Dynamics of Saturable Absorption in the Semiconductor-Doped Glass RG850

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Dynamics of Saturable Absorption in the Semiconductor-Doped Glass RG850

A thesis
Presented in
Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE
June, 2015
BY
Pinyaphat Srikrishna

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Acknowledgements

Dr. Landahl

Dr. Sarma

Dr. Gonzalez

…and all the friends and family that helped along the way.
# TABLE OF CONTENTS

## LIST OF FIGURES

5

## LIST OF TABLES

6

## ABSTRACT

7

## CHAPTER

I. MOTIVATION

1.1 Saturable Absorption

8

1.2 Semiconductor-Doped Glass

9

1.3 RG850

11

1.4 Approach

11

II. THEORY

13

2.1 Carrier Generation and Recombination in Semiconductors

13

2.2 Heat Generation

16

2.3 Diffusion

18

2.4 Surface and Bulk Recombination

21

III. EXPERIMENTAL SETUP

22

3.1 Pump probe spectroscopy

22

3.2 Optical Setup

23

3.3 Signal Detection and Recovery

26
# LIST OF FIGURES

**Figure**

1. Energy-wave vector (E-k) diagram of the photogeneration mechanisms.
   (a) Direct bandgap semiconductor. (b) Indirect bandgap semiconductor. ........ 14

2. Heat flow inside RG850, including dimensions ........................................ 17

3. The Gaussian distributions in two dimensions ........................................... 19

4. The pump probe spectroscopy. ................................................................. 23

5. Experimental setup for the pump-probe-spectroscopy experiments. .............. 25

6. Lock-in amplifiers diagram. ..................................................................... 27

7. Results from time-resolved pump-probe absorption measurement of RG850 .... 28

8. Fast time-scale results from time-resolved pump-probe absorption ............... 29

9. Measured laser spectra before and after transmission through the RG850 ...... 34

10. Transient absorption change of RG850 with specific laser powers and double-exponential curve fits ................................................................. 37

11. Slow-time constant determined from double-exponential fit ..................... 38

12. Fast-time constant determined from the double-exponential fit .................. 39

13. Data from Fig. 11 fitted to an inverse laser power relationship ................. 44
LIST OF TABLES

TABLE

1. The calculations of carriers per pulse and carrier density .................................. 31
2. Effective lifetime estimates for RG850 ................................................................. 41
ABSTRACT

The semiconductor-doped glass RG850 is a commercially available optical filter material that has recently been found to also be useful as a saturable absorber for intense ultrafast light pulses. This thesis presents the first experimental study of the time-dependent saturable absorption of RG850 and compares it to a simple electronic model. Even at low light intensities, our data display two distinct decay time constants. This may be indicative of the nanocrystalline structure of this material. We find that the slow-time constant is independent of laser intensity (173 +/- 14 ps), but that the fast-time constant decreases with increasing laser intensity. The ultrafast nonlinear response observed implies that RG850 could be useful in optical computing or other high-speed applications, and that further insights into the mechanism could be gained from additional studies such as time-resolved optical and x-ray spectroscopy.
CHAPTER 1

Motivation

This chapter describes the motivation for this study, namely understanding the mechanism of optical saturable absorption in the semiconductor-doped glass RG850. This chapter also describes the RG850 material, and provides an overview of the entire thesis.

1.1 Saturable Absorption

Saturable absorption is an example of a nonlinear optics effect [1]. Although photons do not usually interact with each other in vacuum, it becomes possible for light to affect light via interaction within a material. These phenomena are rarely observed in everyday life where the intensity of ambient light is usually too low and the magnitude of the nonlinear optical coefficients too small in most materials. High power lasers have made it possible to study these effects in the laboratory, and ultrafast lasers have allowed high powers such as the nearly MW of peak power laser used in this thesis work to be produced on a small optical tabletop. This subject is called “nonlinear optics” because the optical properties depend not just on the material itself (“linear optics”) but also on the intensity of the incident light.

Qualitatively, saturable absorption can be described as a phenomenon where an initially dark piece of optical material (such as the filter glass in sunglasses) becomes lighter when placed under a bright light. This is the opposite phenomenon to “photochromic” sunglasses which actually darken under bright conditions. The central question of this thesis is, once a
material becomes more transparent due to saturable absorption, how long does it stay that way before going dark again? And more quantitatively, can measuring this timescale as a function of incident light intensity help establish the saturable absorption mechanism?

Saturable absorbers have many uses in both optics labs and commercial applications. They form one of the building blocks of optical computers: like transistors where the flow of electrons can be modulated with a control signal, an optical transistor may consist of a saturable absorber that can switch one light beam with another [2]. They are used today in several optical devices where it is useful to prevent the transmission of low intensity optical signals. The particular observation that motivated this study was that a particular semiconductor-doped glass, RG850, is extremely effective at cleaning up the output of high power lasers which often suffer from low-intensity satellite pulses which can disrupt experiments. Saturable absorbers are also used in some ultrafast laser oscillators [3], where saturable absorption encourages laser operation modes where all of the available cavity optical energy is in a single intense pulse that experiences less absorption than lower intensity modes.

1.2 Semiconductor-Doped Glass

Semiconductor-doped glasses often exhibit strong optical nonlinearities and a fast response time [4]. Semiconductor-doped glasses are made of two components: a transparent glass matrix within which “micocrystals” (in fact, nanoscale particles of <100 nm dimensions) of semiconductors are embedded. The traditional processes of manufacturing semiconductor-doped glasses start by adding semiconductor compositions to a silicate glass and heating to
1300°C [5]. Afterward, the glass is cooled down and still colorless, indicating that the semiconductor compositions are not yet uniformly dispersed. The next stage, the glass is reheated to a temperature of about 600 – 700 °C [5]. The microcrystals randomly disperse themselves homogeneously throughout the entire glass, in this stage indicating the microcrystals of semiconductors have grown to the average size. Hence, the microcrystal sizes can be controlled by the temperature and heated time, although in practice there is usually large size dispersion [6]. Semiconductor-doped glasses contain microcrystals with size in the range of 8 – 12 nm [7]. The optical nonlinearity properties of semiconductor-doped glass have been found to depend on diameter of the microcrystals. This diameter can be greater or less than the Bohr radius of the exciton [8]. The difference in diameter explains the difference in their absorption edges [9], as does defects within the semiconductor-doped glasses which perform as electron-hole traps that can lead to nonlinear optical effects [6]. It is very difficult to grow semiconductor crystals of proper dimensions with required band edge, absorption coefficient, and overall optical quality. The advantages of semiconductor-doped glasses are that they are simple and inexpensive to manufacture even to extremely small thickness. In addition, semiconductor-doped glasses have high absorption with a steep absorption edge and fast carrier relaxation times. They can also be produced with very high optical quality, meaning that they can have smooth polished surfaces and uniform thickness. The main application of semiconductor-doped glasses is short wavelength cut-off optical filters. Sets of optical filters containing different absorption edges made of semiconductor-doped glasses are available from different glassmakers, including Schott [10, 11], Hoya [12], and Thorlabs [13].
1.3 RG850

The semiconductor glass used in this study is RG850. The “RG” stand for “Red Glass”, meaning that it transmits longer wavelengths [11]. The “850” stands for the approximate transmission edge, which is 850 nm in the near infra-red. It has been widely available for several decades. The composition of the RG850 nanocrystals is complex and non-uniform. It primarily contains the nanocrystals ZnSe, CdS$_x$Se$_{1-x}$ and CdSe$_x$Te$_{1-x}$ [9]. RG850 has rapid charge carrier relaxation due to ZnSe microcrystal which is a direct bandgap material (discussed in Chapter 2). The exciton Bohr radii of CdS, CdSe, and CdTe are 3, 5.6, and 7.4 nm respectively, which are comparable to the average crystal radius of 11 nm [9]. The particular sample used in this thesis had a thickness of 3 mm, a density of 2.93 g/cm$^3$, and a temperature coefficient of 0.24 nm / °C.

RG850 has a very steep absorption edge, a characteristic that makes it very desirable as a color filter [10, 11]. Its transmission jumps from 1% at 800 nm to 50% at 850 nm. Therefore the sample is mostly but not entirely transparent at our laser wavelength, which is centered at 830 nm and has a spectral width of 20 nm full-width at half-maximum.

1.4 Approach

Our approach was to measure the sample transmission as a function of time following the absorption of an intense “pump” light pulse. This was done by sending a low intensity “probe” pulse through the sample with a varying time-delay after the initial intense pulse. This allowed us to map out the dynamics of the saturable absorption process. In other words, we could watch as the sample returned to its initial transparency level. By repeating the measurement at
different pump laser intensities, we were able to also determine how the intensity changed these dynamics. We propose a model to explain the data based on charge recombination. In this model, electrons are initially excited by the absorption of laser light. The proximity of the absorption edge to the laser wavelength combined with the microcrystalline structure of the material means that there are not a large number of electrons available for absorption. As the laser intensity increases, these absorption electrons are depleted, leaving the sample more transparent. As the electronic excitations of the crystal relax, it returns to its initial transparency value. Finally, the implications of a fast, nonlinear mechanism for semiconductor-doped glass saturable absorption are discussed.
This chapter describes the different theoretical models that might be used to describe saturable absorption in semiconductor-doped glasses. Components of the theory include electron generation, recombination, heat generation, and thermal diffusion. The time dependencies of both thermal and electronic properties are identified.

### 2.1 Carrier Generation and Recombination in Semiconductors

In a semiconductor at zero Kelvin, the valence band is completely full with electrons and the conduction band is completely empty. A small energy gap separates these two bands [14, 15]. In the valence band at this temperature, each atom shares electrons that form bonds. Charge carriers are generated by the absorption of photons if the photon energy is higher than the energy gap of semiconductor [16]. When photons are incident on a semiconductor, electrons are moved from the valence band to the conduction band by absorbing energy and momentum. In the valence band, a vanishing electron is represented by a hole. This type of carrier generation is called photogeneration. However, the carrier generation can also result from other processes (e.g. thermal or electrical) [14]. Carrier generation occurs rapidly, over a few femtoseconds.

The reverse process of carrier generation is recombination [14]. In electron-hole recombination, a higher lying electron in the conduction band recombines with a hole in the
valence band, and emits the excess energy as a either as a photon (radiative recombination) with the energy closed to the bandgap energy of semiconductor or as heat (non-radiative recombination). To summarize, absorption requires photon energy $h\nu \geq E_g$, the semiconductor bandgap; while radiative emission produces photons with $h\nu = E_g$. An incident photon with energy less than $E_g$ will be transmitted through the semiconductor.

![Energy-wave vector (E-k) diagram of the photogeneration mechanisms](image)

Figure 1. Energy-wave vector (E-k) diagram of the photogeneration mechanisms [15, 17, 18, 19]. (a) Direct bandgap semiconductor. (b) Indirect bandgap semiconductor.

The bandgap can be classified as direct or indirect [17]. Fig. 1 shows energy-wave vector (E-k) diagrams of the photogeneration mechanisms for both types of materials. In the case of a direct bandgap, the maximum of the valence band and the minimum of the conduction band have the same wave number, $k$ or the same momentum. In an indirect bandgap semiconductor, the maximum of the valence band and the minimum of the conduction band have a different
wave number. Therefore, the excitation of an electron in an indirect bandgap material needs to be accompanied by an exchange of momentum with the crystal lattice, which can also be described as the absorption or generation of “phonons”. This more complicated process typically results in weaker light absorption as well as longer recombination times than in a direct bandgap material [17].

The simplest form of recombination is radiative recombination [14], in which an electron-hole pair annihilates to emit light. In this sense, it is the opposite of photogeneration. Because two particles (electron and hole) are required, the rate of this recombination process scales as $n^2$, where $n$ is the number of photogenerated carriers. Although quadratic in $n$, the radiative recombination process is expected to dominate in direct bandgap materials, since the process does not require phonons of the proper energy and momentum to be present. A common application of radiative recombination is in Light Emitting Diodes.

Most real semiconductor materials, including RG850, are not pure bulk crystalline materials. Both impurities and surfaces can lead to the presence of intermediate “trap” states, located within the bandgap (above the valence band energy and below the conduction band energy). The recombination therefore depends only on a single charge carrier, and is very sensitive to the number of trap states. In practice, the impurity level can be engineered into the material to alter this recombination rate, which otherwise simply depends linearly on $n$. This recombination process is usually referred to as Shockley-Read-Hall recombination [14].

A third recombination process is frequently found in semiconductors, and depends on the third power of $n$, or $n^3$. This process would be expected to dominate when large numbers
of charge carriers are present, such as would be found at the high laser intensities used during saturable absorption. Referred to as Auger recombination, this is a three-body process. An electron and hole recombine, but instead of releasing the recombination energy as a photon, it gets converted into kinetic energy and momentum of a third charge carrier which remains within the material.

We can combine these recombination rates into a simple rate equation as a function of carrier density $n$ [18],

$$\frac{dn}{dt} = -An - Bn^2 - Cn^3$$  \hspace{1cm} (1)

where $A$ is the Shockley–Read–Hall recombination coefficient, $B$ is the radiative recombination coefficient, and $C$ is Auger recombination coefficient. Equation (1) anticipates that any electronic effects in the sample would be likely to have nonlinear decay dynamics characterized by this ordinary differential equation.

2.2 Heat Generation

The energy of the light absorbed by semiconductors can be released as light (through radiative recombination) or carrier kinetic energy (through Auger decay) but is also likely to result in some heating of the material. In addition to phonon-mediated decay in indirect gap semiconductors discussed above, even in direct-gap materials incident photon energy exceeding the bandgap energy will generally be transferred to the lattice in the form of thermal energy, $E_{th} = E_g - h\nu$. Even the high-energy carriers produced in Auger decay are likely to eventually deposit their energy into the lattice via carrier-carrier and carrier-lattice scattering.
Although this process is longer than photogeneration, it is still relatively rapid, on the order of a few picoseconds.

Figure 2. Heat flow inside RG850, including dimensions relevant to these measurements.
2.3 Diffusion

Following photogeneration, both heat and charge will diffuse through a material at their own characteristic diffusion speeds. However for RG850 we expect that bulk electron diffusion will not occur, since the semiconductor structures are embedded in an insulating material (glass) as described in Chapter 1. However we will consider thermal diffusion. Specifically the sample excitation geometry may be approximated in two-dimensions with a cylindrical symmetry shown in Fig. 2: a circular laser beam that is a few microns in radius penetrates hundreds of microns deep in the sample material.

The initial transverse distribution of temperature is given by the Gaussian distribution, because the laser beam also has a Gaussian intensity profile in the transverse direction. At time $t = 0$, the initial temperature is the highest at point $x = 0$ and $y = 0$ then heat is immediately transferred to the other points of the sample when time increases. The two dimensional Gaussian distribution is given as

$$f(x, y) = \Theta_0 e^{-a(x^2+y^2)}$$ \hspace{1cm} (2)

where $\Theta_0$ is temperature at initial time $t_0$ at point $x = 0$ and $y = 0$ and $a$ is the laser diameter.

The two-dimension Gaussian distribution is shown in Fig. 3.
Heat flow is calculated using the two-dimensional diffusion equation. The fundamental solution for the two-dimensional heat equation is

$$\theta(x, y, t) = \frac{1}{4\pi Dt} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(u, v) e^{-\frac{(x-u)^2+(y-v)^2}{4Dt}} dudv$$

(3)

where $D$ is thermal diffusivity.

Substituting Equation (2) into Equation (3),

$$\theta(x, y, t) = \frac{1}{4\pi Dt} \theta_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left[-au^2 - av^2 - \left\{ \frac{x^2 - 2xu + u^2 + y^2 - 2yv + v^2}{4Dt} \right\} \right] dudv$$

or,
\[
\theta(x, y, t) = \frac{1}{4\pi Dt} \theta_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[ \frac{-4aDtu^2 - 4aDt v^2 - x^2 - y^2 + 2xu + 2yv - u^2 - v^2}{4Dt} \right] dudv
\]

This double integral can be rewritten
\[
\theta(x, y, t) = \frac{1}{4\pi Dt} \theta_0 \exp \left[ \frac{-a(x^2 + y^2)}{1+4aDt} \right] \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[ \frac{-(1+4aDt)}{4Dt} \left( u - \frac{x}{1+4aDt} \right)^2 + \left( v - \frac{y}{1+4aDt} \right)^2 \right] dudv
\]

Two substitutions allow for the integral to be solved analytically:

\[
A = \sqrt{\frac{1+4aDt}{4Dt}} \left[ u - \frac{x}{1+4aDt} \right]
\]

and

\[
du = \sqrt{\frac{4Dt}{1+4aDt}} dA
\]

\[
B = \sqrt{\frac{1+4aDt}{4Dt}} \left[ v - \frac{y}{1+4aDt} \right]
\]

and

\[
v = \sqrt{\frac{4Dt}{1+4aDt}} dB
\]

leading to
\[
\theta(x, y, t) = \frac{1}{4\pi Dt} \theta_0 \sqrt{\frac{4Dt}{1+4aDt}} \sqrt{\frac{4Dt}{1+4aDt}} \exp \left[ \frac{-a(x^2 + y^2)}{1+4aDt} \right] \int_{-\infty}^{\infty} \exp \left[ - A^2 \right] dA \int_{-\infty}^{\infty} \exp \left[ - B^2 \right] dB
\]

which may be directly evaluated to
\[
\theta(x, y, t) = \frac{1}{(1+4aDt)} \theta_0 \exp \left[ \frac{-a(x^2 + y^2)}{1+4aDt} \right]
\]

(4)

When \( x = 0 \) and \( y = 0 \), we find
\[ \theta(x = 0, y = 0, t) = \frac{1}{(1 + 4aDt)} \theta_0 \]  \tag{5}

where \( \theta_0 \) and \( \theta \) are temperature at initial time \( t_0 \) and temperature at all subsequent times respectively, \( a \) is laser diameter, \( D \) is thermal diffusivity, and \( t \) is time. Equation (5) indicates that any thermal effects in the sample would be expected to have a \( t^{-1} \) time dependence.

### 2.4 Surface and Bulk Recombination

Shockley–Read–Hall carrier lifetimes contain information about both surface and bulk properties of the material including structural quality, doping level, and the injection of carriers. The total carrier recombination lifetime \( \tau_T \) is the summation of the reciprocal of surface recombination lifetime \( \tau_S \) and bulk recombination lifetimes \( \tau_B \) \[18, 19, 20\],

\[ \frac{1}{\tau_T} = \frac{1}{\tau_B} + \frac{1}{\tau_S} \]  \tag{6}

where \( \tau_B \) is bulk recombination lifetime (slow-time constant due to the recombination away from the surfaces), and \( \tau_S \) is surface recombination lifetime. Furthermore, the surface recombination lifetime is related to other sample parameters \[14\],

\[ \frac{1}{\tau_S} = \frac{2\alpha^2 D}{1 + \sqrt{1 + \frac{8\alpha^2 D^2}{S^2}}} \]  \tag{7}

where \( \alpha \) is absorption depth, \( D \) is thermal diffusivity, and \( S \) is the surface recombination velocity. Equation (6) indicates that even at low carrier excitation, a material made of microcrystals such as RG850 might be expected to have two distinct carrier lifetimes.
3.1 Pump probe spectroscopy

In our experiment, an ultrafast time-resolved pump-probe technique is used to measure the time-dependent optical absorption of the ZnSe semiconductor doped glass RG850. The concept of the transient absorption pump-probe approach is shown in Fig. 4. In this method, the time resolution of the experiment depends on the pulse duration of the laser, which in our case is 50 fs. The output from this “ultrafast” laser is split into two unequal parts: pump pulse and probe pulse. When the intense pump pulse is incident on our sample, electrons are excited from the valence to the conduction band, leaving holes behind in the conduction band. Increasing the power of the pump pulse will create a higher population of electrons in the conduction band and leave behind more holes in the valence band. The sample is not damaged at the power levels used in this experiment, and so it eventually must relax back to its original, equilibrium state by electronic and/or thermal processes, as discussed in Chapter 2.

Our 3 mm thick sample (see Fig. 2) has a 0.45 mm absorption depth, resulting in low total transmission. A delayed probe pulse, too weak to affect the relaxation dynamics, is also directed on to the sample at the same position. As the delay of the probe pulse is increased, the sample’s optical transmission approaches its equilibrium value. The largest departure from equilibrium properties are seen when the probe pulse most closely follows the pump pulse (i.e. at small time delays). If the probe pulse delay is adjusted such that it arrives before the pump
pulse, only the equilibrium behavior of the sample is measured [4]. The spacing between pump pulses is chosen to be long enough (in our case 10 ns) that the sample has completely recovered before the experiment is repeated [18].

Figure 4. Pump probe spectroscopy. Illustrative pump-probe delays shown in the upper figure result in the time-dependent optical absorption shown in the lower figure. In a photobleaching experiment such as this one, the largest transmission signal is seen when the probe pulse follows the pump pulse with only a brief delay, such as with the labeled “Probe 1” pulse.

3.2 Optical Setup

The laser used for the experiment utilizes a Ti:Sapphire crystal as its gain medium. The Ti:Sapphire crystal is pumped with a commercial “VERDI” (Coherent, Inc.) 5 W green laser
operating at 532 nm. This corresponds to the peak absorption wavelength of Ti:Sapphire. Ti:Sapphire has an extremely broad emission spectrum that is centered at 800 nm. This large bandwidth enables it to lase over a large number of wavelengths and is a pre-requisite for generating fast pulses. In our case, the laser is operated over a 20 nm bandwidth, which has a Fourier Transform of 50 fs. A nonlinear mechanism inside the Ti:Sapphire crystal itself (the optical Kerr effect) serves to lock the phases of all of the laser modes within this bandwidth together to synthesize a single short pulse which circulates within the 10 ns long laser cavity. A 90% reflective output coupler mirror allows 10% of the optical power in the pulse to exit the cavity for use in our experiments on each round trip. Due to the regular spacing of the pulses, this ultrafast laser is referred to as a “laser oscillator” and is shown schematically within the rest of our experiment in Fig. 5. The first optical component after the oscillator is a set of prisms used for “dispersion control” which allow the phase relationship of the broad bandwidth of laser modes to be maintained despite propagation through many different optical components in the experiment.

Following the prism compressor, the laser is divided into the pump and probe pulses by a beam splitter. The intensity of the pump pulse may be adjusted from 20 to 200 mW by inserting different calibrated neutral-density optical filters into its beampath. A calibrated calorimetric power meter is used to verify the pump pulse average power. The pump pulse travels a fixed distance but the probe pulse beampath includes a stepper motor-driven 25 mm long delay stage that is controlled by LabView so the delay time between pump and probe pulse can be varied between -10 and +75 ps. LabView is programmed to provide both a fine
timescan at short delays where the data is changing rapidly as well as a coarse displacement scan over longer times. The fine scan uses a step size of 1 micron over 1 mm to yield 1000 data points. The coarse scan steps over 22 mm in 0.1 mm step sizes to acquire 220 data points. The total acquisition time for both scans is 72 minutes.

Figure 5. Experimental setup for the pump-probe-spectroscopy experiments.
3.3 Signal Detection and Recovery

After the sample has been excited by the pump pulse, a change in the sample transmission is monitored by the probe pulse. The peak intensity of the transmitted probe pulse is measured by a silicon photodiode. The probe pulse’s intensity is very small due to the large absorption of the RG850 sample, and furthermore the changes in probe pulse absorption due to the pump may also be very small. Therefore a lock-in amplifier is used to selectively amplify the small changes in the probe signal. In our apparatus, we modulate the pump beam using a mechanical chopper at 1 kHz and use the lock-in amplifier to extract modulations of the probe beam at this frequency. This is a general version of a phase-sensitive detection technique, and is described schematically in Fig. 6. Briefly, the lock-in amplifier uses a bandpass filter which can detect input signals at a narrow bandwidth near 1 kHz. Most naturally occurring noise however is inherently broadband and falls off monotonically at higher frequencies. Thus, the noise signal within this narrow frequency range will be very small, and the resulting signal-to-noise ratio may be quite large, allowing signals to be recovered which are well below the inherent noise limit at all frequencies. This integrated noise level is close to 1 mV for most electronics, and we were able to obtain noise levels of 1 μV or less using the 1 kHz mechanical chopper. In principle, even greater sensitivity could be obtained using a higher frequency modulation, which could be accomplished using electro-optic (rather than mechanical) techniques. To compensate for small drifts in probe beam power, a normalization diode monitors the probe beam before the sample, and is used as a reference by the lock-in
amplifier. The data taken using these techniques that is analyzed in this thesis are shown in Figs. 7 and 8.

During the pump-probe measurements, the pump pulse is also monitored using an optical grating fiber-coupled spectrometer. The pump pulse is too weak to be measured by the spectrometer in the current apparatus.

Figure 6. Lock-in amplifier diagram [20]. The phase shifter circuit will shift the reference phase with respect to input signal by adjusting the reference phase to 0° or 180° to get maximum output. The input signal and reference are multiplied in a phase-sensitive detector or analog multiplier. Because the measurements are always disturbed by the large noise signals, the amplifier gain is adjusted to keep the amplified signals at a measurable level and is set very low so the noise signal is not to large. Thereafter, the result is filtered by a low pass filter or a basic RC circuit. The noise signals are attenuated by the low pass filter. The signal is only detected by the phase-sensitive detector and low pass filter if it approximately coincides to the modulation frequency in the reference signal.
Figure 7. Results from time-resolved pump-probe absorption measurement of RG850 using 800 nm wavelength femtosecond laser excitation. Different incident laser powers are shown offset for clarity. Lock-in amplifier gain was adjusted for each incident power level, resulting in different noise levels for each scan. The data inside the rectangle was taken at small step sizes and is shown in Fig. 8.
Figure 8. Fast time-scale results from time-resolved pump-probe absorption measurement of RG850 using 800 nm wavelength femtosecond laser excitation. Different incident laser powers are shown offset for clarity using the same arrangement as in Fig 7. The data inside the rectangle in Fig. 7 are displayed in this plot.
CHAPTER 4
Measurement of ZnSe Density

In this chapter, both laser and sample parameters are used to calculate the density, mass, and number of charge carriers generated in our experiments. These numbers will be used in the following chapter to investigate an electronic model for RG850 saturable absorption.

4.1 The carriers per pulse and carrier density

In our experiments, the ultrafast laser pulse has a few micron spot size, 100 MHz repetition rate, and 800 nm center wavelength. The measurement and analysis procedure has been performed with the laser power ranging between 20 mW to 186 mW by attenuating the output from an ultrafast laser pulse with a range of neutral density filters. The neutral density filters are a set of filters that absorb light without any significant reflection, scattering, or alteration of the spectrum.

From the Plank relation,

\[ E = \frac{hc}{\lambda} \]  

where \( h \) is Planck’s constant, \( c \) is speed of light, and \( \lambda \) is wavelength, the energy per photon of 800 nm center wavelength is 1.67 eV or \( 2.49 \times 10^{-19} \) J. The energy bandgap of RG850 is 1.46 eV or \( 2.49 \times 10^{-19} \) J, corresponding to 850 nm (in agreement with the manufacturing code RG850). The energy of our laser photons are therefore above the bandgap of RG850 and so charge carriers
are generated upon absorption. The total number of photons per pulse can be determined by dividing the average laser power by the repetition rate and photon energy. For example, given an ultrafast laser power is 186 mW, the number of photon per pulse is

\[
\frac{186 \text{ mJ}}{2.49 \times 10^{-19} \text{ J} \times \frac{1 \text{s}}{100 \times 10^6 \text{ pulse}}} = 0.75 \times 10^{10} \frac{\text{photons}}{\text{pulse}} \tag{9}
\]

One absorbed photon generates one electron-hole pair. Since the majority of the pump pulse is absorbed, we find that 0.75x10^{10} electrons per pulse are moved to the conduction band for 186 mW laser pulse power. Carrier density can be computed by dividing the amount of carriers per pulse by the volume of an ultrafast laser pulse on the sample. The volume of laser pulse on the sample is obtained from a few micron laser spot size and 3 mm thick RG850.

\[
\text{Carrier Density} = \frac{0.75 \times 10^{10} \frac{\text{photons}}{\text{pulse}}}{(1 \mu\text{m})^2(3 \text{ mm})} = 2.50 \times 10^{18} \text{ cm}^{-3} \tag{10}
\]

From our calculations the range of carrier densities corresponding to the laser powers between 49-186 mW will be 6.57x10^{17}-2.50x10^{18} cm^{-3}. The calculations of carriers per pulse and carrier density are given in Table 1.

<table>
<thead>
<tr>
<th>Laser Power (mW)</th>
<th>Carriers per pulse (carriers)</th>
<th>Carrier Density (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.08x10^{10}</td>
<td>2.68x10^{17}</td>
</tr>
<tr>
<td>49</td>
<td>0.20x10^{10}</td>
<td>6.57x10^{17}</td>
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<tr>
<td>113</td>
<td>0.46x10^{10}</td>
<td>1.52x10^{18}</td>
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<td>166</td>
<td>0.67x10^{10}</td>
<td>2.23x10^{18}</td>
</tr>
<tr>
<td>186</td>
<td>0.75x10^{10}</td>
<td>2.50x10^{18}</td>
</tr>
</tbody>
</table>
From Table 1 increasing the energy of power of the laser pulse will increase the concentration of the carriers per pulse and also carrier density. For comparison, in semiconductors the equilibrium density of electrons and holes in conduction band and valence band is usually less than $10^{20}$ cm$^{-3}$ [7].

4.2 Internal transmittance of RG850

The internal transmittance is defined as the ratio of the intensity of transmitted laser pulse to the intensity of incident laser pulse [7, 15]. The intensity of transmitted laser pulse is attenuated according to the exponential function as given by

$$\text{Internal Transmittance} = \frac{I_{out}}{I_{in}} = e^{-d/\Delta d} \quad (11)$$

where $I_{out}$ and $I_{in}$ are intensity of transmitted laser pulse from sample and intensity of incident laser pulse to sample respectively, $d$ is the thickness of sample, and $\Delta d$ is absorption depth. The absorption depth is the distance that a laser pulse penetrates inside the element before the intensity of the laser pulse drops due to $1/e$ of its original value. We calculated the absorption depth of RG850 by using this equation corresponding to the internal transmittance from RG850 data sheet at 800 nm wavelength and thickness of RG850. The internal transmittance at 800 nm wavelength of RG850 is $1.2 \times 10^{-3}$ and the thickness of our RG850 sample is 3 mm. This small transmission is in agreement with the use of a laser photon energy which is above the bandgap, and yields an absorption depth of

$$\Delta d = \frac{-3 \text{ mm}}{\ln(1.2 \times 10^{-3})} = 0.446 \text{ mm.} \quad (12)$$
We used this absorption depth to calculate the mass of RG850. The density of RG850 is 2.93 $g/cm^3$ and the radius of the focused laser was estimated to be 0.5 micron from the focusing optics used. The mass of RG850 absorbing laser light is therefore

$$mass = \rho \Delta d \pi r^2 = 2.93 \frac{g}{cm^3} \times 0.446 \ mm \times 3.14 \times (0.5 \ \mu m)^2 \times 0.00103 \ \mu g. \quad (13)$$

### 4.3 Total transmittance of RG850

Total transmission is the ratio of transmitted signals in the sample to the reference signals as a function of wavelength. We measured the spectrum of the Ti:sapphire laser both when it was mode locked (producing ultrashort pulses) and operating in Continuous Wave (CW) mode. The mode-locked signal was measured both directly and after passing through the RG850 sample. The three normalized spectra are shown in Fig. 9.
Figure 9. Measured laser spectra before (green) and after (blue) transmission through the RG850 sample at low intensity. The output spectra of the laser in CW mode is shown in red. All spectra have been normalized to maximum intensity.

From Fig. 9 the peaks of the CW mode and incident pulsed laser are at 815 nm and 830 nm respectively, but after transmission through the RG850 sample the pulsed laser spectrum peaks at 839 nm. The redshift is due to the wavelength-dependent absorption of RG850, which increases dramatically at 850 nm, with the exact transition wavelength determined by temperature as described in the previous section. For each temperature the total transmission can be determined by integrating over all wavelengths,
\[ Total\ Transmission = \frac{\int_{-\infty}^{\infty} I(\lambda)T(\lambda - \Delta\lambda)d\lambda}{\int_{-\infty}^{\infty} I(\lambda)d\lambda} \quad (14) \]

where \( I(\lambda) \) is output laser spectra and \( T(\lambda - \Delta\lambda) \) is spectral transmittance. It is the total transmission that is measured in the pump-probe experiments presented in this thesis.
CHAPTER 5

Charge Carrier Analysis

Nonlinear behavior at short-timescales suggests using an electronic model. The simple carrier recombination model used appears to recapitulate our data. Notably, it ignores electron diffusion, which we do not expect to play a role in this microcrystalline material.

5.1 Double Exponential Decay

Measuring the transmitted probe pulse as a function of time delay for all specific laser powers, we observed that the optical transmission of RG850 rapidly increases, and then decays. The sample had fast recovery seen as a sharp decay component at early times which is followed by a slow relaxation as shown in Fig. 7. The two-component behavior suggests representing our data with a double exponential decay function

\[ y = e^{-\frac{t}{\tau_1}} + e^{-\frac{t}{\tau_2}} \]  \hspace{1cm} (15)

where \( y \) is transmission, \( t \) is time, and \( \tau_1 \) and \( \tau_2 \) are time constants. This allows us to separate our results into two parts: a fast time constant of decay \( \tau_1 \) at early time and followed by a slow time constant of decay \( \tau_2 \). We fitted all decay curves by double exponential decay function as shown in Fig. 10.
Figure 10. Transient absorption change of RG850 with specific laser powers and double-exponential curve fits. Different laser powers are shown offset for clarity. The fine time-point scans shown inside the rectangle are displayed in the inset. The double exponential fit is shown as the dark solid line.
Strikingly, the fast time constant monotonically decreases with increasing laser power, while the slow time constant appears to be laser power independent. The slow- and fast-time constants are plotted as a function of incident laser power in Fig. 10 and Fig. 11, respectively. Error bars are determined both from the residuals as well as the noise levels in the fits shown in Fig. 9.

Figure 11. Slow-time constant determined from double-exponential fit shown in Fig. 9. The time constant does not correlate with the incident laser power 166 mW data point.
Figure 12. Fast-time constant determined from the double-exponential fit shown in Fig. 9. The time-constants decrease monotonically with incident laser power.

The time constants of fast decay $\tau_1$ are approximately in picosecond and time constants of slow decay $\tau_2$ are approximately in hundreds of picoseconds. These can be compared with only a few other values for similar materials reported in previous literature, such as H. Wang et al. [21] and A. K. G. Tapia et al. [22]. H. Wang et al. used time-resolved photoluminescence technique for bulk ZnSe and found values of fast time constants about 43.3 ps, 37.5 ps, 33.4 ps, and 26.1 ps and the values of slow time constants about 2.36 ns, 2.96 ns, 4.43 ns, and infinity at
temperature 77 K, 110 K, 150 K, and 296 K respectively. A. K. G. Tapia et al. used optical-pump terahertz-probe spectroscopy techniques for bulk ZnSe and found value of fast time constant about 23.98 ps and the value of slow time constant about 0.88 ns.

5.2 Surface recombination

One possible explanation of the two lifetimes is that one is from surface recombination while the other is from bulk recombination, as discussed in Chapter 2. This hypothesis is particularly attractive since semiconductor-doped glass has a very large effective surface area due the nanocrystallites. To test this, we estimated the surface recombination lifetimes of RG850 by using Eq. 7. We used the same surface recombination velocity as H. Wang et al [21], \( S = 5.8 \times 10^5 \) cm/s, \( \alpha = 22.42 \text{ cm}^{-1} (=1/(0.446 \text{mm})) \) at room temperature, but inserted our carrier density estimates from Chapter 4. The calculations are displayed in Table 2. The surface recombination lifetime is so long (hundreds of microseconds), that it would have no effect on our measured effective lifetimes for these measurements at sub-nanosecond timescales.
Table 2 Effective lifetime estimates for RG850

<table>
<thead>
<tr>
<th>Laser Power (mW)</th>
<th>Measured slow timescale, $\tau_B$ (picosecond)</th>
<th>Estimated Surface Recombination Lifetime, $\tau_S$ (millisecond)</th>
<th>Effective Lifetime, $\tau_T$ (picosecond)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>184.98</td>
<td>0.1326</td>
<td>184.98</td>
</tr>
<tr>
<td>49</td>
<td>181.09</td>
<td>0.1170</td>
<td>181.09</td>
</tr>
<tr>
<td>113</td>
<td>180.01</td>
<td>0.1326</td>
<td>180.01</td>
</tr>
<tr>
<td>166</td>
<td>149.59</td>
<td>0.1326</td>
<td>149.59</td>
</tr>
<tr>
<td>186</td>
<td>169.22</td>
<td>0.1243</td>
<td>169.22</td>
</tr>
</tbody>
</table>

These results indicated bulk recombination is the dominant to total recombination lifetime in our sample. Determining exactly what types of bulk recombination processes such as the Shockley–Read–Hall recombination, radiative recombination, and Auger recombination are taking place however requires a more sophisticated model using the recombination rate equation.

5.3 Bulk recombination

One possibility that could explain multiple decay constants, as well as intensity-dependent (nonlinear) decay constants is if multiple recombination processes are involved in the recombination dynamics. These processes were reviewed in Chapter 1. In order to acquire all coefficients: (the Shockley–Read–Hall recombination coefficient, the radiative recombination coefficient, and the Auger recombination coefficient), it would be necessary to fit our entire set
of experimentally determined transient transmission curves over the full range of incident laser powers to solutions of the nonlinear ordinary differential equation for these processes[1]. Instead we make two major assumptions and consider two limiting cases which allows a considerable simplification of the analysis.

First, we assume that electron diffusion play no role in the dynamics. This is in contrast to most published studies of bulk semiconductor electrical properties, where diffusion of charge carriers away from the photogeneration spot is a dominating factor in the dynamics. In particular, the rapid decrease in carrier density caused by diffusion results in significant reduction in the higher order nonlinear recombination rates. We make this assumption because of the structure of the RG850 material. The individual crystallites of ZnSe are separated by large distances of non-conducting glass material, through which the charges can not travel. Thus each photogenerated charge carrier pair is confined to a small volume from which it can not escape, except by recombination. This confinement feature is likely responsible for the large size of the saturable absorption effect.

Second, we assume that we are unable to measure the Auger term, which depends on the third power of electron density. This is based on the fact that only two time constants are observed, and the Auger effect should only dominate at the highest carrier densities and shorter timescales. This leaves us with a modified carrier recombination equation,

$$\frac{dn}{dt} = -An - Bn^2$$  

(16)

Next, we consider the limiting case of small carrier concentration, which should be valid at long times after most of the charge carriers have recombined,
\[
\frac{dn}{dt} = -An. \quad (17)
\]

Eq. (17) is simply the ordinary differential equation for linear decay, and it is intensity-independent. Normalizing the carrier density using \( N = n/n_0 \), where \( n(t=0) = n_0 \) and \( N(0)=1 \), Eq. (17) becomes

\[
\frac{dN}{dt} = -AN, \quad (18)
\]

and taking the weighted average of the data shown in Fig. 11 we obtain \( A^{-1} = \tau_2 = 173 \pm 14 \) ps for the linear recombination coefficient for RG850.

At high carrier concentrations, present at early times, Eq. 16 can be approximated as

\[
\frac{dn}{dt} = -Bn^2 \quad (19)
\]

or using the normalized carrier density \( N \),

\[
\frac{dN}{dt} = -Bn_0N^2 \quad (20)
\]

This can be thought of as a linear rate equation where the instantaneous time constant is

\[
\tau_1N = \frac{1}{Bn_0} \quad (21)
\]

This relationship implies that the short-time constant should decrease as the laser power (and therefore initial carrier density) increases, as observed in our data. Curve fitting the data in Fig. 11 to an inverse laser power relationship (Fig. 13) yields an approximation for \( \tau_1 = 92 \pm 46 \) mW-ps.
Figure 13. Data from Fig. 11 fitted to an inverse laser power relationship. The response time of the saturable absorption gets faster as the laser power increases.

Using the estimate from Eq. 10 of $10^{16} \text{1/(mW-cm)}^3$ for the photogenerated charge density, our data allows us to estimate the magnitude of the ultrafast nonlinearity in RG850 saturable absorption as $10^{18} \text{ps/cm}^3$. To the best of our knowledge, this is the first time this parameter has been estimated for a semiconductor-doped glass.
CHAPTER 6

Conclusions

Ultrafast pump-probe spectroscopy was used to observe the transient bleaching response in the semiconductor-doped glass RG850 following above-gap intense optical excitation. We found RG850 exhibited saturable absorption, in agreement with previous observations. Furthermore, we found that the dynamics could be explained with a simple electronic recombination model, neglecting diffusion which should not play a role in semiconductor-doped glass. At short timescales we observed a nonlinear response of the material, where the decay time decreased as incident laser intensity increased. We have estimated the order of magnitude of this nonlinearity. This nonlinear ultrafast response we have observed may prove useful for designing high-speed optical devices. For instance, the few picosecond duration photobleaching we observed in these experiments would make optical logic operations at 100 GHz possible. In principle, extrapolating from the response we measured, charge carrier concentrations of $10^{21} \text{ cm}^{-3}$ (which are routinely obtained in table-top systems) might be able to induce ultrafast reversible photobleaching at the femtosecond timescale.

A complete understanding of this phenomenon will require additional theoretical work, perhaps in conjunction with other ultrafast measurements. In particular, measuring the optical absorption changes at different wavelengths might help explain exactly which competing nonlinear processes determine the fastest timescale behavior.
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