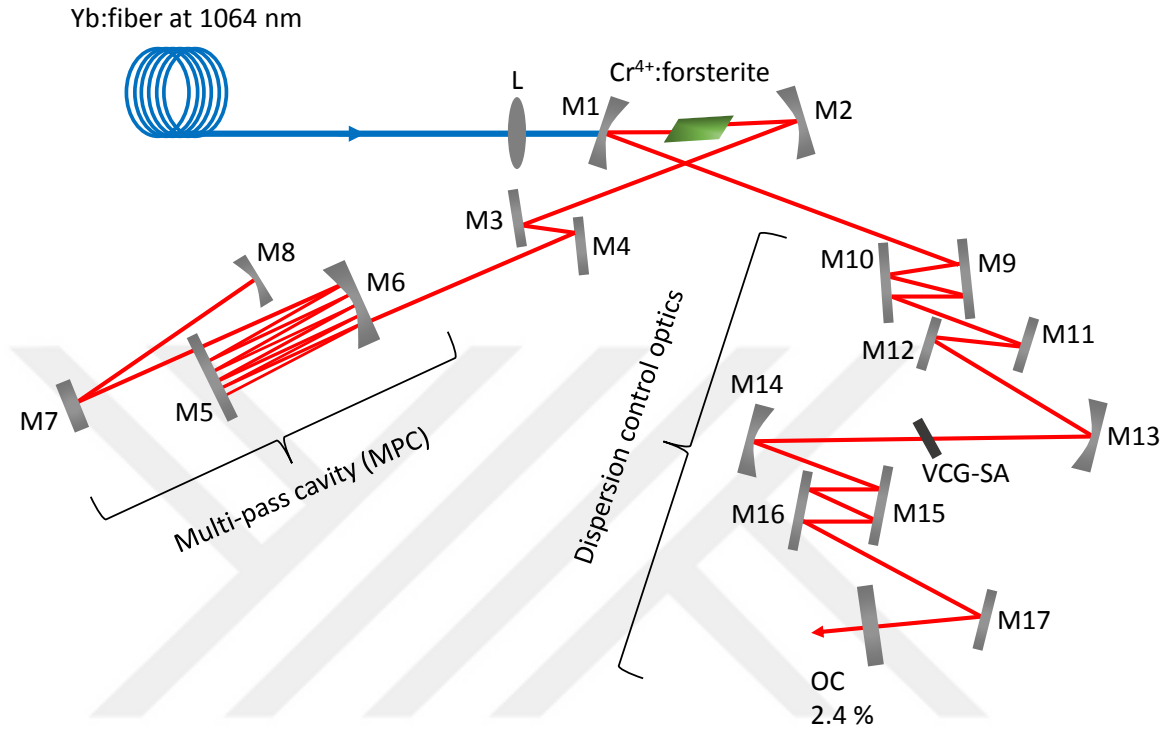


Figure 5.2.1 Experimental setup of the multipass-cavity Cr⁴⁺:forsterite laser with the voltage-controlled graphene-based saturable absorber (VCG-SA) and the 2.4% output coupler (OC).
(Adapted with permission from [54], (The Optical Society)).

Figure 5.2.2 shows the continuous-wave power performance of the MPC Cr⁴⁺:forsterite laser with and without the VCG-SA. Slope efficiency of the laser without the VCG-SA was measured to be 6.7%. Insertion of the VCG-SA at 0V of bias led to a considerable decrease in the slope efficiency and the measured efficiency was 0.5%. However, as the applied bias increased, the slope efficiency of the laser also increased up to 1.6% at 3V as expected. To further investigate the voltage-dependent output power characteristics of the laser, output power of the laser was measured with respect to the bias voltage at a fixed input pump power of 7.1 W. Since the absorption of graphene was blocked due to the Fermi level shift in graphene, output power of the laser increased from 11 to 69 mW with respect to the

applied bias as can be seen from Fig. 5.2.3 (a). Since the absorption of the graphene electrodes was blocked one by one as explained earlier in the previous section, the two-step behavior was also observed here.

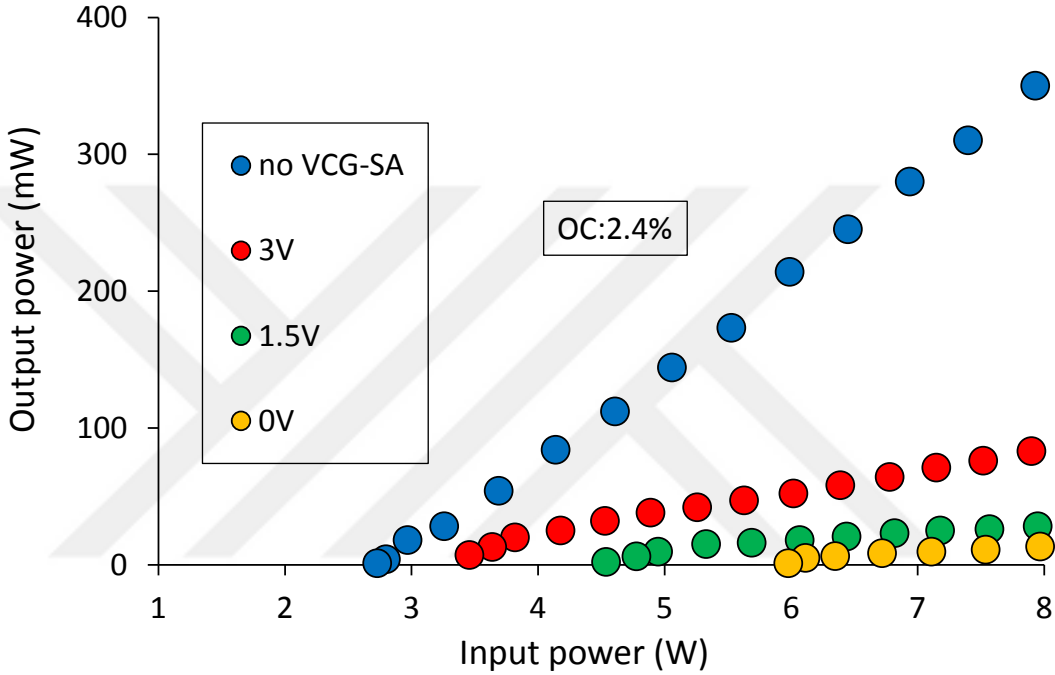


Figure 5.2.2. Power efficiency curves of the multipass-cavity Cr⁴⁺:forsterite laser with and without the voltage-controlled graphene saturable absorber (VCG-SA) by using the 2.4% output coupler. (Adapted with permission from [54], (The Optical Society)).

Based on the measured threshold pump powers and the loss analysis formula given in Chapter 3 ($(P_p)_{th} = A(L + T)$), the voltage-dependent optical insertion loss of the VCG-SA was estimated as depicted in Fig. 5.2.3 (b). Single-pass optical insertion loss of the VCG-SA could be decreased from 5.9% to 1.3% by changing the applied bias from 0V to 3V respectively. The results shown in Fig. 5.2.3 (b) clearly demonstrated that the absorption of the graphene electrodes could be dynamically controlled and the optical insertion loss of the graphene-based device could be decreased with the application of few

volts of bias. Since the graphene electrodes became completely transparent at 3V of applied bias, the remaining losses at 3V were probably due to the substrates and the electrolyte.

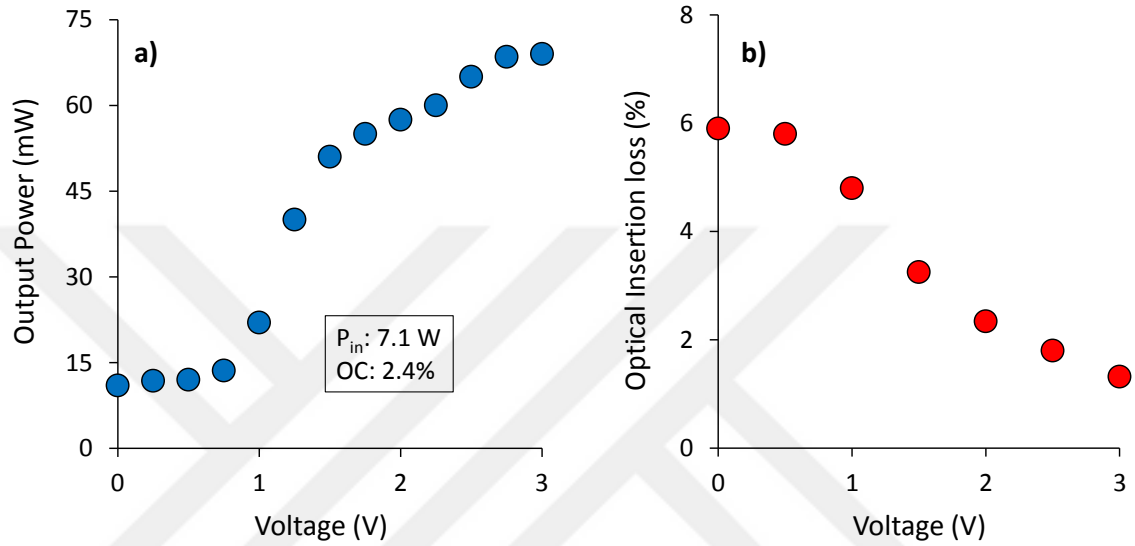


Figure 5.2.3. (a) Measured variation in the output power of the laser with the VCG-SA as a function of the applied bias at a fixed input power of 7.1 W. (b) The estimated change in the single-pass optical insertion loss of the VCG-SA as a function of the applied voltage. (Adapted with permission from [54], (The Optical Society)).

In our previous experiments, conducted with the graphene saturable absorbers [24, 40], two different output couplers (e.g. 2.4% and 4.7%) were used to characterize the performance of the laser. However, as can be seen from Fig. 5.2.4, our laser was not tolerable to optical insertion losses larger than nearly 10%. Together with the insertion loss of the VCG-SA, shown in Fig.5.2.3 (b), it was not possible to operate our laser with the output coupling levels greater than 2.4%. Hence, the continuous-wave and the mode-locked operation of the laser with the VCG-SA were explored by using only the 2.4% output coupler.

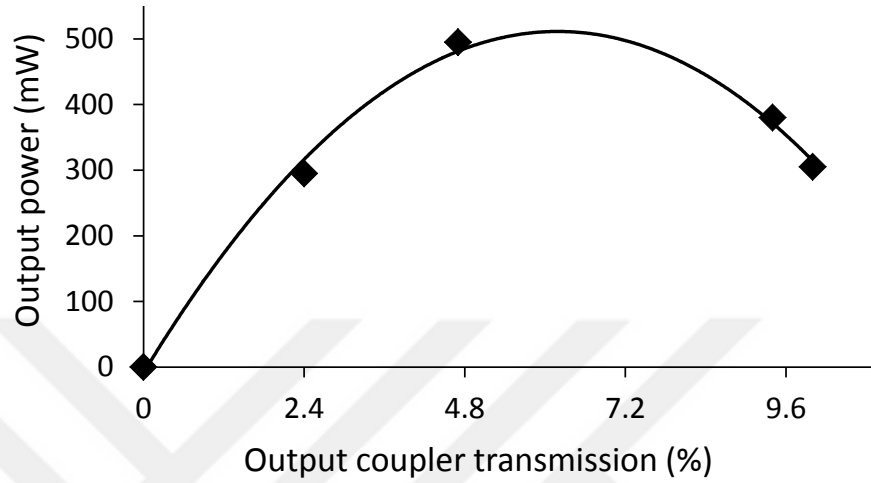


Figure 5.2.4. Measured output power of the multipass-cavity Cr⁴⁺:forsterite laser with respect to the different output coupler transmissions at a fixed input power of 7.1 W. (Adapted with permission from [24], (The Optical Society)).

5.3 Mode-Locked Operation Results

Since the same Cr⁴⁺:forsterite laser was used in the mode locking experiments, the net dispersion of the cavity, the pulse repetition rate and the estimated waist on the VCG-SA was -4440 fs², 4.51 MHz, and nearly 100 μ m respectively [54]. For bias voltages between 0.5-1V, single-pulse mode-locked operation was initiated by translating the output coupler. Since the absorption of the graphene electrodes was completely blocked due to the Pauli blocking at the photon energy of our laser wavelength (1250 nm, 1 eV), it was not possible to initiate mode-locked operation for voltages beyond 1V. For voltages smaller than 0.5V, the insertion loss of the VCG-SA caused insufficient intracavity energy levels and hence, mode-locked operation could not be observed as described in Fig.5.3.1. Figures 5.3.2 and 5.3.3 further summarize the characterization results of the VCG-SA mode-locked MPC Cr⁴⁺:forsterite laser at the applied voltages of 0.5V and 1V respectively [54].

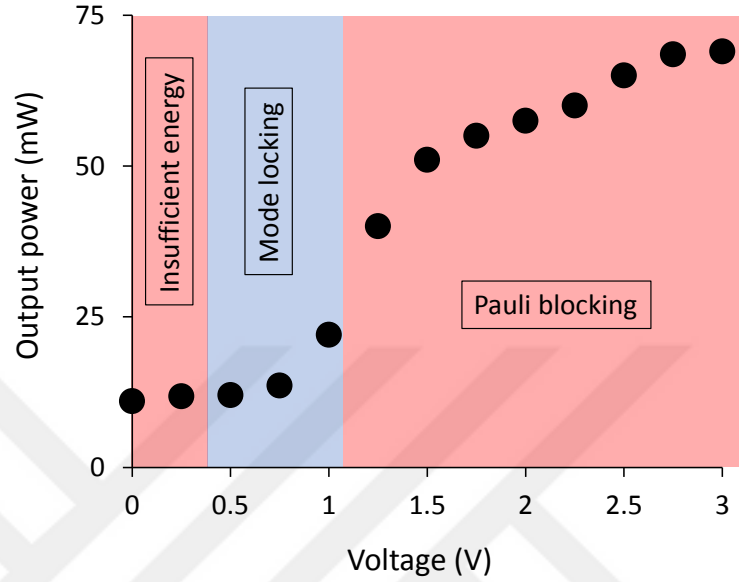


Figure 5.3.1. Mode-locked operation range (blue) of the laser as a function of the applied voltage.

The VCG-SA mode-locked laser resonator produced, nearly transform-limited 89-fs (84-fs) pulses with a time-bandwidth product of 0.35 (0.32) and a peak power of 30 kW (37 kW) at 0.5V (1V) of applied bias [54]. The RF spectra further indicated that stable mode-locked operation was achieved with the VCG-SA modulator. The mode locking results clearly shows that the VCG-SA operated as an effective fast saturable absorber and the femtosecond pulse characteristics did not depend on the applied voltage. Furthermore, at the highest single-pulse mode-locked operation output power, the incident fluence on the VCG-SA was estimated to be 364 $\mu\text{J}/\text{cm}^2$ (424 $\mu\text{J}/\text{cm}^2$) at 0.5V (1V) of applied bias and no damage was observed on the device up to this fluence level [54]. Summary of the mode locking results at 0.5V and 1V of applied bias are further shown in Table 5.3.1.

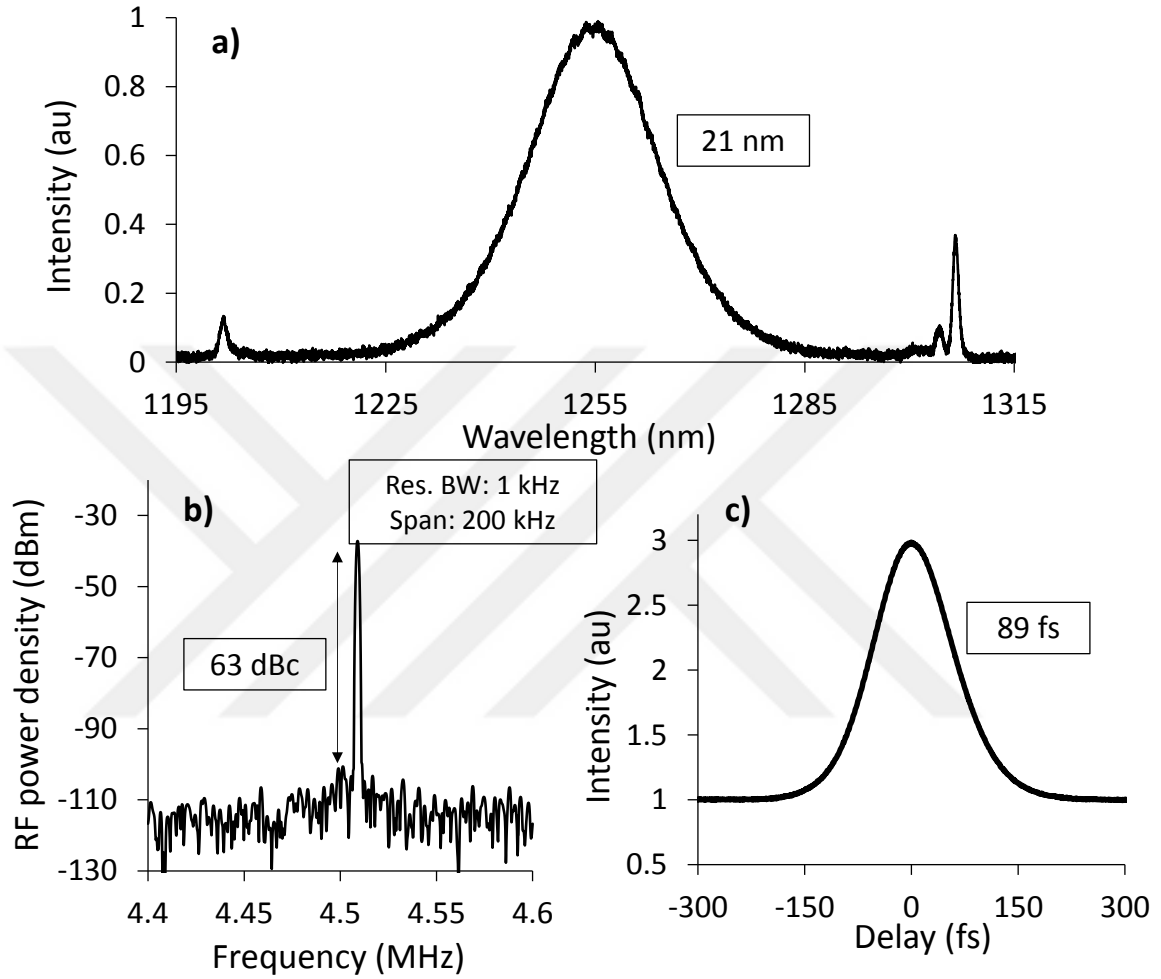


Figure 5.3.2. (a) Spectrum, (b) RF spectrum, and (c) autocorrelation trace of the VCG-SA mode-locked multipass-cavity Cr^{4+} :forsterite laser measured at 0.5V of applied bias. (Adapted with permission from [54], (The Optical Society)).

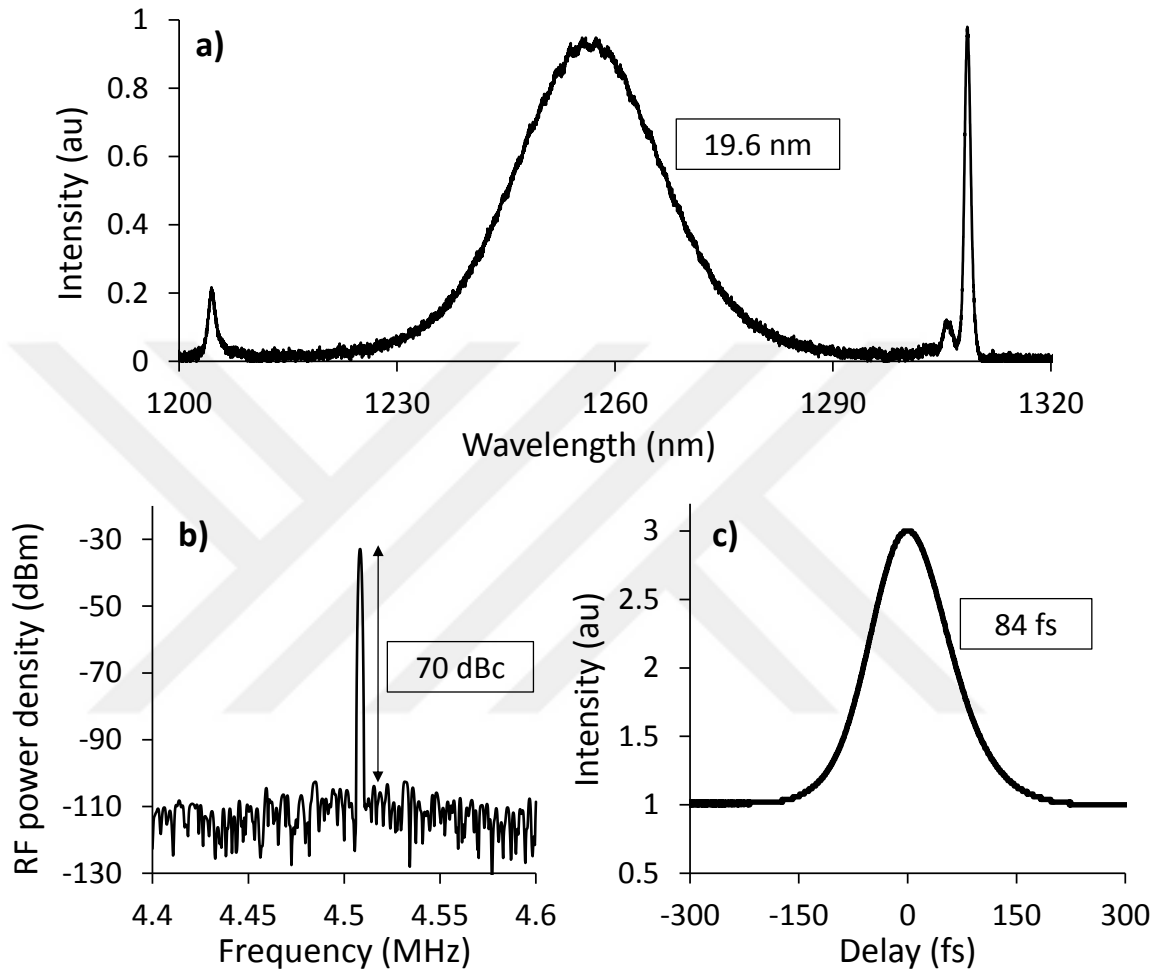


Figure 5.3.3. (a) Spectrum, (b) RF spectrum, and (c) autocorrelation trace of the VCG-SA mode-locked Cr^{4+} :forsterite laser measured at 1V of applied bias. (Adapted with permission from [54], (The Optical Society)).

Table 5.3.1. Summary of the laser parameters for the VCG-SA mode-locked multipass-cavity Cr⁴⁺:forsterite laser at 0.5V and 1V of bias.

Applied voltage (V)	Mode-locked output power (mW)	Pulse energy (nJ)	Pulse peak power (kW)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
0.5	12	2.6	30	1256	21	89	0.35
1	14	3.1	37	1255	19.6	84	0.32

In conclusion, this work was the first demonstration of a graphene-based supercapacitor saturable absorber for femtosecond pulse generation from a laser [54]. The superior supercapacitor architecture enabled the dynamic control of the absorption in graphene while maintaining a sufficient level of saturable absorption for the mode locking. Our voltage-dependent linear optical characterization results further indicated that the modulation of absorption could be achieved up to the visible wavelengths even with few volts of applied bias. The voltage-dependent nonlinear optical response of graphene was also investigated by using a femtosecond pump-probe setup. The estimated saturation fluence and the modulation depth monotonically increased and decreased respectively as a function of the applied bias. Voltage-controlled graphene-based saturable absorber mode-locked multipass-cavity Cr⁴⁺:forsterite laser produced nearly transform-limited sub-100-fs pulses and the results indicated that the femtosecond pulse characteristics were independent of the applied voltage.

CHAPTER 6

MODE-LOCKED OPERATION OF A FEMTOSECOND Cr⁴⁺:FORSTERITE LASER BY USING VOLTAGE-CONTROLLED GRAPHENE-GOLD SATURABLE ABSORBER

In Chapter 5, the graphene-based supercapacitor architecture with two graphene electrodes, which was used to generate sub-100-fs pulses from the multipass-cavity Cr⁴⁺:forsterite laser operating near 1250 nm, was described. In Chapter 6, a second more versatile graphene-based supercapacitor device, comprising the same electrolyte (Diethymethyl (2-methoxyethyl) ammonium bis (trifluoro- methylsulfony) imide [DEME][TFSI], $\epsilon_r = 14$) sandwiched between a graphene and a notched gold electrode, will be presented. The superior architecture of the voltage-controlled graphene-gold-based saturable absorber (VCG-gold-SA) consists of only one graphene electrode and eliminates the additional insertion losses due to the second graphene electrode. The VCG-gold-SA was used to generate sub-100-fs pulses from the same multipass-cavity Cr⁴⁺:forsterite laser and to the best of our knowledge, it was the first demonstration of a graphene-gold based supercapacitor mode-locked femtosecond laser [55]. With the VCG-gold-SA, the modulation of absorption in the graphene electrode could be achieved again at low operating voltages, which were in the range of 0-2V. In Chapter 6, the voltage-dependent linear optical characterization of the VCG-gold-SA will be presented and then, its voltage-dependent continuous-wave and mode-locked operation performance in a solid-state laser will be described.

6.1 Fabrication and Optical Characterization of Voltage-Controlled Graphene-Gold Saturable Absorber

Voltage-controlled graphene-gold supercapacitor saturable absorber (VCG-gold-SA) was fabricated by C. Kocabas's group at Bilkent University. The graphene electrode of the VCG-gold-SA was synthesized by using chemical vapor deposition (CVD) technique as described in Chapter 4 and 5, and transfer-printed onto a 1-mm thick infrasil substrate. The second electrode was a gold coated infrasil substrate with a 5mm notch to allow the transit of the beam. The gold electrode was fabricated with thermal evaporation method [55]. The 5-mm notch on the gold electrode was patterned with shadow evaporation technique by using a 5-mm Ti adhesive layer under the gold layer [55]. Figure 6.1.1 shows, photograph (a) and schematic drawing (b) of the VCG-gold-SA.

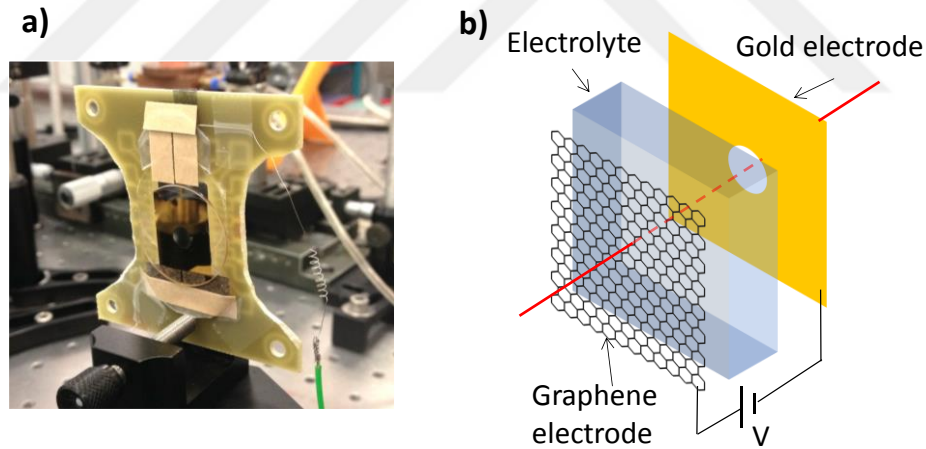


Figure 6.1.1. (a) Photograph of the voltage-controlled graphene-gold saturable absorber. **(b)** Schematic of the supercapacitor architecture comprising an electrolyte sandwiched between the graphene and the gold electrode. (Adapted with permission from [55], (The Optical Society)).

The voltage-dependent optical response of the VCG-gold-SA was measured by using a spectrophotometer. As can be seen from Fig. 6.1.2, by applying few volts only (0-2V), transmission of the device could be increased up to a wavelength as short as 600 nm.

Figure 6.1.3 (a) demonstrates that the measured fractional change in the optical transmission of the VCG-gold-SA as a function of bias voltage for three selected wavelengths and for the operation wavelength of the Cr⁴⁺:forsterite laser (Fig.6.1.3 (b)). As expected, when the wavelength decreases, the photon energy increases and a larger bias voltage is required to cause the same amount of fractional transmission change due to Pauli blocking. Furthermore, at the operation wavelength of our laser, a maximum fractional change of 1% could be obtained.

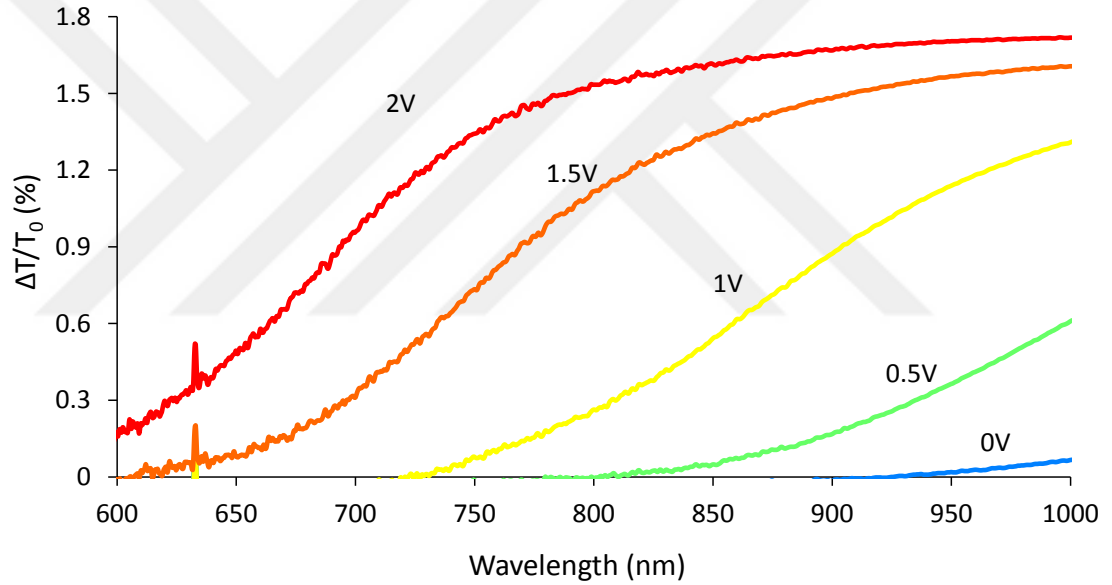


Figure 6.1.2. Measured fractional change in the transmission of the voltage-controlled graphene-gold saturable absorber as a function of the wavelength at different applied voltages. (Adapted with permission from [55], (The Optical Society)).

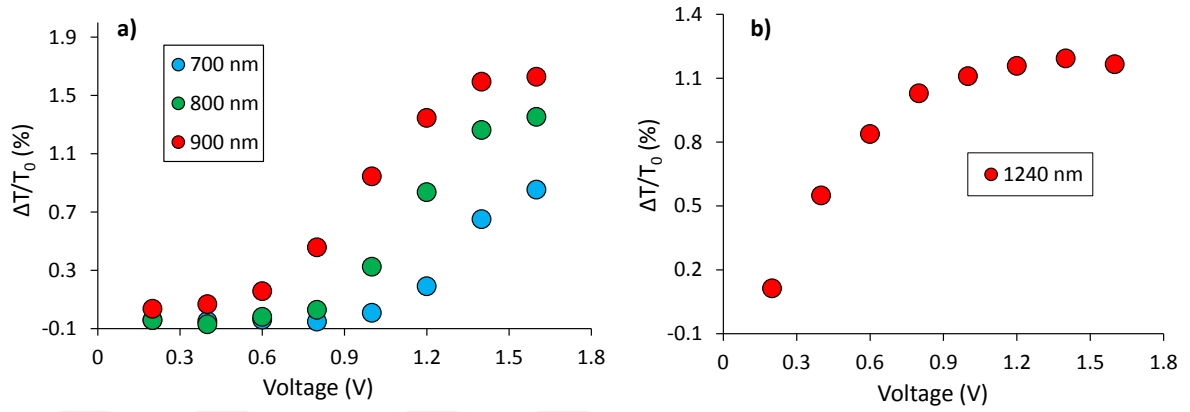


Figure 6.1.3. (a) Measured variation of the fractional change in the transmission spectrum of the VCG-gold-SA as a function of the voltage at three selected wavelengths and (b) near the operation wavelength of our laser. (Adapted with permission from [55], (The Optical Society)).

Figure 6.1.4 further delineates that the Fermi level shift scales linearly with the applied bias and for photon energies smaller than twice the Fermi level shift, the VCG-gold-SA becomes transparent due to the Pauli blocking.

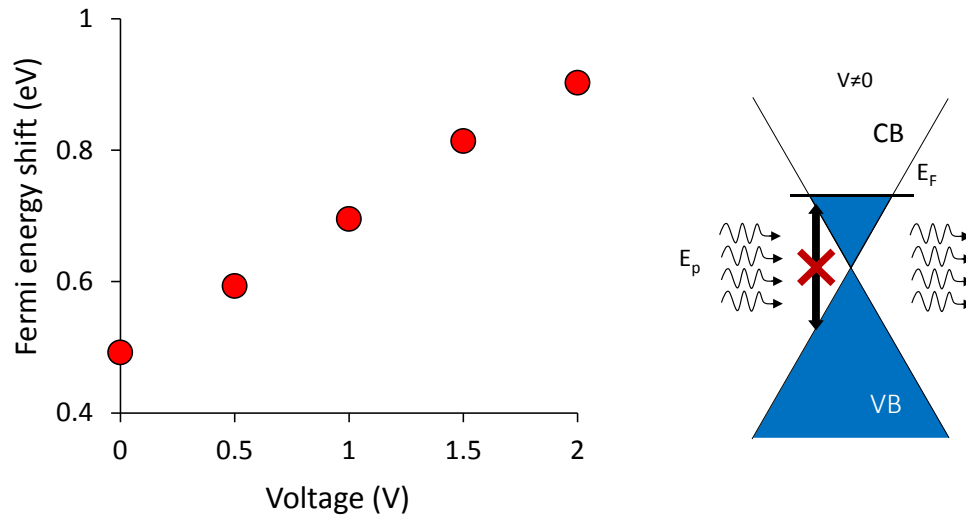


Figure 6.1.4. Estimated Fermi level shift of the VCG-gold-SA as a function of bias voltage. (Adapted with permission from [55], (The Optical Society)).

6.2 Voltage-Dependent Continuous-Wave Operation Results

To test the mode locking performance of the voltage-controlled graphene-gold-based supercapacitor saturable absorber (VCG-gold-SA), the multipass-cavity Cr⁴⁺:forsterite laser, which was described in detail in Chapter 4 and 5, was used. The VCG-gold-SA was also placed between the two curved high reflector mirrors as described in Chapter 4 and 5. The continuous-wave operation performance of the multipass-cavity Cr⁴⁺:forsterite without the VCG-gold-SA was same with the previous chapter. As expected, insertion of the VCG-gold-SA to the resonator reduced the output power of the laser from 350 mW to nearly 16 mW [55]. However, as depicted in Fig. 6.2.1 (a), application of the bias voltage reduced the loss of the device and hence, the output power of the laser increased up to 54 mW at 2V of bias. The optical insertion loss analysis was also done for the VCG-gold-SA by using the measured threshold pump power data at different bias voltages. As shown in Fig.6.2.1 (b), the optical insertion loss of the VCG-gold-SA decreased from 4.3% (0V) to 2% (2V) by increasing the applied bias [55]. Figure 6.2.1 (b) also compares the single-pass optical insertion losses for the VCG-SA and the VCG-gold-SA. The advantage of the VCG-gold-SA can be seen clearly from this comparison. Since approximately 1V is needed per graphene electrode to block the absorption near 1250 nm, the VCG-gold-SA reached lower loss levels at low operating voltages in relation to the supercapacitor architecture, which involved two graphene electrodes [54]. In Fig. 6.2.1 (b), the remaining losses of the VCG-gold-SA at the applied voltage of 2V were higher than the previous design. This was mainly due to the use of different substrates (e.g. infrasil and quartz) with lower optical quality. Furthermore, since the operation of the supercapacitor was based on the ionic gating, the electric field was created within the ultrathin electrical double layers (EDLs) as described before and hence, the area of transit for the beam was neutral and the notched structure did not affect the electric field formation across the EDLs.

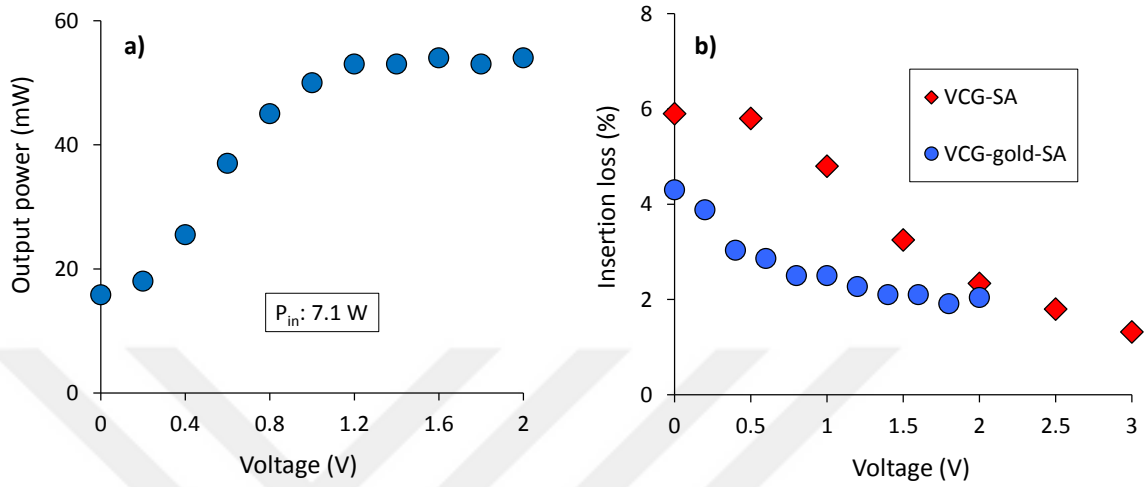


Figure 6.2.1. (a) Measured variation in the output power at a fixed input power of 7.1 W as a function of the applied voltage. **(b)** Estimated voltage-dependent optical insertion losses of the VCG-SA and the VCG-gold-SA. (Adapted with permission from [55], (The Optical Society)).

6.3 Mode-Locked Operation Results

The operation parameters of the multipass-cavity Cr⁴⁺:forsterite laser were similar to the previous chapter. The net dispersion of the resonator with the VCG-gold-SA, the estimated waist on the modulator, and the pulse repetition rate was -4432 fs², 115 μm, and 4.51 MHz respectively [55]. Since the 0V insertion loss of the VCG-gold-SA was still high, the mode-locked operation was conducted with the 2.4% output coupler. However, due to the increase in the intracavity energy, mode-locked operation could be initiated for bias voltages smaller than 0.5V as opposed to the VCG-SA mode-locked laser. Furthermore, the input threshold pump power required to initiate the mode-locked operation could be decreased from 7.15 W (0V) to 5.14 W (0.8V) by increasing applied bias as shown in Fig.6.3.1. Since the threshold pump power required to initiate mode locking depends on the insertion loss of the VCG-gold-SA, it followed a similar trend with the estimated insertion loss curve and varied more strongly with applied bias in the 0-0.4V range [55]. For bias

voltages between 0-0.8V, single-pulse mode-locked operation could be initiated by translating the output coupler [55]. Since the use of a gold electrode also included an additional Fermi level shift of 0.2V due to the unintentional doping, absorption of the graphene electrode was completely blocked at 0.8V of applied bias due to the Pauli blocking for the 1250 nm (photon energy of nearly 1 eV) as opposed to the VCG-SA, which was blocked at 1V. Hence, for voltages larger than 0.8V, it was not possible to initiate VCG-gold-SA mode-locked operation for the wavelength of our laser due to the insufficient amount of saturable absorption [55].

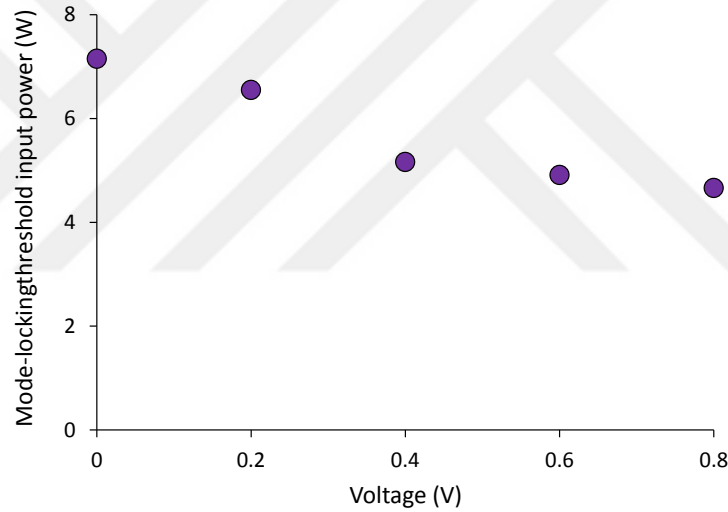


Figure 6.3.1. Measured threshold pump power to initiate VCG-gold-SA mode-locked operation.
(Adapted with permission from [55], (The Optical Society)).

The VCG-gold-SA mode-locked multipass-cavity (MPC) Cr⁴⁺:forsterite laser produced 89-fs (90-fs and 80-fs) nearly transform-limited pulses with a time-bandwidth product of 0.35 (0.35 and 0.33) at the applied bias of 0.4V (0.6V and 0.8V) near 1240 nm. The corresponding pulse peak power was 32 kW (34 kW and 42 kW) for 0.4V (0.6V and 0.8V) [55]. Similar to the mode-locked spectra shown in Chapter 4 and 5, Kelly sidebands were also observed in the VCG-gold-SA mode-locked spectra. Figures 6.3.2, 6.3.3, and 6.3.4

summarize, the mode-locked spectra and the autocorrelation traces of the femtosecond pulses, which were generated from the VCG-gold-SA mode-locked MPC Cr⁴⁺:forsterite laser at three different bias voltages. Figure 6.3.5 further shows, the RF spectra of the generated pulses, which indicated that the stability of the mode-locked operation was voltage-independent and the laser was operated without pulsing instabilities.

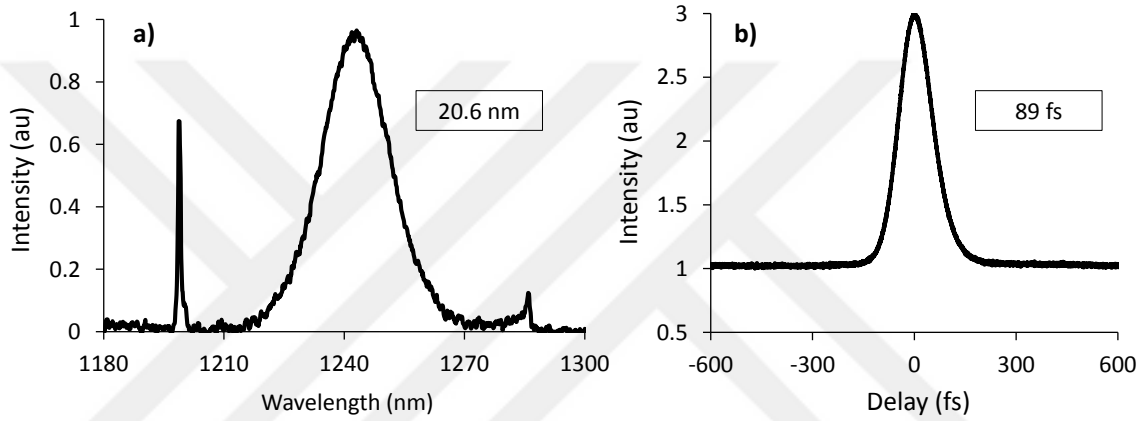


Figure 6.3.2. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.4V of applied bias. (Adapted with permission from [55], (The Optical Society)).

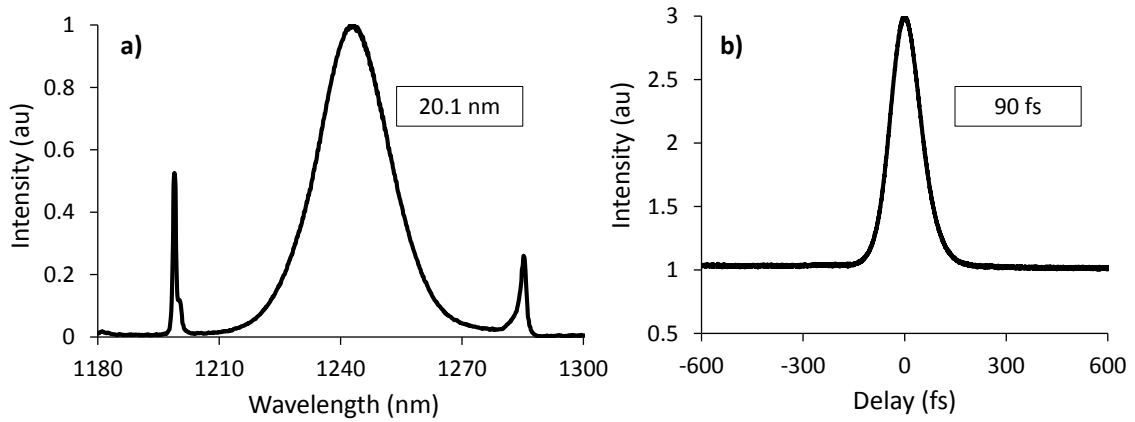


Figure 6.3.3. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.6V of applied bias.

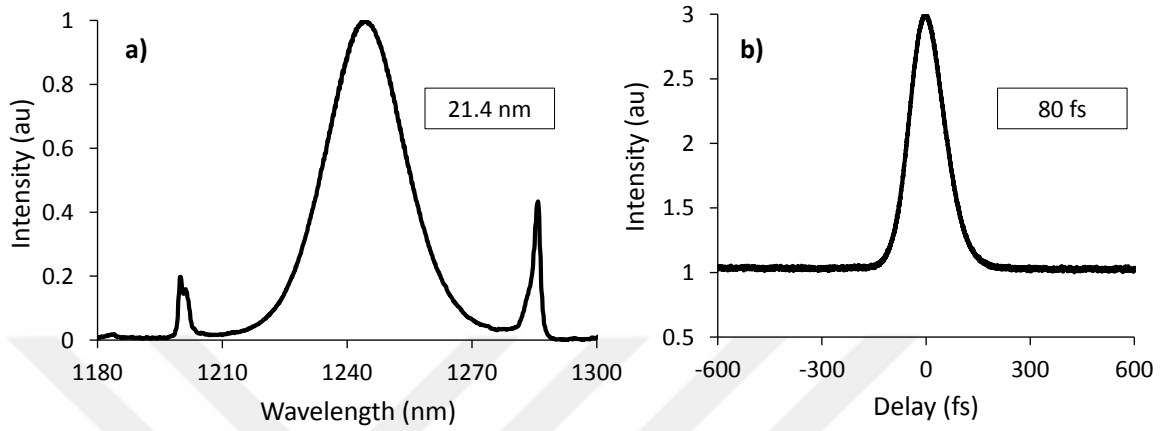


Figure 6.3.4. (a) Mode-locked spectrum and (b) autocorrelation trace of the VCG-gold-SA mode-locked laser at the 0.8V of applied bias. (Adapted with permission from [55], (The Optical Society)).

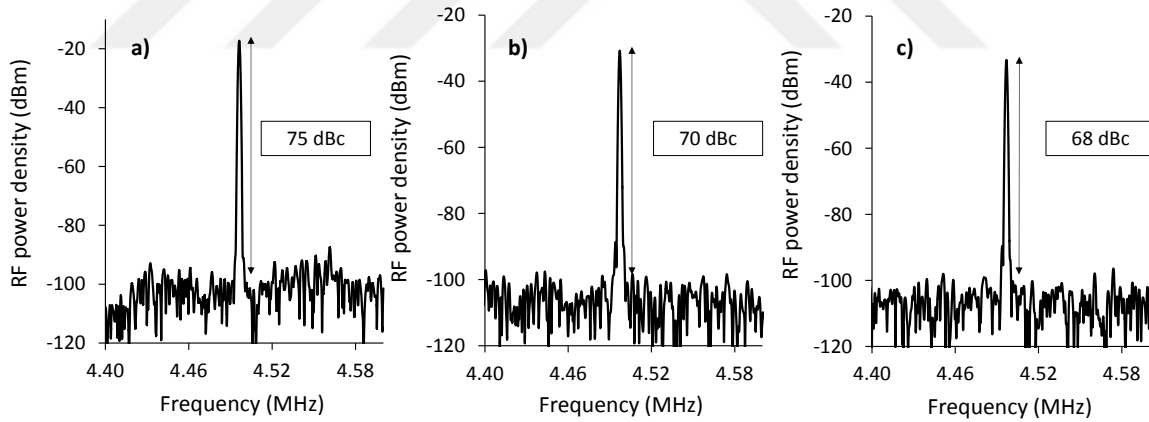


Figure 6.3.5. (a) Measured RF spectra of the VCG-gold-SA mode-locked laser at 0.4V, (b) at 0.6V, and (c) at 0.8V of applied bias. During the measurements, the resolution bandwidth and the span were 1 kHz and 200 kHz respectively. (Adapted with permission from [55], (The Optical Society)).

Table 6.3.1 gives summary of the mode locking results obtained at different bias voltages. The results demonstrate that the applied voltage had no effect on the pulse characteristics

and the VCG-gold-SA was operated as an effective fast saturable absorber, which initiated the mode-locked operation. Hence, the pulse characteristics depended only on the cavity nonlinearities. In addition, at the highest single-pulse mode-locked operation voltage of 0.8V, the incident fluence on the VCG-SA was estimated to be 335 $\mu\text{J}/\text{cm}^2$ and no damage was observed on the device up to this fluence level.

Table 6.3.1. Summary of the femtosecond laser parameters for the VCG-gold-SA mode-locked MPC Cr⁴⁺:forsterite laser at 0.4V, 0.6V, and 0.8V of bias.

Applied voltage (V)	Mode-locked output power (mW)	Pulse energy (nJ)	Pulse peak power (kW)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
0.4	13	2.88	32	1242	20.6	89	0.35
0.6	14	3.1	34	1243	20.1	90	0.35
0.8	15	3.3	42	1242	21.4	80	0.33

In conclusion, the first operation of a graphene-gold-based supercapacitor saturable absorber was demonstrated to generate sub-100-fs pulse near 1240 nm [55]. In the previous study, presented in Chapter 5, it was not possible to initiate mode-locked operation for bias voltages smaller than 0.5V. However, the superior architecture of the graphene-gold supercapacitor enabled the operation of the voltage-controlled saturable absorber to generate femtosecond pulses even at lower applied voltages in the range of 0-0.8V. Similar to the previous work, the voltage-dependent linear transmission of the device was measured and nearly 1% modulation of absorption was obtained at the operation wavelength of our laser. Voltage-controlled graphene-gold-based saturable absorber mode-locked multipass-cavity Cr⁴⁺:forsterite laser produced nearly transform-limited sub-100-fs pulses and the pulse characteristics were voltage independent.

CHAPTER 7

MODE-LOCKED OPERATION OF A FEMTOSECOND Ti^{3+} :SAPPHIRE LASER BY USING VOLTAGE-CONTROLLED GRAPHENE-GOLD SATURABLE ABSORBER

In our experiments, presented in Chapter 5 and 6, novel graphene-based supercapacitor architectures were demonstrated to initiate mode-locked operation of a multipass-cavity Cr^{4+} :forsterite laser operating near 1250 nm [54, 55]. Our preliminary design (voltage-controlled graphene saturable absorber, VCG-SA), presented in Chapter 5, involved a high dielectric electrolyte sandwiched between the two graphene electrodes. The supercapacitor architecture enabled the control of absorption in the graphene electrodes up to the visible region even with low operating voltages (0-3V) [54]. To further reduce the insertion loss of the VCG-SA at the zero bias, a second more versatile supercapacitor architecture involving the same electrolyte sandwiched between the graphene and the notched gold electrode (voltage-controlled graphene-gold saturable absorber, VCG-gold-SA) was utilized as a modulator to generate femtosecond pulses again near 1250 nm and results are summarized in Chapter 6 [55]. With regard to the graphene-based supercapacitor saturable absorbers, the next challenge involves pushing the modulation capability of such graphene-based supercapacitors to as low a wavelength as possible at low operating voltages. Hence, to achieve this aim, a Ti^{3+} :sapphire laser operating near 800 nm was used to test the mode locking performance of the voltage-controlled graphene-gold based saturable absorber (VCG-gold-SA). In Chapter 7, experimental setup of the Ti^{3+} :sapphire laser will be described and voltage-dependent continuous-wave and mode-locked operation results will be presented.

In order to balance the cavity nonlinearities, two different dispersion control schemes were used during the experiments. In the first part of Chapter 7, the voltage-dependent

continuous-wave and mode-locked results obtained from the first configuration consisted of only the dispersion control mirrors (DCMs) will be given. In the remaining sections of Chapter 7, the second configuration consisted of a pair of prism will be presented. Since the same VCG-gold-SA was used during the experiments, the fabrication steps and the voltage-dependent optical characterization results will not be discussed again here and they can be found in Chapter 6.

7.1 Voltage-Dependent Continuous-Wave Operation Results Obtained with Dispersion Control Mirrors

Figure 7.1.1 shows the sketch of the x-cavity Ti³⁺:sapphire laser, which consisted of only the dispersion control mirrors (DCMs) to balance the nonlinearities inside the cavity. As can be seen from the sketch, a Brewster-cut 2.3-mm-long Ti³⁺:sapphire crystal, which had a pump absorption of 74% at 532 nm, was positioned between the two curved high reflector DCMs (M1 and M2), each with a radius of curvature of 50 mm and a group delay dispersion (GDD) of nearly -50 fs². Furthermore, a focusing lens (L) with a focal length of 50 mm was used to focus the pump beam inside the crystal to an estimated waist of 17 μm. The Ti³⁺:sapphire resonator further contained four flat dispersion control mirrors (M3, M4, M5 and M6) each with a nearly -50 fs² group delay dispersion and a flat 3% output coupler (OC). To increase the negative GDD inside the resonator, the laser beam was reflected two times from the flat DCMs, M3 and M4. During the experiments, the Ti³⁺:sapphire crystal was held inside a copper holder and kept at a constant temperature of 20 °C by water cooling. As can be seen from Fig. 7.1.1, a second pair of curved high reflectors (M7 and M8), each with a radius of curvature of 150 mm, was used to obtain a sufficient incident fluence on the saturable absorber and the VCG-gold-SA was positioned between these mirrors. With this configuration, the waist on the VCG-gold-SA was estimated to be approximately 70 μm.

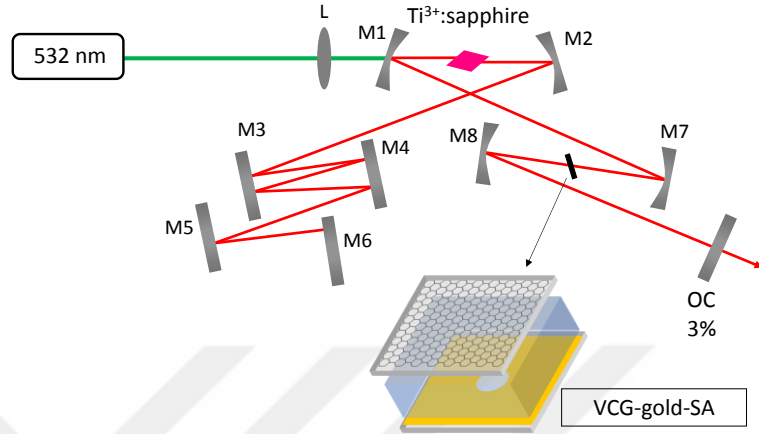


Figure 7.1.1. Sketch of the Ti^{3+} :sapphire laser consisted of only the dispersion control mirrors and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA).

The continuous-wave operation of the laser for this configuration was characterized with and without the VCG-gold-SA. As depicted in Fig.7.1.2, empty cavity Ti^{3+} :sapphire laser operating with 3% output coupler (i.e. without the DCMs and the VCG-gold-SA) produced an output power of 380 mW for 1.6 W of input power. The efficiency of the free-running resonator was around 26%. After introducing the DCMs, the output power and the laser efficiency decreased to 330 mW and 23.5% respectively. Figure 7.1.2 further shows that the insertion of the VCG-gold-SA at zero bias led to a decrease in the output power (58 mW) and the slope efficiency (5.6%) of the laser. However, by increasing the applied bias, output power of the laser increased from 58 mW to 110 mW at 2V as shown in Fig. 7.1.3 (a). Based on the measured threshold pump powers at different bias voltages and by using the loss analysis formula, introduced in Chapter 3, the optical insertion loss of the VCG-gold-SA was estimated at the laser operation wavelength of 800 nm. Figure 7.1.3 (b) demonstrates that the insertion loss of the VCG-gold-SA could be decreased from 4.2% to 1.32% by varying the applied bias from 0V to 2V. Figures 7.1.2 and 7.1.3 clearly shows that the absorption of the graphene electrode could be controlled via Pauli blocking by applying low bias voltages (0-2V) even at a wavelength as low as 800 nm.

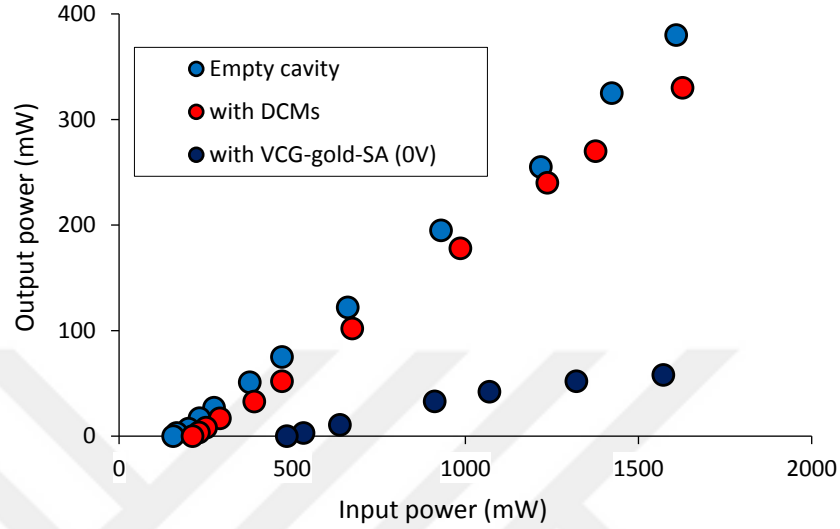


Figure 7.1.2. Power efficiency curves for the Ti^{3+} :sapphire laser with and without the dispersion control mirrors (DCMs) and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) at zero bias.

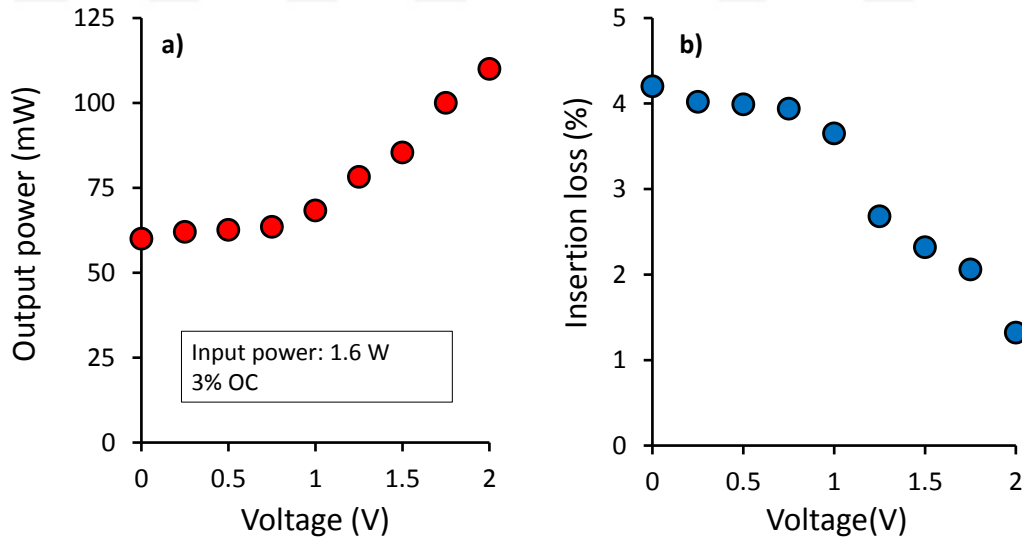


Figure 7.1.3. (a) Measured variation in the output power of the Ti^{3+} :sapphire laser as a function of the applied voltage at a fixed input power of 1.6 W. **(b)** Estimated single-pass insertion loss of the VCG-gold-SA as a function of the applied bias.

7.2 Mode-Locked Operation Results Obtained with Dispersion Control Mirrors

Mode-locked operation could be achieved for voltages in the range of 0-1.6V. For voltages greater than 1.6V, the saturable absorption in the graphene electrode was blocked at the wavelength of 800 nm (photon energy of nearly 1.55 eV) due to Pauli blocking. Figure 7.2.1 shows the representative mode-locked spectra, autocorrelation traces, and RF spectra measured at different bias voltages respectively. As can be seen from Fig. 7.2.1 (a), the shortest wavelength, where we could obtain mode-locked operation was as short as 795 nm [56]. Furthermore, as the applied bias increased, the pulse width decreased from 203 fs (0V) to 106 fs (1.6V) indicating that we could decrease the optical insertion loss and increase the intracavity energy (Figure 7.2.1 (b)). Together with the dispersion control mirrors and the second x-cavity extensions, the total round-trip optical path length of the resonator gave nearly 117.7 MHz pulse repetition rate and voltage-independent stable mode locking could be obtained at all bias voltages as shown in Fig.7.2.1 (c). Figure 7.2.1 and 7.2.2 further delineate that for voltages less than 1.2V, the measured spectral widths were in the range of 3-5 nm and the corresponding time-bandwidth products were nearly transform-limited. However, higher applied voltages resulted in higher intracavity energies and hence, the generated pulses became chirped with time-bandwidth products approaching to 0.6. By taking into account the positive dispersion due to the intracavity elements such as the Ti^{3+} :sapphire crystal, air, and the VCG-gold-SA and the negative group delay dispersion (GDD) due to the DCMs, the net GDD of the resonator for this configuration was estimated to be -248 fs^2 . Since, the net dispersion of the resonator was fixed and the DCMs introduced unbalanced GDD to the cavity (see Figure 7.3.1), the generated pulses became chirped as shown in Figs. 7.2.1 (a) and 7.2.2.

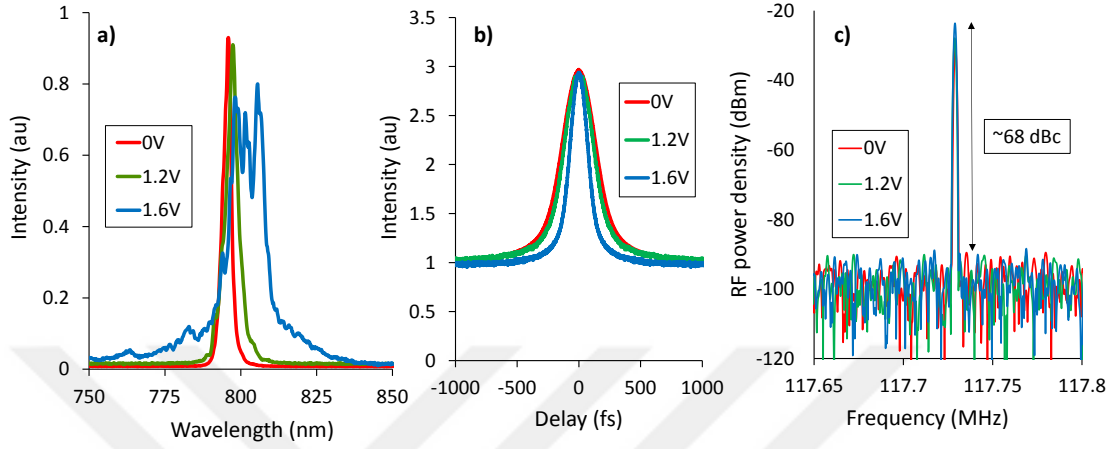


Figure 7.2.1. (a) Measured mode-locked spectra, (b) autocorrelation traces, and (c) RF spectra (1 kHz resolution bandwidth) of the generated pulses at three different voltages.

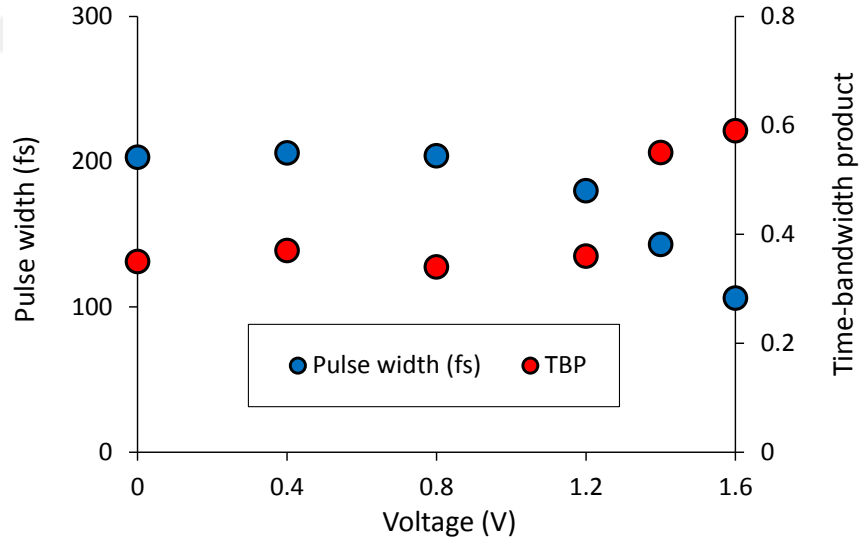


Figure 7.2.2. Variation in the measured pulse widths and the corresponding time-bandwidth products (TBP) as a function of the applied voltage for the resonator, which consisted of only the dispersion control mirrors.

Table 7.2.1 summarizes the results obtained from the VCG-gold-SA mode-locked Ti^{3+} :sapphire laser, which consisted of only the DCMs to balance the nonlinearities inside the resonator. As can be seen, femtosecond pulse characteristics, such as spectral width, pulse duration, time-bandwidth product, and pulse energy were voltage-dependent and hence, they can be controlled by changing the applied voltage. Furthermore, for this configuration, the estimated waist on the VCG-gold-SA was around 70 μm , which corresponded to an incident fluence of nearly 60 $\mu\text{J}/\text{cm}^2$ at the highest single pulse mode-locked operation voltage of 1.6V, and no damage were observed on the device for this fluence level.

Table 7.2.1. Mode-locking results obtained from the VCG-gold-SA mode-locked Ti^{3+} :sapphire laser. For this case, the resonator consisted of only the dispersion control mirrors.

Applied voltage (V)	Mode-locked output power (mW)	Pulse energy (nJ)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
0	15	0.13	795	3.5	203	0.35
0.4	15	0.13	795	4	206	0.37
0.8	16.5	0.14	797	3.3	204	0.34
1.2	17.6	0.15	797	4.3	180	0.36
1.4	23.5	0.2	801	8.5	143	0.55
1.6	30	0.25	802	12	106	0.59

As can be seen from Table 7.2.1, for the applied voltages up to 1.2V, the pulse characteristics were nearly the same with each other and it followed a similar trend with the estimated insertion loss of the VCG-gold-SA shown in Fig. 7.1.3 (b). However, for greater bias voltages, the insertion loss of the graphene electrode started to decrease due to Pauli blocking near 800 nm and hence, more dramatic changes were observed in the pulse characteristics.

7.3 Voltage-Dependent Continuous-Wave Operation Results Obtained with a Prism Pair

To provide adjustable dispersion at each applied voltage and to eliminate unbalanced group delay dispersion (GDD) oscillations introduced by the dispersion control mirrors (DCMs), three of the DCMs were replaced with an SF-14 prism pair. As can be seen from Fig. 7.3.1, SF-14 prism pair provides more smooth dispersion profile. Furthermore, its dispersion can be adjusted by changing the tip-to-tip separation of the prisms and by aligning its insertion amount as discussed in Chapter 2.

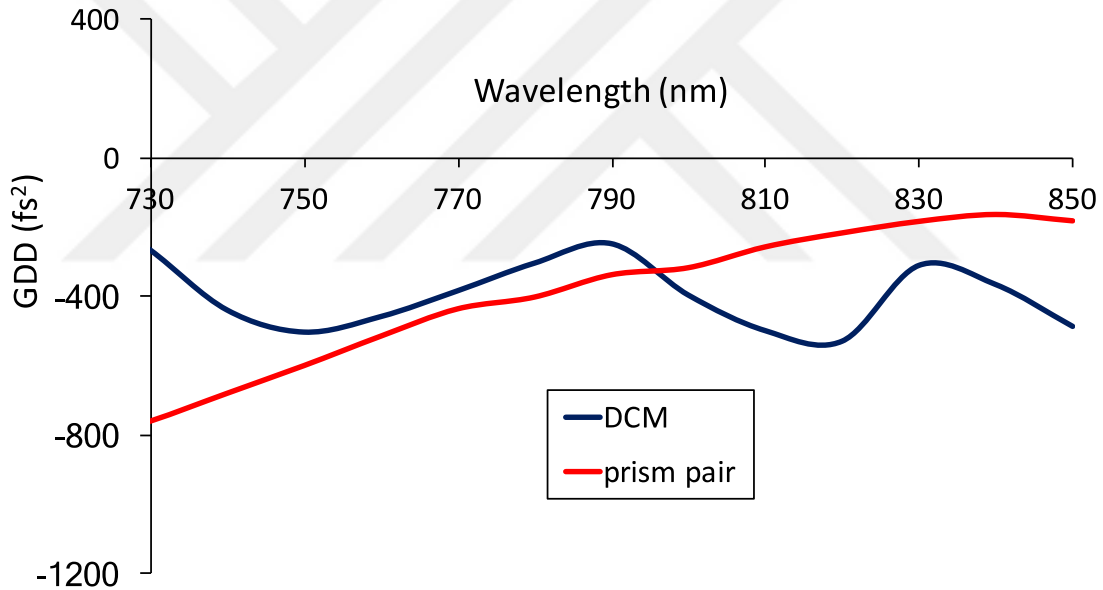


Figure 7.3.1. Estimated negative group delay dispersion (GDD) introduced by the dispersion control mirrors (DCMs) and an SF-14 prism pair with 13 cm tip-to-tip separation.

Figure 7.3.2 shows, sketch of the Ti^{3+} :sapphire laser with the VCG-gold-SA and the SF-14 prism pair (P1 and P2). In this configuration, the resonator consisted of the SF-14 prism pair (P1 and P2), which was placed at the Brewster's incidence to minimize the insertion

losses, the VCG-gold-SA, a flat high reflector (M3) with -50 fs^2 GDD, and the 3% output coupler. The curved and flat high reflectors (M1, M2, M3, M4 and M5) and the output coupler were the same with the previous configuration.

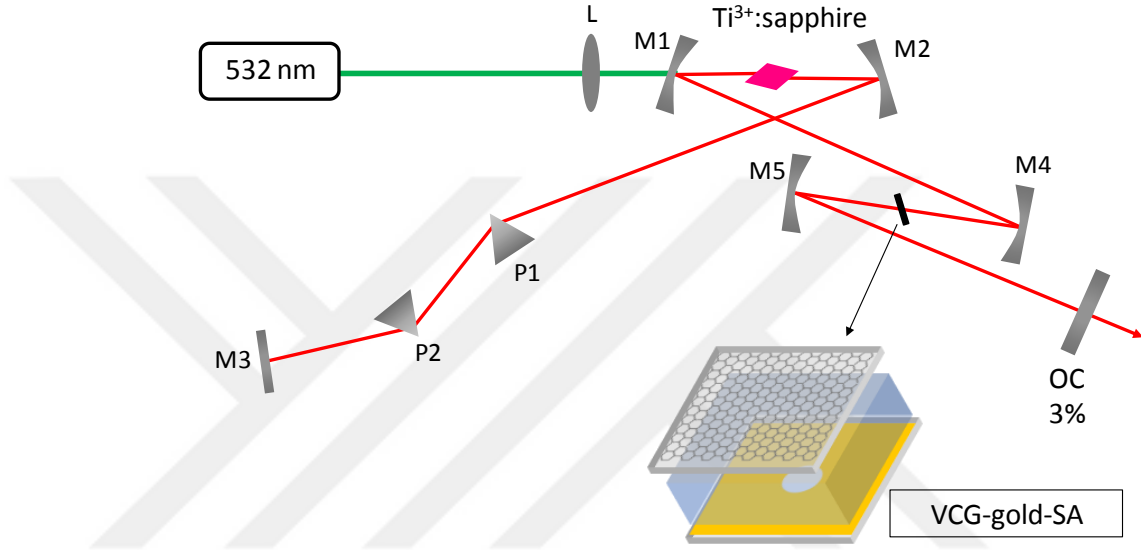


Figure 7.3.2. Sketch of the Ti^{3+} :sapphire laser resonator consisted of the prism pair and the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA). (Adapted with permission from [56], (The Optical Society)).

With this configuration, a similar continuous-wave power performance was obtained from the Ti^{3+} :sapphire laser. After the insertion of the SF-14 prism pair and the VCG-gold-SA at the zero bias, power efficiency of the laser reduced from 26% to 18.5% and to 6.4% respectively. Figure 7.3.3 gives the power efficiency curves for the empty resonator, with the prism pair, and for the composite cavity.

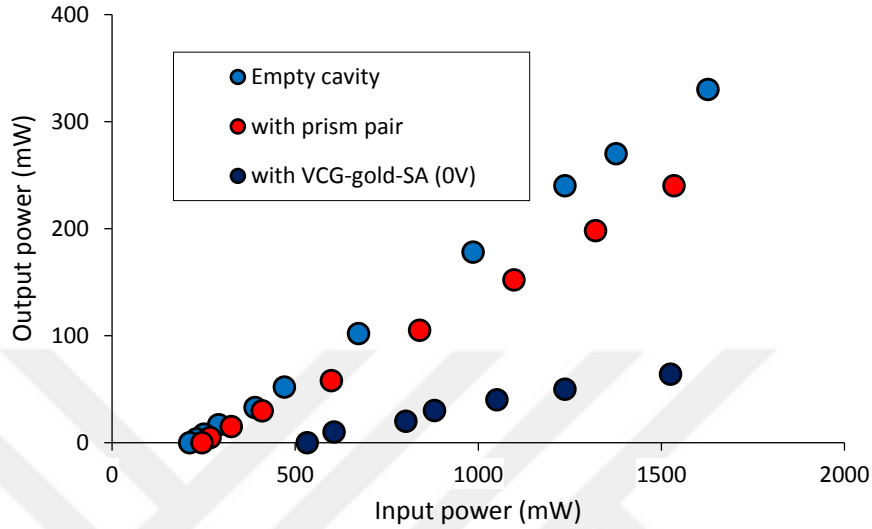


Figure 7.3.3. Power efficiency curves for the empty cavity Ti^{3+} :sapphire laser, with the SF-14 prism pair, and with the voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) at the zero bias.

Introducing the VCG-gold-SA to the resonator at the zero-bias led to a decrease in the output power of the laser from 240 mW to 58 mW as expected. However, as the bias voltage increased from 0V to 2V, the optical insertion loss of the VCG-gold-SA decreased and hence, output power of the laser increased from 58 mW to 113 mW due to Pauli blocking. Figure 7.3.4 demonstrates a similar voltage-dependent improvement in the output power of the laser and an expected decrease in the optical insertion loss, which was estimated from the measured threshold pump powers at different bias voltages. Since the application of the voltage bias creates the high electric field within the ultrathin electrical double layers, which are formed on the both electrodes, architecture of the supercapacitor did not affect the electric field formation. Hence, the 5-mm notch or the thickness of the electrolyte did not have an influence on the operation performance of the VCG-gold-SA. To test this, the output power of the laser was measured by translating the VCG-gold-SA across the notch at a fixed voltage of 1.5V and at a fixed input power of 1.6 W. As shown

in Fig. 7.3.5, the response of the device was nearly the same across the notch, except near the edges.

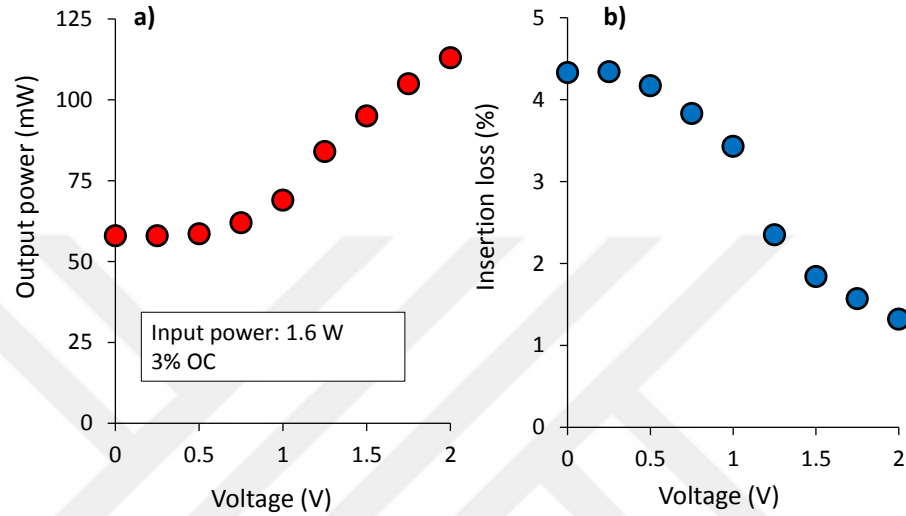


Figure 7.3.4. (a) Voltage-dependent output power of the Ti^{3+} :sapphire laser with the SF-14 prism pair. **(b)** Estimated insertion loss of the voltage-controlled graphene-gold saturable absorber as a function of the applied voltage. (Adapted with permission from [56], (The Optical Society)).

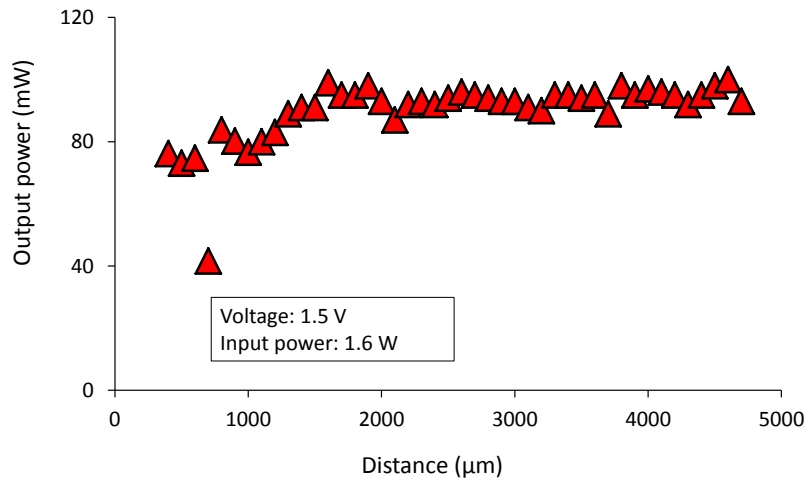


Figure 7.3.5. Measured output power of the laser across the 5-mm notch at a fixed voltage of 1.5V for 1.6 W of fixed input pump power.

7.4 Mode-Locked Operation Results Obtained with a Prism Pair

In this case, by taking into account the negative GDD due to the SF-14 prism pair with a tip-to-tip separation of 13 cm and the DCMs (M1, M2, and M3), the net GDD of the resonator was estimated to be -182 fs^2 . Furthermore, the pulse repetition rate and the estimated waist on the VCG-gold-SA was 131.7 MHz and $65 \text{ }\mu\text{m}$ respectively. Similar to the previous configuration, mode-locked operation could be easily initiated by translating the output coupler for the resonator with the prism pair. For this configuration, mode-locked operation could be achieved for applied voltages in the range of 0V to 1.2V. Figures 7.4.1 and 7.4.2 summarizes the mode locking results obtained from the VCG-gold-SA mode-locked resonator with the prism pair for 0.8V and 1.2V of applied voltages respectively. For the prism pair case, the resonator operated near 830 nm. For 0.8V, 52-fs nearly transform-limited pulses were generated with a time-bandwidth product of 0.33. In the case of 1.2V, the intracavity energy of the resonator increased due to the decreased insertion losses and hence, by adjusting the prism pair for the higher intracavity levels, nearly 48-fs pulses transform-limited with a time-bandwidth product of 0.37 could be obtained [56]. For both cases, measured RF spectra further indicated that a stable mode-locked operation was achieved.

As expected from Pauli blocking of the graphene electrode, the optical insertion loss of the VCG-gold-SA could be reduced by increasing the applied voltage and hence, higher intracavity energies could be obtained at higher bias voltages as shown in Fig. 7.4.3 (a). Since the adjustable dispersion could be achieved with the prism pair, the net negative GDD of the resonator was controlled at each applied voltage and shorter pulse durations could be obtained with nearly transform-limited time-bandwidth products. Therefore, in the mode locking experiments conducted with the prism pair, the generated pulses were nearly transform-limited at all bias voltages as shown in Fig. 7.4.3 (b).

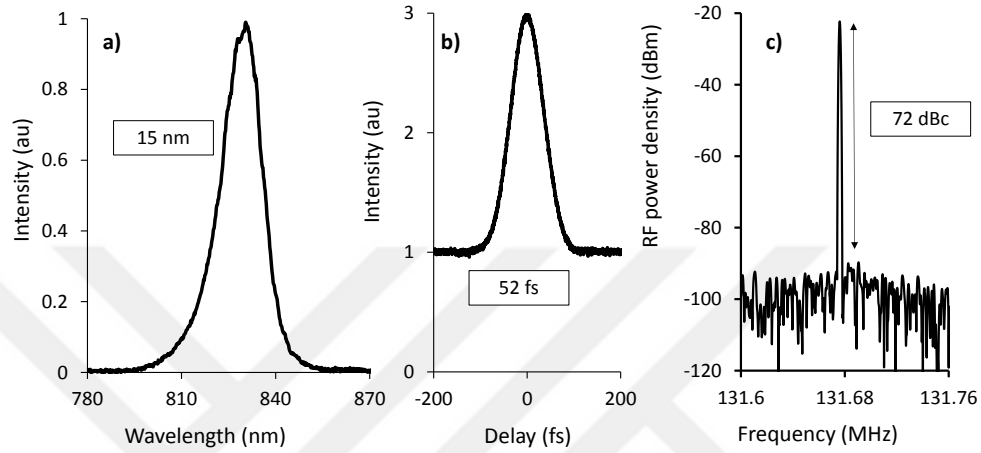


Figure 7.4.1. (a) Mode-locked spectrum, (b) autocorrelation trace, and (c) RF spectrum (1 kHz resolution bandwidth) of the generated pulses at 0.8V of applied bias. (Adapted with permission from [56], (The Optical Society)).

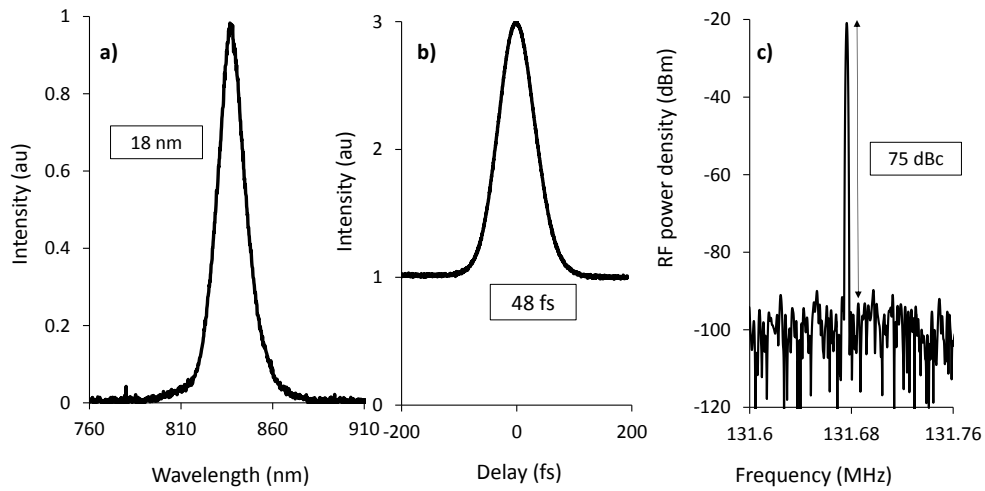


Figure 7.4.2. (a) Mode-locked spectrum, (b) autocorrelation trace, and (c) RF spectrum (1 kHz resolution bandwidth) of the generated pulses at 1.2V of applied bias.

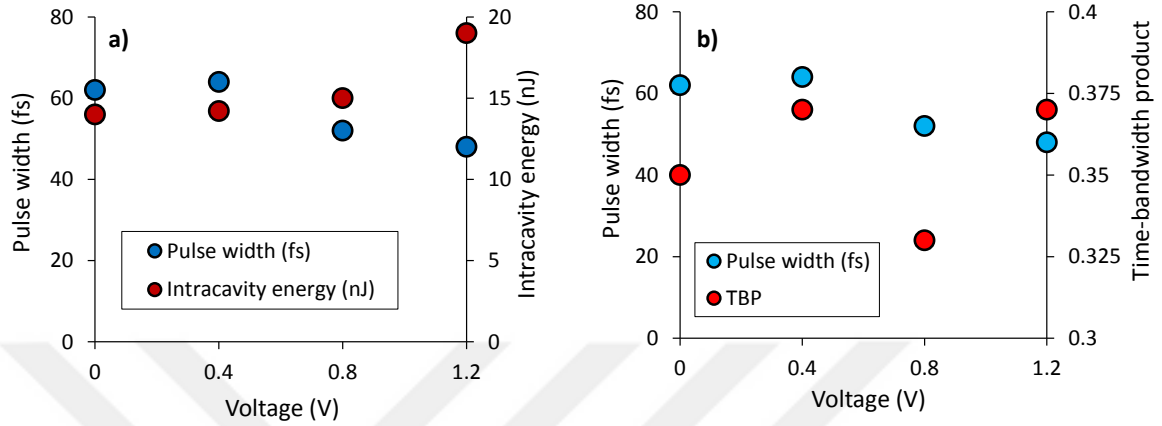


Figure 7.4.3. (a) Measured pulse durations and corresponding intracavity energies and (b) the time-bandwidth products (TBP) as a function of the applied voltage. (Adapted with permission from [56], (The Optical Society)).

Table 7.4.1 gives summary of the mode locking results obtained with the prism pair configuration. Mode-locked operation could be initiated for applied voltages in the range of 0-1.2V as opposed to the dispersion control mirror configuration (0-1.6V). The difference between the applied voltage range was mainly due to the different levels of insertion losses of the DCMs and the prism pair introduced to the resonator. As can be seen from Table 7.4.1, by increasing the applied voltage, pulses with higher energies could be obtained. At the highest single pulse mode-locked operation voltage of 1.2V, the estimated incident fluence on the VCG-gold-SA was $143 \mu\text{J}/\text{cm}^2$ and no damage was observed on the VCG-gold-SA up to this fluence level. Since the generated pulses were nearly transform-limited at all bias voltages, the net GDD of the resonator was further determined from the soliton area theorem, which connects the intracavity energy to the pulse duration and the dispersion as discussed in Chapter 2. By using the nonlinear refractive index value (n_2) of the Ti^{3+} :sapphire crystal [144] and the measured intracavity energies and pulse durations, the net GDD of the resonator was determined to be -184 fs^2 , which was in good agreement with our estimated value of -182 fs^2 . Furthermore, since the nonlinear refractive index of

the Ti^{3+} :sapphire medium is high enough to initiate the Kerr-lens mode locking (KLM), the initiation mechanism of the mode-locked operation was also checked by increasing the applied bias and translating the output coupler. For voltages greater than 1.2V, translating the output coupler did not initiate mode-locked operation and hence, this verified that the mode locking was achieved solely by the saturable absorber action of the graphene electrode.

Table 7.4.1. Summary of the femtosecond laser parameters for the VCG-gold-SA mode-locked Ti^{3+} :sapphire laser with the prism pair.

Applied voltage (V)	Mode-locked output power (mW)	Pulse energy (nJ)	Center wavelength (nm)	Spectral width (nm)	Pulse duration (fs)	Time-bandwidth product
0	55	0.42	833	13	62	0.35
0.4	56	0.43	833	13.5	64	0.37
0.8	59	0.45	828	15	52	0.33
1.2	76	0.57	836	18	48	0.37

In conclusion, use of the VCG-gold-SA to generate femtosecond pulses at a wavelength as short as 795 nm was demonstrated for the first time to the best of our knowledge [56]. The optical insertion loss of the VCG-gold-SA could be decreased and hence, the intracavity energy of the laser could be increased even with low operating voltages of the order of 0-2V. Two different dispersion control schemes were used and the transform-limited pulses as short as 48 fs was obtained by using an SF-14 prism pair, which introduced adjustable dispersion to the resonator. The generated pulses were nearly transform-limited at all bias voltages for the prism pair configuration. Therefore, by using the nonlinear refractive index value of the Ti^{3+} :sapphire gain medium and the measured laser parameters (e.g. pulse width and intracavity energy), the net group delay dispersion of the resonator was determined and the value came to be in agreement with the estimated group delay dispersion.

CHAPTER 8

CONCLUSIONS

In this thesis, a brief background of the optical properties and the optical characterization methods for graphene and graphene-based supercapacitor saturable absorbers were presented in Chapter 1. In Chapter 2, characteristics of ultrashort pulses, their propagation in nonlinear media, and principles behind different mode locking techniques (e.g. Kerr-lens and saturable absorber mode locking) were discussed. This was followed by the description of the important laser parameters, such as laser threshold, output power, and slope efficiency in Chapter 3. Design principles for the solid-state lasers with multipass-cavity (MPC) extensions were also discussed in the remaining parts of Chapter 3.

During this PhD research, linear and nonlinear optical response and mode locking performance of graphene and graphene-based saturable absorbers were investigated in detail. The nonlinear optical characterization experiments were conducted by using novel optical characterization tools, such as Raman and transient absorption spectroscopy and the linear characteristics were measured by using a spectrophotometer. The femtosecond pulse generation performance of graphene and graphene-based supercapacitor saturable absorbers were conducted in two different solid-state laser resonators: the multipass-cavity Cr^{4+} :forsterite (1250 nm) laser and the x-cavity Ti^{3+} :sapphire (800 nm) laser. Both gain media have numerous novel applications and are essential coherent light sources. Therefore, investigation of the mode-locked operation of such lasers is crucial to improve their performance.

Graphene and graphene-based supercapacitor saturable absorbers, which were used in the experiments, were fabricated by C. Kocabas's group at Bilkent University. The experimental results, obtained during this PhD study, were presented under four main chapters (Chapters 4, 5, 6, and 7).

In Chapter 4, the experimental results obtained from a graphene on quartz and a graphene on yttrium aluminium garnet (YAG) saturable absorber mode-locked multipass-cavity (MPC) Cr^{4+} :forsterite laser were presented. Graphene saturable absorbers were fabricated by chemical vapor deposition (CVD) technique and transfer-printed on quartz and YAG substrates, which had excellent optical quality and transparency at the operation wavelength of our laser. The graphene saturable absorber (GSA) samples were then characterized by using spectrophotometry, Raman spectroscopy and transient absorption spectroscopy techniques. The linear transmission measurements indicated that both GSAs (GSA on quartz and GSA on YAG) were monolayer samples and had a nearly constant broadband absorption of 2.3%, as discussed in Chapter 1. Raman spectroscopy results further showed that they were nearly defect-free samples. The saturable absorber parameters, such as recovery time, saturation fluence and modulation depth of the GSAs were explored by using pump-probe spectroscopy and the fast saturable absorber characteristics of our samples were inferred from the experimental results.

To test the mode locking performance of both GSAs, the samples were placed inside the multipass-cavity (MPC) Cr^{4+} :forsterite laser. Following the design parameters that were introduced in Chapter 3, the MPC extension was built step by step and each step was described in detail in Chapter 4. The advantage of the MPC extension stems from the relationship between the pulse repetition rate and the pulse energy. As stated in Chapter 2, when the optical path length increases, the pulse repetition rate decreases and hence, energy of the pulses can be scaled up at low average output power levels. In other words, the MPC extension enables the scaling of the energy per pulse at the same input pump power. Therefore, this advantage not only reduces the cost of a system, but also eliminates thermally-induced effects in light-matter applications where thermal effects are undesirable. In our experiments, the MPC extension enabled us to test the compatibility of

such graphene saturable absorbers in an energy-scaled laser for the first time to the best of our knowledge.

The other experimental step involved a careful dispersion management to balance the cavity nonlinearities and to generate solitary optical pulses as described in Chapter 2. To achieve this, specially designed double chirped (DCM) and Gires-Tournouis interferometer mirrors (GTI) were used during the experiments.

In the experiments, each GSA was separately introduced to the MPC Cr⁴⁺:forsterite resonator and the continuous-wave power performance of the laser was investigated prior to the mode locking experiments. Afterwards, mode-locked operation of the laser was initiated by translating the output coupler of the resonator. In the first case, where we used the GSA on quartz substrate, the resonator produced nearly transform-limited pulses as short as 100 fs with a peak power of 53 kW. When the GSA on YAG was employed to initiate mode locking, nearly transform-limited pulses with a duration of 93 fs and a peak power of 53 kW were generated. To the best of our knowledge, these were the highest peak powers obtained from a (GSA) mode-locked Cr⁴⁺:forsterite laser at room temperature. Further increase in the pulse peak power resulted in pulsing instabilities during mode-locked operation. To investigate the reason behind this limitation, the nonlinear refractive index value of the Cr⁴⁺:forsterite gain medium was estimated and used to determine the critical power for self-focusing inside the gain medium as described in Chapter 2. Since the estimated critical power for self-focusing was in agreement with the experimentally observed highest cavity peak power, we concluded that the self-focusing inside the Cr⁴⁺:forsterite gain medium was the major reason that limited further power scaling.

The favorable optical characteristics of graphene, such as nearly constant broadband absorption, saturation, and ultrafast response, make it an effective saturable absorber for femtosecond pulse generation from lasers operating in the near and mid-infrared as demonstrated in Chapter 4. However, one major drawback of graphene arises from its

round-trip small-signal insertion of nearly 5%. This excessive insertion loss amount can lead to operational challenges especially in low gain lasers or lasers operating at low input pump power levels.

The insertion loss of even monolayer graphene can be reduced by changing its broadband absorption. To achieve this, the Fermi level of graphene can be shifted and hence, its absorption can be blocked via Pauli exclusion principle. Different approaches, such as chemical or electrostatic doping of graphene to shift the Fermi level have been demonstrated. The drawbacks of such approaches were discussed in detail in Chapter 1. For example, in the case of the chemical doping, the Fermi level shift is fixed and cannot be dynamically controlled. For the electrostatic doping case, graphene-based solid-state capacitors have been proposed. However, as explained in Chapter 1, operation wavelength of the solid-state capacitors is limited to the infrared because they require high operating voltages to change the absorption at high photon energies and this may lead to dielectric breakdown.

In the case of a supercapacitor structure, which was described in Chapter 1, the application of a voltage bias polarizes the high dielectric electrolyte and enables ultrathin electrical double layer (EDL) formation. Since, the electric field, which electrostatically dopes the graphene electrode of the supercapacitor, was generated within the few nanometer thick EDLs, the Fermi level can be shifted to vary the absorption even with few volts of applied bias. Graphene-based supercapacitors of this kind have been proposed for the first time by our groups to generate femtosecond pulses from different solid-state lasers. The experimental results, obtained from the supercapacitor mode-locked lasers were presented in Chapters 5, 6, and 7.

Our first supercapacitor design involved, a high dielectric electrolyte sandwiched between two graphene electrodes. This device is referred to as the voltage-controlled graphene

saturable absorber (VCG-SA) and fabricated by our collaborators from Bilkent University. The fabrication details of the VCG-SA can be found in Chapter 5.

Prior to the mode locking experiments conducted with the VCG-SA, optical characterization of the device was performed by using spectrophotometry and transient absorption spectroscopy techniques as shown in Chapter 5. The voltage-dependent linear optical response of the VCG-SA indicated that the modulation of absorption could be achieved up to the visible region (up to 2.4 eV) even with few volts of applied bias (0V-3V) due to the novel supercapacitor architecture. Furthermore, the time-dependent nonlinear optical characterization experiments, conducted with a pump-probe spectrometer, demonstrated that the VCG-SA had fast carrier recovery times of the order of picoseconds and the effective inter/intraband transition rates may depend on the voltage. Saturable absorber parameters of the VCG-SA were also measured by using the same setup. A monotonic increase in the saturation fluence and a monotonic decrease in the modulation depth of the VCG-SA were observed with respect to the applied voltage.

The VCG-SA was tested inside the same MPC Cr⁴⁺:forsterite laser operating near 1250 nm, which was described in Chapter 4. The voltage-dependent continuous-wave and the mode-locked operation results were presented in detail in Chapter 5. The continuous-wave results indicated that the insertion of the VCG-SA at zero bias led to a considerable decrease in the output power of the laser. However, by increasing the applied voltage, the insertion loss of the device could be reduced and the output power of the laser could be increased as demonstrated in Chapter 5. Mode-locked operation with the VCG-SA could be obtained in the bias range of 0.5V-1V. For voltages smaller than 0.5V, intracavity pulse energy of the laser was not sufficient to initiate mode-locked operation. Since the saturable absorption is completely blocked at our laser wavelength of 1250 nm (photon energy of approximately 1 eV) due to the Pauli blocking, mode-locked operation was not observed for voltages beyond 1V. The VCG-SA mode-locked resonator produced nearly transform limited

femtosecond pulses in the voltage range of 0.5V-1V. Ultrashort pulses as short as 84 fs were generated from the MPC Cr⁴⁺:forsterite laser at 1V of applied bias. To the best of our knowledge, this was the first demonstration of a graphene-based supercapacitor saturable absorber with a voltage reconfigurable insertion loss to generate femtosecond pulses from a laser. The detailed pulse characterization results were presented in Chapter 5.

To further reduce the insertion losses at zero bias, one of the graphene electrodes of the VCG-SA was replaced with a notched gold electrode. The new voltage-controlled graphene-gold saturable absorber (VCG-gold-SA) design comprised the same electrolyte sandwiched between the graphene and the gold electrode. Similar to the experiments that were described in Chapter 5, the voltage-dependent linear optical characterization was performed and nearly 1% of modulation in absorption was achieved at the operation wavelength of the MPC Cr⁴⁺:forsterite laser (1250 nm) at 2V of applied bias.

Voltage-dependent continuous-wave and mode-locked operation of the same MPC Cr⁴⁺:forsterite laser with the VCG-gold-SA were presented in Chapter 6. Since one of the graphene electrodes was removed, the insertion loss of the device decreased from 6% to nearly 4% at zero volts of applied bias. Similar voltage-dependent continuous-wave characterization was performed with the VCG-gold-SA and further details can be found in Chapter 6. The improved design led to a decrease in the mode locking threshold pump power of the laser and hence, mode-locked operation could also be initiated for voltages less than 0.5V. Since the gold electrode caused unintentional doping of the graphene electrode, absorption of the graphene electrode was completely blocked for voltages beyond 0.8V. Therefore, mode-locked operation could not be initiated due to Pauli blocking. The VCG-gold-SA mode-locked laser produced 80-fs, nearly transform-limited pulses at 0.8V of applied bias and this study was also the first demonstration of a graphene-gold-based supercapacitor saturable absorber mode-locked laser.

In Chapters 5 and 6, use of the graphene-based supercapacitor saturable absorbers to generate femtosecond pulses from a laser operating around near infrared was presented. However, we also mentioned that the modulation of absorption in graphene supercapacitors can be achieved in a much broader wavelength range even at low applied voltages, as opposed to the graphene-based solid-state capacitors. To achieve this aim, a Ti^{3+} :sapphire laser, operating near 800 nm, was used for femtosecond pulse generation by using VCG-gold as a fast saturable absorber.

In Chapter 7, experimental setup of the Ti^{3+} :sapphire laser, which consisted of two different dispersion control elements, was described. The first configuration consisted of only the dispersion control mirrors (DCMs) and the net group delay dispersion (GDD) of the resonator was fixed. For this configuration, the voltage-dependent continuous-wave power performance of the laser was investigated and the experimental results were presented in Chapter 7. The VCG-gold-SA mode-locked resonator consisting of only the DCMs produced femtosecond pulses at a wavelength as short as 795 nm for applied voltages between 0V-1.6V. As the applied voltage increased, the loss of the VCG-gold-SA decreased and hence, the intracavity pulse energy of the laser also increased as expected. Since the net GDD of the resonator was fixed, increased intracavity energy resulted in unbalanced cavity nonlinearities and hence, the generated pulses became chirped for applied voltages greater than 1.2V. Therefore, to adjust the dispersion at each voltage and to eliminate the undesired GDD oscillations due to the DCMs, three of the DCMs were replaced with an SF-14 prism pair as shown in Chapter 7. In this second configuration, the generated pulses were nearly transform-limited at all bias voltages (0-1.2V) and the pulse duration could be shortened by increasing the applied voltage (i.e. increasing the intracavity energy). The voltage-dependent pulse characteristics were investigated in detail in Chapter 7. In the prism pair configuration, the laser operated near 830 nm and produced nearly transform-limited pulses as short as 48 fs (at 1.2V). The results presented in Chapter

7 showed, to our knowledge, the first demonstration of the VCG-gold supercapacitor as a fast saturable absorber at a wavelength as short as 795 nm. Together with the previous results, obtained near 1250 nm and presented in Chapters 5 and 6, it was demonstrated that the voltage-controlled graphene-based supercapacitor architectures have the potential to be utilized as versatile fast saturable absorbers with controllable insertion losses to generate femtosecond pulses from lasers operating over a broad wavelength range and with different levels of gain.

BIBLIOGRAPHY

1. P. R. Wallace, "The Band Theory of Graphite," *Physical Review Letters* **71**, 622-634 (1947).
2. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science* **306**, 666-669 (2004).
3. A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials* **6**, 183-191 (2007).
4. C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene," *Science* **321**, 385-388 (2008).
5. J. H. Chen, C. Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, "Intrinsic and extrinsic performance limits of graphene devices on SiO₂," *Nature Nanotechnology* **3**, 206-209 (2008).
6. A. B. Kuzmenko, E. van Heumen, F. Carbone, and D. van der Marel, "Universal Optical Conductance of Graphite," *Physical Review Letters* **100**, 117401 (2008).
7. J. H. Lee, E. K. Lee, W. J. Joo, Y. Jang, B. S. Kim, J. Y. Lim, S. H. Choi, S. J. Ahn, J. R. Ahn, M. H. Park, C. W. Yang, B. L. Choi, S. W. Hwang, and D. Whang, "Wafer-scale growth of single-crystal monolayer graphene on reusable hydrogen-terminated germanium," *Science* **344**, 286-289 (2014).
8. W. Gao, L. B. Alemany, L. Ci, and P. M. Ajayan, "New insights into the structure and reduction of graphite oxide," *Nature Chemistry* **1**, 403-408 (2009).
9. Q. Cao and J. A. Rogers, "Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects," *Advanced Materials* **21**, 29-53 (2009).
10. K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, "Electronic and magnetic properties of nanographite ribbons," *Physical Review B* **59**, 8271-8282 (1999).
11. M. Bacon, S. J. Bradley, and T. Nann, "Graphene Quantum Dots," *Particle & Particle Systems Characterization* **31**, 415-428 (2014).
12. E. F. Sheka and N. A. Popova, "Molecular theory of graphene oxide," *Physical Chemistry Chemical Physics* **15**, 13304-13322 (2013).
13. A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics* **81**, 109-162 (2009).
14. K. S. Novoselov, V. I. Falko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, "A roadmap for graphene," *Nature* **490**, 192-200 (2012).

15. R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. Peres, and A. K. Geim, "Fine structure constant defines visual transparency of graphene," *Science* **320**, 1308 (2008).
16. L. M. Malard, K. F. Mak, A. H. C. Neto, N. M. R. Peres, and T. F. Heinz, "Observation of intra- and inter-band transitions in the transient optical response of graphene," *New Journal of Physics* **15**(2013).
17. K. F. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, and T. F. Heinz, "Measurement of the Optical Conductivity of Graphene," *Physical Review Letters* **101**(2008).
18. K. F. Mak, L. Ju, F. Wang, and T. F. Heinz, "Optical spectroscopy of graphene: From the far infrared to the ultraviolet," *Solid State Communications* **152**, 1341-1349 (2012).
19. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, "Raman Spectrum of Graphene and Graphene Layers," *Physical Review Letters* **97**, 187401 (2006).
20. A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology* **8**, 235-246 (2013).
21. J. M. Dawlaty, S. Shivaraman, M. Chandrashekhhar, F. Rana, and M. G. Spencer, "Measurement of ultrafast carrier dynamics in epitaxial graphene," *Applied Physics Letters* **92**, 042116 (2008).
22. J. Z. Shang, Z. Q. Luo, C. X. Cong, J. Y. Lin, T. Yu, and G. G. Gurzadyan, "Femtosecond UV-pump/visible-probe measurements of carrier dynamics in stacked graphene films," *Applied Physics Letters* **97**(2010).
23. I. Gierz, J. C. Petersen, M. Mitran, C. Cacho, I. C. E. Turcu, E. Springate, A. Stohr, A. Kohler, U. Starke, and A. Cavalleri, "Snapshots of non-equilibrium Dirac carrier distributions in graphene," *Nature Materials* **12**, 1119-1124 (2013).
24. S. Ozharar, I. Baylam, M. N. Cizmeciyan, O. Balci, E. Pince, C. Kocabas, and A. Sennaroglu, "Graphene mode-locked multipass-cavity femtosecond Cr⁴⁺: forsterite laser," *Journal of Optical Society of America B* **30**, 1270-1275 (2013).
25. S. Kumar, M. Anija, N. Kamaraju, K. S. Vasu, K. S. Subrahmanyam, A. K. Sood, and C. N. R. Rao, "Femtosecond carrier dynamics and saturable absorption in graphene suspensions," *Applied Physics Letters* **95**(2009).
26. W. B. Cho, J. H. Yim, S. Y. Choi, S. Lee, U. Griebner, V. Petrov, and F. Rotermund, "Mode-locked self-starting Cr:forsterite laser using a single-walled carbon nanotube saturable absorber," *Optics Letters* **33**, 2449-2451 (2008).
27. W. B. Cho, J. W. Kim, H. W. Lee, S. Bae, B. H. Hong, S. Y. Choi, I. H. Baek, K. Kim, D.-I. Yeom, and F. Rotermund, "High-quality, large-area monolayer graphene for efficient bulk laser mode-locking near 1.25 μm ," *Optics Letters* **36**, 4089-4091 (2011).

28. I. H. Baek, H. W. Lee, S. Bae, B. H. Hong, Y. H. Ahn, D.-I. Yeom, and F. Rotermund, "Efficient Mode-Locking of Sub-70-fs Ti:Sapphire Laser by Graphene Saturable Absorber," *Applied Physics Express* **5**, 032701 (2012).
29. F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," *Nature Photonics* **4**, 611-622 (2010).
30. C.-C. Lee, T. R. Schibli, G. Acosta, and J. S. Bunch, "Ultra-short optical pulse generation with single-layer graphene," *Journal of Nonlinear Optical Physics & Materials* **19**, 767-771 (2010).
31. W. D. Tan, C. Y. Su, R. J. Knize, G. Q. Xie, L. J. Li, and D. Y. Tang, "Mode locking of ceramic Nd:yttrium aluminum garnet with graphene as a saturable absorber," *Applied Physics Letters* **96**, 031106-031103 (2010).
32. Q. Bao, H. Zhang, Z. Ni, Y. Wang, L. Polavarapu, Z. Shen, Q.-H. Xu, D. Tang, and K. Loh, "Monolayer graphene as a saturable absorber in a mode-locked laser," *Nano Research* **4**, 297-307 (2011).
33. J.-L. Xu, X.-L. Li, J.-L. He, X.-P. Hao, Y.-Z. Wu, Y. Yang, and K.-J. Yang, "Performance of large-area few-layer graphene saturable absorber in femtosecond bulk laser," *Applied Physics Letters* **99**, 261107-261104 (2011).
34. L. Zhang, Y. G. Wang, H. J. Yu, S. B. Zhang, W. Hou, X. C. Lin, and J. M. Li, "High power passively mode-locked Nd:YVO₄ laser using graphene oxide as a saturable absorber," *Laser Physics* **21**, 2072-2075 (2011).
35. J. Ma, G. Q. Xie, P. Lv, W. L. Gao, P. Yuan, L. J. Qian, H. H. Yu, H. J. Zhang, J. Y. Wang, and D. Y. Tang, "Graphene mode-locked femtosecond laser at 2 μ m wavelength," *Optics Letters* **37**, 2085-2087 (2012).
36. Z. Sun, T. Hasan, and A. C. Ferrari, "Ultrafast lasers mode-locked by nanotubes and graphene," *Physica E: Low-dimensional Systems and Nanostructures* **44**, 1082-1091 (2012).
37. E. Ugolotti, A. Schmidt, V. Petrov, J. W. Kim, D.-I. Yeom, F. Rotermund, S. Bae, B. H. Hong, A. Agnesi, C. Fiebig, G. Erbert, X. Mateos, M. Aguilo, F. Diaz, and U. Griebner, "Graphene mode-locked femtosecond Yb:KLuW laser," *Applied Physics Letters* **101**, 161112-161114 (2012).
38. M. N. Cizmeciyan, J. W. Kim, S. Bae, B. H. Hong, F. Rotermund, and A. Sennaroglu, "Graphene mode-locked femtosecond Cr:ZnSe laser at 2500nm," *Optics Letters* **38**, 341-343 (2013).
39. F. Canbaz, N. Kakenov, C. Kocabas, U. Demirbas, and A. Sennaroglu, "Graphene mode-locked Cr:LiSAF laser at 850 nm," *Optics Letters* **40**, 4110-4113 (2015).
40. I. Baylam, S. Ozharar, M. N. Cizmeciyan, O. Balci, E. Pince, C. Kocabas, and A. Sennaroglu, "Femtosecond Pulse Generation from an Extended Cavity Cr⁴⁺:forsterite Laser using Graphene on YAG," in *Advanced Solid-State Lasers Congress* (2013)

41. F. Canbaz, N. Kakenov, C. Kocabas, U. Demirbas, and A. Sennaroglu, "Sub-20 Femtosecond Pulse Generation with a Graphene Mode-locked Solid-State Laser," in *Lasers Congress 2016 (ASSL, LSC, LAC)* (2016)
42. H. T. Liu, Y. Q. Liu, and D. B. Zhu, "Chemical doping of graphene," *Journal of Materials Chemistry* **21**, 3335-3345 (2011).
43. C. C. Lee, C. Mohr, J. Bethge, S. Suzuki, M. E. Fermann, I. Hartl, and T. R. Schibli, "Frequency comb stabilization with bandwidth beyond the limit of gain lifetime by an intracavity graphene electro-optic modulator," *Optics Letters* **37**, 3084-3086 (2012).
44. C. C. Lee, S. Suzuki, W. Xie, and T. R. Schibli, "Broadband graphene electro-optic modulators with sub-wavelength thickness," *Optics Express* **20**, 5264-5269 (2012).
45. E. O. Polat and C. Kocabas, "Broadband Optical Modulators Based on Graphene Supercapacitors," *Nano Letters* **13**, 5851-5857 (2013).
46. C. F. Chen, C. H. Park, B. W. Boudouris, J. Horng, B. S. Geng, C. Girit, A. Zettl, M. F. Crommie, R. A. Segalman, S. G. Louie, and F. Wang, "Controlling inelastic light scattering quantum pathways in graphene," *Nature* **471**, 617-620 (2011).
47. X. T. Gan, K. F. Mak, Y. D. Gao, Y. M. You, F. Hatami, J. Hone, T. F. Heinz, and D. Englund, "Strong Enhancement of Light-Matter Interaction in Graphene Coupled to a Photonic Crystal Nanocavity," *Nano Letters* **12**, 5626-5631 (2012).
48. A. Majumdar, J. Kim, J. Vuckovic, and F. Wang, "Electrical Control of Silicon Photonic Crystal Cavity by Graphene," *Nano Letters* **13**, 515-518 (2013).
49. M. M. Huang, Y. P. Jiang, P. Sasisanker, G. W. Driver, and H. Weingartner, "Static Relative Dielectric Permittivities of Ionic Liquids at 25 degrees C," *Journal of Chemical and Engineering Data* **56**, 1494-1499 (2011).
50. J. J. Yoo, K. Balakrishnan, J. S. Huang, V. Meunier, B. G. Sumpter, A. Srivastava, M. Conway, A. L. M. Reddy, J. Yu, R. Vajtai, and P. M. Ajayan, "Ultrathin Planar Graphene Supercapacitors," *Nano Letters* **11**, 1423-1427 (2011).
51. J. R. Miller, R. A. Outlaw, and B. C. Holloway, "Graphene Double-Layer Capacitor with ac Line-Filtering Performance," *Science* **329**, 1637-1639 (2010).
52. Y. W. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, and R. S. Ruoff, "Carbon-Based Supercapacitors Produced by Activation of Graphene," *Science* **332**, 1537-1541 (2011).
53. Y. Wang, Z. Q. Shi, Y. Huang, Y. F. Ma, C. Y. Wang, M. M. Chen, and Y. S. Chen, "Supercapacitor Devices Based on Graphene Materials," *Journal of Physical Chemistry C* **113**, 13103-13107 (2009).
54. I. Baylam, M. N. Cizmeciyan, S. Ozharar, E. O. Polat, C. Kocabas, and A. Sennaroglu, "Femtosecond pulse generation with voltage-controlled graphene saturable absorber," *Optics Letters* **39**, 5180-5183 (2014).

55. I. Baylam, O. Balci, N. Kakenov, C. Kocabas, and A. Sennaroglu, "Graphene-gold supercapacitor as a voltage controlled saturable absorber for femtosecond pulse generation," *Optics Letters* **41**(2016).
56. I. Baylam, A. Muti, C. Cihan, S. Ozharar, C. Kocabas, and A. Sennaroglu, "Femtosecond Pulse Generation with Graphene-Gold Supercapacitor Saturable Absorbers near 800 nm," in *Lasers Congress 2016 (ASSL, LSC, LAC)* (2016)
57. V. Gerginov, C. E. Tanner, S. A. Diddams, A. Bartels, and L. Hollberg, "High-resolution spectroscopy with a femtosecond laser frequency comb," *Optics Letters* **30**, 1734-1736 (2005).
58. C. Calabrese, A. M. Stingel, L. Shen, and P. B. Petersen, "Ultrafast continuum mid-infrared spectroscopy: probing the entire vibrational spectrum in a single laser shot with femtosecond time resolution," *Optics Letters* **37**, 2265-2267 (2012).
59. C. H. Chuang and C. Burda, "Contribution of Femtosecond Laser Spectroscopy to the Development of Advanced Optoelectronic Nanomaterials," *Journal of Physical Chemistry Letters* **3**, 1921-1927 (2012).
60. U. Keller, "Ultrafast solid-state lasers," *Progress in Optics*, Vol 46 **46**, 1-115 (2004).
61. G. J. Tearney, M. E. Brezinski, B. E. Bouma, S. A. Boppart, C. Pitris, J. F. Southern, and J. G. Fujimoto, "In vivo endoscopic optical biopsy with optical coherence tomography," *Science* **276**, 2037-2039 (1997).
62. B. E. Bouma, G. J. Tearney, I. P. Bilinsky, B. Golubovic, and J. G. Fujimoto, "Self-phase-modulated Kerr-lens mode-locked Cr:forsterite laser source for optical coherence tomography," *Optics Letters* **21**, 1839-1841 (1996).
63. D. Huang, E. A. Swanson, C. P. Lin, J. S. Schuman, W. G. Stinson, W. Chang, M. R. Hee, T. Flotte, K. Gregory, C. A. Puliafito, and et al., "Optical coherence tomography," *Science* **254**, 1178-1181 (1991).
64. C.-K. Sun, C.-C. Chen, S.-W. Chu, T.-H. Tsai, Y.-C. Chen, and B.-L. Lin, "Multiharmonic-generation biopsy of skin," *Optics Letters* **28**, 2488-2490 (2003).
65. K. Konig, "Multiphoton microscopy in life sciences," *Journal of Microscopy* **200**, 83-104 (2000).
66. W. R. Zipfel, R. M. Williams, and W. W. Webb, "Nonlinear magic: multiphoton microscopy in the biosciences," *Nature Biotechnology* **21**, 1368-1376 (2003).
67. J. J. Macklin, J. D. Kmetec, and C. L. Gordon, "High-Order Harmonic-Generation Using Intense Femtosecond Pulses," *Physical Review Letters* **70**, 766-769 (1993).
68. D. Vonderlinde, T. Engers, G. Jenke, P. Agostini, G. Grillon, E. Nibbering, A. Mysyrowicz, and A. Antonetti, "Generation of High-Order Harmonics from Solid-Surfaces by Intense Femtosecond Laser-Pulses," *Physical Review A* **52**, R25-R27 (1995).

69. C. Spielmann, N. H. Burnett, S. Sartania, R. Koppitsch, M. Schnurer, C. Kan, M. Lenzner, P. Wobrauschek, and F. Krausz, "Generation of coherent X-rays in the water window using 5-femtosecond laser pulses," *Science* **278**, 661-664 (1997).
70. A. Sennaroglu, *Photonics and Laser Engineering : Principles, Devices, and Applications* (McGraw-Hill, New York, 2010).
71. J. C. Diels and W. Rudolph, *Ultrashort Laser Pulse Phenomena: Fundamentals, Techniques, and Applications on a Femtosecond Time Scale* (Academic Press, 2006).
72. D. Huang, M. Ulman, L. H. Acioli, H. A. Haus, and J. G. Fujimoto, "Self-Focusing-Induced Saturable Loss for Laser Mode-Locking," *Optics Letters* **17**, 511-513 (1992).
73. F. Shimizu, "Frequency Broadening in Liquids by a Short Light Pulse," *Physical Review Letters* **19**(1967).
74. H. A. Haus, "Mode-locking of lasers," *IEEE Journal of Selected Topics in Quantum Electronics* **6**, 1173-1185 (2000).
75. B. Chassagne, A. Ivanov, J. Oberle, G. Jonusauskas, and C. Rulliere, "Experimental determination of the nonlinear refractive index in an operating Cr:forsterite femtosecond laser," *Optics Communications* **141**, 69-74 (1997).
76. J. L. Shen, C. Y. Chang, W. C. Chou, M. C. Wu, and Y. F. Chen, "Temperature dependence of the reflectivity in absorbing Bragg reflectors," *Optics Express* **9**, 287-293 (2001).
77. R. Szipocs, K. Ferencz, C. Spielmann, and F. Krausz, "Chirped multilayer coatings for broadband dispersion control in femtosecond lasers," *Optics Letters* **19**, 201-203 (1994).
78. F. X. Kartner, N. Matuschek, T. Schibli, U. Keller, H. A. Haus, C. Heine, R. Morf, V. Scheuer, M. Tilsch, and T. Tschudi, "Design and fabrication of double-chirped mirrors," *Optics Letters* **22**, 831-833 (1997).
79. B. Golubovic, R. R. Austin, M. K. Steiner-Shepard, M. K. Reed, S. A. Diddams, D. J. Jones, and A. G. Van Engen, "Double Gires-Tournois interferometer negative-dispersion mirrors for use in tunable mode-locked lasers," *Optics Letters* **25**, 275-277 (2000).
80. J. Kuhl and J. Heppner, "Compression of Femtosecond Optical Pulses with Dielectric Multilayer Interferometers," *IEEE Journal of Quantum Electronics* **22**, 182-185 (1986).
81. E. B. Treacy, "Optical Pulse Compression with Diffraction Gratings," *IEEE Journal of Quantum Electronics* **5**, 454-458 (1969).
82. P. Maine, D. Strickland, P. Bado, M. Pessot, and G. Mourou, "Generation of Ultrahigh Peak Power Pulses by Chirped Pulse Amplification," *IEEE Journal of Quantum Electronics* **24**, 398-403 (1988).

83. R. L. Fork, O. E. Martinez, and J. P. Gordon, "Negative dispersion using pairs of prisms," *Optics Letters* **9**, 150-152 (1984).
84. A. Sennaroglu, *Solid-State Lasers and Applications* (Taylor & Francis, 2010).
85. K. Gurs, "Modulation and mode locking of the continuous ruby laser," *IEEE Journal of Quantum Electronics* **3**(1967).
86. S. H. and T. C. L., "Zeeman effect and nonlinear interactions between oscillating laser modes," *Quantum Electronics III*, 469-498 (1964).
87. DiDomenico, "Small-signal analysis of internal (coupling type) modulation of lasers," *Journal of Applied Physics* **35**, 2870-2876 (1964).
88. L. E. Hargrove, R. L. Fork, and M. A. Pollack, "Locking Of He-Ne Laser Modes Induced by Synchronous Intracavity Modulation," *Applied Physics Letters* **5**, 4-5 (1964).
89. Y. A., "Internal modulation in multimode laser oscillations," *Journal of Applied Physics* **36**, 388 (1965).
90. D. Kuizenga and A. Siegman, "FM and AM mode locking of the homogeneous laser - Part II: Experimental results in a Nd:YAG laser with internal FM modulation," *IEEE Journal of Quantum Electronics* **6**, 709-715 (1970).
91. D. J. Kuizenga and A. E. Siegman, "FM and AM mode locking of the homogeneous laser-Part I: Theory," *IEEE Journal of Quantum Electronics* **QE-6**, 694-708 (1970).
92. R. Ell, U. Morgner, F. X. Kartner, J. G. Fujimoto, E. P. Ippen, V. Scheuer, G. Angelow, T. Tschudi, M. J. Lederer, A. Boiko, and B. Luther-Davies, "Generation of 5-fs pulses and octave-spanning spectra directly from a Ti : sapphire laser," *Optics Letters* **26**, 373-375 (2001).
93. P. B. Corkum and F. Krausz, "Attosecond science," *Nat Phys* **3**, 381-387 (2007).
94. F. Zhang, S. Han, Y. Q. Liu, Z. P. Wang, and X. G. Xu, "Dependence of the saturable absorption of graphene upon excitation photon energy," *Applied Physics Letters* **106**(2015).
95. Q. L. Bao, H. Zhang, Y. Wang, Z. H. Ni, Y. L. Yan, Z. X. Shen, K. P. Loh, and D. Y. Tang, "Atomic-Layer Graphene as a Saturable Absorber for Ultrafast Pulsed Lasers," *Advanced Functional Materials* **19**, 3077-3083 (2009).
96. U. Keller, K. J. Weingarten, F. X. Kartner, D. Kopf, B. Braun, I. D. Jung, R. Fluck, C. Hönninger, N. Matuschek, and J. A. d. Au, "Semiconductor saturable absorber mirrors (SESAM's) for femtosecond to nanosecond pulse generation in solid-state lasers," *IEEE Journal of Selected Topics in Quantum Electronics* **2**, 435-453 (1996).
97. S. Iijima, "Helical Microtubules of Graphitic Carbon," *Nature* **354**, 56-58 (1991).
98. H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umez, S. Suzuki, Y. Ohtsuka, and Y. Achiba, "Optical properties of single-wall carbon nanotubes," *Synthetic Metals* **103**, 2555-2558 (1999).

99. W. B. Cho, J. H. Yim, S. Y. Choi, S. Lee, A. Schmidt, G. Steinmeyer, U. Griebner, V. Petrov, D. I. Yeom, K. Kim, and F. Rotermund, "Carbon Nanotubes: Boosting the Non Linear Optical Response of Carbon Nanotube Saturable Absorbers for Broadband Mode-Locking of Bulk Lasers," *Advanced Functional Materials* **20**, (2010).
100. H. R. Chen, C. Y. Tsai, H. M. Cheng, K. H. Lin, P. H. Yen, C. H. Chen, and W. F. Hsieh, "High-quality and Large-size Topological Insulator Bi₂Te₃-Gold Saturable Absorber Mirror for Mode-Locking Fiber Laser," *Scientific Reports* **6** (2016).
101. W. J. Liu, L. H. Pang, H. N. Han, W. L. Tian, H. Chen, M. Lei, P. G. Yan, and Z. Y. Wei, "70-fs mode-locked erbium-doped fiber laser with topological insulator," *Scientific Reports* **6** (2016).
102. L. Gao, T. Zhu, W. Huang, and Z. Q. Luo, "Stable, Ultrafast Pulse Mode-Locked by Topological Insulator Bi₂Se₃ Nanosheets Interacting With Photonic Crystal Fiber: From Anomalous Dispersion to Normal Dispersion," *IEEE Photonics Journal* **7** (2015).
103. J. Boguslawski, J. Sotor, G. Sobon, J. Tarka, J. Jagiello, W. Macherzynski, L. Lipinska, and K. M. Abramski, "Mode-locked Er-doped fiber laser based on liquid phase exfoliated Sb₂Te₃ topological insulator," *Laser Physics* **24** (2014).
104. M. B. Hisyam, M. F. M. Rusdi, A. A. Latiff, and S. W. Harun, "Generation of Mode-Locked Ytterbium Doped Fiber Ring Laser Using Few-Layer Black Phosphorus as a Saturable Absorber," *IEEE Journal of Selected Topics in Quantum Electronics* **23** (2017).
105. Y. Chen, H. R. Mu, P. F. Li, S. H. Lin, B. N. Shivananju, and Q. L. Bao, "Optically driven black phosphorus as a saturable absorber for mode-locked laser pulse generation," *Optics Engineering* **55** (2016).
106. J. F. Li, H. Y. Luo, B. Zhai, R. G. Lu, Z. N. Guo, H. Zhang, and Y. Liu, "Black phosphorus: a two-dimension saturable absorption material for mid-infrared Q-switched and mode-locked fiber lasers," *Scientific Reports* **6** (2016).
107. G. Cerullo, S. D. Silvestri, and V. Magni, "Self-starting Kerr-lens mode locking of a Ti:sapphire laser," *Optics Letters* **19**, 1040-1042 (1994).
108. L. J. Qian, X. Liu, and F. W. Wise, "Femtosecond Kerr-lens mode locking with negative nonlinear phase shifts," *Optics Letters* **24** (1999).
109. V. L. Kalashnikov and I. G. Poloyko, "Investigation of the Kerr-Lens mode locking ability of Cr:ZnSe solid-state laser," **1**, 1-14 (2002).
110. F. X. Kaertner, "Ultrafast optics, Kerr-Lens and Additive Pulse Mode Locking," p. 258.
111. M. N. Cizmeciyan, H. Cankaya, A. Kurt, and A. Sennaroglu, "Kerr-lens mode-locked femtosecond Cr²⁺:ZnSe laser at 2420 nm," *Optics Letters* **34**, 3056-3058 (2009).

112. D. E. Spence, Kean, P. N., Sibbett, W., "60-fsec pulse generation from a self-mode-locked Ti:sapphire laser," *Optics Letters* **16** (1991).
113. H. Hora, P. Lalouis, L. Giuffrida, D. Margarone, G. Korn, S. Eliezer, G. H. Miley, S. Moustazis, G. Mourou, and C. P. J. Barty, "Picosecond-petawatt laser-block ignition for avalanche fusion of boron by ultrahigh acceleration and ultrahigh magnetic fields," *J. Phys. Conf. Ser.* **717** (2016).
114. M. L. Spaeth, K. R. Manes, M. Bowers, P. Celliers, J. M. Di Nicola, P. Di Nicola, S. Dixit, G. Erbert, J. Heebner, D. Kalantar, O. Landen, B. MacGowan, B. Van Wonterghem, P. Wegner, C. Widmayer, and S. Yang, "National Ignition Facility Laser System Performance," *Fusion Sci. Technol.* **69**, 366-394 (2016).
115. S. K. D. P. P. Pronko, J. Squier, J. V. Rudd, D. Du, G. Mourou, "Machining of sub-micron holes using a femtosecond laser at 800 nm," *Optics Communications* **114**, 106-110 (1995).
116. X. Liu, D. Du, and G. Mourou, "Laser ablation and micromachining with ultrashort laser pulses," *IEEE Journal of Quantum Electronics* **33**, 1706-1716 (1997).
117. C. B. Schaffer, A. Brodeur, J. F. Garcia, and E. Mazur, "Micromachining bulk glass by use of femtosecond laser pulses with nanojoule energy," *Optics Letters* **26**, 93-95 (2001).
118. A. F. Chase, D. Z. Chase, J. F. Weishampel, J. B. Drake, R. L. Shrestha, K. C. Slatton, J. J. Awe, and W. E. Carter, "Airborne LiDAR, archaeology, and the ancient Maya landscape at Caracol, Belize," *J. Archaeol. Sci.* **38**, 387-398 (2011).
119. G. T. Forrest, "Diode-Laser Applications - Red Diode-Lasers Read Barcodes and Optical-Data," *Laser Focus-Electro-Optics* **24**, 52-& (1988).
120. P. F. Moulton, "An Investigation of the Co:MgF₂ Laser System," *IEEE Journal of Quantum Electronics* **21**, 1582-1595 (1985).
121. U. Demirbas, M. Schmalz, B. Sumpf, G. Erbert, G. S. Petrich, L. A. Kolodziejski, J. G. Fujimoto, F. X. Kärtner, and A. Leitenstorfer, "Femtosecond Cr:LiSAF and Cr:LiCAF lasers pumped by tapered diode lasers," *Optics Express* **19**, 20444-20461 (2011).
122. F. Druon, F. Balembois, and P. Georges, "New laser crystals for the generation of ultrashort pulses," *Comptes Rendus Physique* **8**, 153-164 (2007).
123. A. Sennaroglu, "Analysis and optimization of lifetime thermal loading in continuous-wave Cr⁴⁺-doped solid-state lasers," *Journal of Optical Society of America B* **18**, 1578-1586 (2001).
124. D. Herriot, H. Kogelnik, and R. Kompfner, "Off-Axis in Spherical Mirror Interferometers," *Applied Optics* **3**, 523-526 (1964).
125. A. Sennaroglu, A. M. Kowalewicz, E. P. Ippen, and J. G. Fujimoto, "Compact femtosecond lasers based on novel multipass cavities," *IEEE Journal of Quantum Electronics* **40**, 519-528 (2004).

126. P. F. Moulton, "Tunable solid-state lasers," *Proceedings of the IEEE* **80**, 348-364 (1992).
127. V. Petricevic, S. K. Gayen, R. R. Alfano, K. Yamagishi, H. Anzai, and Y. Yamaguchi, "Laser action in chromium-doped forsterite," *Applied Physics Letters* **52**, 1040-1042 (1988).
128. A. Seas, Petricevic, V., Alfano, R. R., "Continuous-wave mode-locked operation of a chromium-doped forsterite laser," *Optics Letters* **16** (1991).
129. A. Sennaroglu, "Efficient Continuous-Wave Radiatively Cooled Cr⁴⁺:Forsterite Lasers at Room Temperature," *Applied Optics* **37** (1998).
130. H. Cankaya, S. Akturk, and A. Sennaroglu, "Direct generation of 81 nJ pulses and external compression to a subpicosecond regime with a 4.9 MHz chirped-pulse multipass-cavity Cr⁴⁺:forsterite oscillator," *Optics Letters* **36**, 1572-1574 (2011).
131. I. Baylam, S. Ozharar, H. Cankaya, S. Y. Choi, K. Kim, F. Rotermund, U. Griebner, V. Petrov, and A. Sennaroglu, "Energy scaling of a carbon nanotube saturable absorber mode-locked femtosecond bulk laser," *Optics Letters* **37**, 3555-3557 (2012).
132. P. F. Moulton, "Spectroscopic and Laser Characteristics of Ti-Al₂O₃," *Journal of the Optical Society of America B-Optical Physics* **3**, 125-133 (1986).
133. K. Gurel, V. J. Wittwer, M. Hoffmann, C. J. Saraceno, S. Hakobyan, B. Resan, A. Rohrbacher, K. Weingarten, S. Schilt, and T. Sudmeyer, "Green-diode-pumped femtosecond Ti:Sapphire laser with up to 450 mW average power," *Optics Express* **23**, 30043-30048 (2015).
134. K. Gurel, M. Hoffmann, C. J. Saraceno, V. J. Wittwer, S. Hakobyan, B. Resan, A. Rohrbacher, K. Weingarten, S. Schilt, and T. Sudmeyer, "Ultrafast Diode-Pumped Ti:Sapphire Laser Generating 200-mW Average Power in 68-fs Pulses," *Conference on Lasers and Electro-Optics* (2015).
135. P. Theer, M. T. Hasan, and W. Denk, "Multi-photon imaging using a Ti : sapphire regenerative amplifier," *Confocal, Multiphoton, and Nonlinear Microscopic Imaging* **5139**, 1-6 (2003).
136. S. M. Foreman, A. Marian, J. Ye, E. A. Petrukhin, M. A. Gubin, O. D. Mücke, F. N. C. Wong, E. P. Ippen, and F. X. Kaertner, "Ti:sapphire Lasers for Frequency Metrology Spanning the Visible and Infrared Spectrum Without Nonlinear Fiber," in *Advanced Solid-State Photonics (TOPS)*, (2005)
137. G. Rodriguez, J. P. Roberts, and A. J. Taylor, "Ultraviolet Ultrafast Pump-Probe Laser-Based on a Ti-Sapphire Laser System," *Optics Letters* **19**, 1146-1148 (1994).
138. D. Bruneel, G. Matras, R. Le Harzic, N. Huot, K. Konig, and E. Audouard, "Micromachining of metals with ultra-short Ti-Sapphire lasers: Prediction and optimization of the processing time," *Optics and Laser Engineering* **48**, 268-271 (2010).

139. M. Kalashnikov, H. Cao, K. Osvay, and V. Chvykov, "Polarization-encoded chirped pulse amplification in Ti:sapphire: a way toward few-cycle petawatt lasers," *Optics Letters* **41**, 25-28 (2016).
140. V. Petrov, F. Rotermund, F. Noack, J. Ringling, O. Kittelmann, and R. Komatsu, "Frequency conversion of Ti : sapphire-based femtosecond laser systems to the 200-nm spectral region using nonlinear optical crystals," *IEEE Journal of Selected Topics in Quantum Electronics* **5**, 1532-1542 (1999).
141. A. Mostafazadeh, H. Cankaya, and A. Sennaroglu, "Pulse Energy Optimization in Multipass-Cavity Mode-Locked Femtosecond Lasers," *IEEE Journal of Selected Topics in Quantum Electronics* **21** (2015).
142. O. Salihoglu, S. Balci, and C. Kocabas, "Plasmon-polaritons on graphene-metal surface and their use in biosensors," *Applied Physics Letters* **100**, 213110 (2012).
143. S. M. J. Kelly, "Characteristic sideband instability of periodically amplified average soliton," *Electronics Letters* **28** (1992).
144. E. Sorokin, "Solid-state materials for few-cycle pulse generation and amplification," in *Few-cycle laser pulse generation and its applications*, F. X. Kartner, ed. (Springer-Verlag, Berlin, 2004), pp. 3-71.

VITA

Işinsu Baylam was born in Çankaya, Ankara on January 7, 1988. She received her BS degree in Physics from Bilkent University in 2010. She was admitted to the Master of Science program in Physics Department in 2010 and to the PhD program in the same department in 2012 at Koç University. Her research interests included femtosecond lasers, solid-state lasers in the near infrared region, biomedical applications of lasers and nonlinear optics. She is a student member of OSA.

Publications:

- I. Baylam, S. Ozharar, H. Cankaya, S. Y. Choi, K. Kim, F. Rotermund, U. Griebner, V. Petrov, and A. Sennaroglu, “Energy scaling of a carbon nanotube saturable absorber mode-locked femtosecond bulk laser,” *Opt. Lett.* **37**, 3555-3557 (2012).
- S. Ozharar, I. Baylam, M. N. Cizmeciyan, O. Balci, E. Pince, C. Kocabas, and A. Sennaroglu, “Graphene mode-locked multipass-cavity femtosecond Cr⁴⁺: forsterite laser,” *J. Opt. Soc. Am. B* **30**, 1270-1275 (2013).
- I. Baylam, M. N. Cizmeciyan, S. Ozharar, E. O. Polat, C. Kocabas, and A. Sennaroglu, “Femtosecond pulse generation with voltage-controlled graphene saturable absorber,” *Opt. Lett.* **39**, 5180-5183 (2014).
- I. Baylam, O. Balci, N. Kakenov, C. Kocabas, and A. Sennaroglu, “Graphene-gold supercapacitor as a voltage controlled saturable absorber for femtosecond pulse generation,” *Opt. Lett.* **41**(2016).
- I. Baylam, S. Ozharar, N. Kakenov, C. Kocabas, and A. Sennaroglu, “Femtosecond pulse generation from a Ti:sapphire laser near 800 nm with voltage reconfigurable graphene saturable absorbers,” *Opt. Lett.* (in revision)

Book Chapter:

- I. Baylam, S. Ozharar, N. Kakenov, C. Kocabaş, and A. Sennaroğlu, “Femtosecond Pulse Generation with Voltage-Controlled Graphene Saturable Absorbers,” in *Optical Properties of Graphene*, ISBN: 978-981-314-874-1.

Proceedings:

- I. Baylam, S. Ozharar, H. Cankaya, S. Y. Choi, K. Kim, F. Rotermund, U. Griebner, V. Petrov, and A. Sennaroglu, “Energy scaling of a multipass-cavity mode-locked femtosecond bulk laser with a carbon nanotube saturable absorber,” in *SPIE Photonics West* (2013).
- I. Baylam, S. Ozharar, M. N. Cizmeciyan, O. Balci, E. Pince, C. Kocabas, and A. Sennaroglu, “Femtosecond Pulse Generation from an Extended Cavity Cr:4+ :forsterite Laser using Graphene on YAG,” in *Advanced Solid State Lasers Congress* (2013).
- I. Baylam, M. N. Cizmeciyan, S. Ozharar, E. O. Polat, C. Kocabas, and A. Sennaroglu, “Graphene Supercapacitor as a Voltage Controlled Saturable Absorber for Femtosecond Pulse Generation,” in *CLEO* (2014).
- I. Baylam, N. Kakenov, O. Balci, C. Kocabas, and A. Sennaroglu, “Graphene-Gold Supercapacitor as a Voltage-Controlled Saturable Absorber for Femtosecond Pulse Generation,” in *Advanced Solid State Lasers Congress* (2015).
- I. Baylam, A. Muti, C. Cihan, S. Ozharar, C. Kocabas, and A. Sennaroglu, “Femtosecond Pulse Generation with Graphene-Gold Supercapacitor Saturable Absorbers near 800 nm,” in *Advanced Solid State Lasers Congress* (2016).

Awards:

- | | |
|------------|---|
| Nov. 2016: | Advanced Solid State Lasers Congress (ASSL 2016) Best Student Oral Presentation Award |
| Oct. 2015: | Advanced Solid State Lasers Congress (ASSL 2015) Best Student Oral Presentation Award |

- Sep. 2014: Fotonik 2014 Best Poster Competition (2nd place)
- Feb. 2013: Newport Research Excellence Award (Travel grant for SPIE Photonics West Conference 2013)

