UNIVERSITY OF CYPRUS
DEPARTMENT OF PHYSICS

FEMTOSECOND PUMP-PROBE
TRANSIENT ABSORPTION
SPECTROMETER

MYRTO SAVVA

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Introduction

Laser ultrafast pulses have been key factor in studying and understanding ultrafast processes in novel material over the past decade. Such pulses have time duration of the order of femtoseconds. The ability to study and understand transient processes in material is a gold mine in developing novel devices for optoelectronic applications.

A basic technique which is widely used in time-resolved spectroscopy, is the so-called pump-probe (PP) spectroscopy. In a typical pump-probe technique, an ultrafast pulse is divided into the strong pulse (pump) used to excite the material and the much weaker pulse (probe) which monitors the pump-induced changes in the reflection or transmission. The probe beam is initially utilized to produce white light generation and in turn is directed on to the excitation region of the sample. Narrow band pass filters are then used to select the probing wavelength. This however is a long process since one has to take measurements over broad range of the white light. In this work we are setting up a spectrometer system equipped with a fast CCD array to simultaneously make measurement over a broad range of wavelengths. This is a nontrivial task given the required synchronization of the femtosecond laser amplifier running at 1kHz with the CCD array and the optical chopper.

In Chapter 1 ‘The principles of laser’, some useful definitions and phenomena are introduced, such as linear and nonlinear optical effects which include the Kerr effect and Harmonic Generation. Next, the basic theory of ultrashort pulses is introduced, with an emphasis on their outstanding features for use in time resolved spectroscopy. The supercontinuum generation of white light used as the probe pulse in the time resolved measurements is described as well. Also, the most important aspects of the Generation of
ultrafast pulses are explained, covering the Q-switch lasers, the mode-locking technique, Titanium-Sapphire lasers and Chirped pulse amplification.

Chapter 2 ‘Experimental techniques’ is devoted to the description of experimental set-up of the pump probe spectroscopy as well as the spectrometer system employed in the presented work. Here, important details of the experimental configuration are further presented while the various modifications between a typical pump-probe technique and the pump-probe transient absorption spectrometer are highlighted.

Chapter 3 ‘Data analysis’ is devoted to the description of properties of Polysilicon thin films and their characterization. For this purpose, there is a brief discussion about the ‘free-carrier absorption’ and ‘state filling’ effects which occur during the measuring process. Further, a presentation of the experimental results acquired by measuring the differential transmission takes place for three different thicknesses of the sample material. In addition, the experimental data is analyzed in order to determine the relaxation times of the photo-excited carriers so as to draw conclusions about the carrier dynamics of the sample.

A summary of the key results from the femtosecond time resolved spectroscopy presenting a convergent picture of the ultrafast dynamics in Polysilicon thin films is presented. References are also appended at the end of the thesis.
Chapter 1

The principles of Laser

1.1 Laser

Laser is an amplifier of electromagnetic waves with positive feedback. The term ‘laser’ originated as an acronym for Light Amplification by Stimulated Emission of Radiation, which describes very succinctly how a laser works. Laser consists of the three following basic features: a source of energy, the optical cavity within which the light is contained by two mirrors (one of which is semitransparent) and the active medium which varies among different types of laser. The radiation emitted by the source stimulates the active medium where photons are traveling in the gain medium to produce other identical photons via stimulated emission.

The light that remains in the cavity gives the positive feedback for the amplifier while the laser output is the exiting light. Therefore, the light is amplified by traveling backwards and forwards in the cavity.

The emitted light has numerous wavelengths and phases. When the phases of the different wavelengths are the same, the radiation intensity rises due to constructive light interference upon reflection from the mirrors. This indicates that the optical cavity acts as a frequency filter: only the wavelengths that satisfy the following condition (1.1):
will survive in the cavity and are called longitudinal modes of the cavity.

\[ n \frac{\lambda}{2} = L, n = 1, 2, 3, ... \]  

(1.1)

1.2 Linear Optical Effects

Linear optics, as a fundamental field of optics, describe basic optical effects such as reflection, refraction and diffraction. Linear optics apply in a variety of common optical components and systems like lenses, mirrors, diffraction gratings and so on.

Their most significant properties, which do not apply in nonlinear optical effects, include some of the following: A monochromatic light entering an unvarying linear optical system maintains the same frequency when exiting through the output. Plus, the major
principle of superposition is valid for linear-optical systems. As an example, if a mirror transforms light input A into output B, and input C into output D, then an input consisting of A and C simultaneously give an output of B and D simultaneously. Finally, if the input light is made more intense, then the output light is more intense but otherwise unchanged.

In linear optics, the induced polarization in a medium is proportional to the external optical electric field and can be given as

\[ \vec{P} = \varepsilon_0 \chi \vec{E} \]  

where \( \varepsilon_0 \) is the vacuum permittivity and \( \chi \) is the electric susceptibility of a medium. This is a scalar relationship only in isotropic (linear) materials.

1.2.1 Dispersion

In optics, dispersion is the dependence of refractive index on the frequency (or wavelength) of light. This is a phenomenon which is actually linear and occurs when white light passes through a transparent medium and the beam is then splitted into its seven constituent colours. In particular, transparent materials exhibit normal dispersion, meaning that the refractive index increases with frequency (or decreases with wavelength). As a result, the speed of light in the material is reversely proportional to its refractive index; therefore the blue photons (shorter wavelength) travel more slowly than the red ones. This means that if a transform limited pulse passes through a transparent medium, its duration will increase.

Dispersion of light is due to the fact that white light consists of seven different colors and each color has different angle of deviation. Therefore, when passing through the transparent material (e.g. a prism), different colors deviate through different angles. If the medium exhibits normal dispersion, the red photons will exit the material earlier, and the blue ones later. A spectrum will then be formed, since the seven colors of white light will separate. Out of the seven colors, the red colors deviates the least, so it is present at the top of the spectrum, whereas the violet color deviates the most, hence it is present at
the lower end of the spectrum.

Figure 1.2: This figure presents the dispersion of white light when passing through a prism. Each color has different angle of deviation as shown.

As regards the ultrafast laser spectroscopy, dispersion can be a major problem as it is responsible for broadening the ultrashort pulses. In order to avoid this effect, optical components of femtosecond beam lines (such as lenses, waveplates or polarizers) are made as thin as possible.
1.3 Nonlinear Optical Effects

Nonlinear optical effects occur when a light beam of high intensity is propagating through the optical elements. In such a case, equilibrium conditions cease to apply; hence, positively charged particles move in the direction of the field whilst negatively charged particles move in the opposite direction. Dipole moments are then created due to this relative displacement of positively and negatively charged particles so the material is said to be polarized. The induced polarization, in turn, can be described as the dipole moment per unit volume. This stands for the real materials, which, in general, are anisotropic crystals (i.e. their properties change with direction along the object) and linear susceptibility becomes a $3 \times 3$ matrix:

$$P_i = \varepsilon_o \left( \sum_i \chi^{(1)}_{ij} E_j + \sum_{ij} \chi^{(2)}_{ijkl} E_i E_j + \sum_{ijk} \chi^{(3)}_{ijkl} E_i E_j E_k + ... \right)$$  

(1.3)

When the magnitude of the electric field is small (which implies low light intensity), higher order terms do not contribute to the polarization. In consequence, the relation between the magnitude of polarization and electric field is approximately linear and can be expressed by the equation 1.2. If sufficiently higher intensities of light are used, polarization dependence on the electric field acquires higher order terms (eq. 1.3). These terms may become important and are responsible for the nonlinear optical effects.

Comparing linear optics with nonlinear optics, we can note that optical properties of materials are independent of intensity at linear optics and this is something that does not apply in nonlinear optics. Furthermore, the principle of superposition is violated at nonlinear optics. Lastly, not only can the frequency of light going through a medium change, but also light can control light in nonlinear optics, since two beams of light in the same region of a medium affect each other. The last mentioned contradict the properties of linear optical effects.
1.3.1 Harmonic generation

Harmonic generation is the easiest way of extending the range of frequencies a laser can access. In this manner, despite the small energy losses that may exist during the process, enough amount of produced light can be achieved for performing time-resolved spectroscopy with an efficiency of about tens of percent.

Using harmonic generation from light of frequency $\omega$, light with frequencies of integer multiples of $\omega$ can be obtained. If an electric field described by a plane electromagnetic wave is assumed:

$$E = E_0 e^{-i(\omega t - kz)}$$  \hspace{1cm} (1.4)

where $k = \frac{2\pi}{\lambda} = \frac{\omega}{c} n$ is the wave vector (wave number in one-dimensional case), and the electric field is strong enough, combined with the equation 1.3 for nonlinear polarization, the second order term of polarization becomes important and gives the following dependence:

$$P^{(2)} \sim e^{-i(2\omega t - 2kz)}$$  \hspace{1cm} (1.5)

This relationship expresses that the material produces light waves of twice the frequency of the incident wave. In other words, this is a case of second harmonic generation (SHG), which is often referred to as ‘frequency doubling’. SHG is a nonlinear optical process, since it only occurs at anisotropic materials, given that the second order nonlinear dielectric susceptibility $\chi^{(2)}$ equals to zero in isotropic materials. This means that SHG can only exist in media with no inversion symmetry and vanishes in centrosymmetric media. Therefore, this explains why nonlinear crystals such as BBO or KDP are popular for the production of second-harmonic radiation.

Apart from SHG, which is only a subcategory, the general case of such wave interaction is the sum-frequency generation (SFG). As a matter of fact, every condition that applies to the SHG does also apply to the general sum-frequency generation. In SFG, the frequencies of the incident waves differ from each other and the two incoming waves come from different directions.
Figure 1.3: Energy diagram of SHG and SFG in linear and nonlinear optics. In linear optics, the input frequency equals to the output frequency in both reflection and refraction. On the contrary, in nonlinear optics, the incident frequencies are summed up generating a resulting frequency at the output.

As with any second order phenomenon in nonlinear optics, there are some restrictive terms required in order for SHG (as well as for SFG) to be observed and are the following conditions:

1. **Phase-matching condition**

   A proper phase relationship between the interacting waves must be maintained along the propagation direction. This indicates that both the incident and generated waves must travel within the crystal in the same phase velocity, having equal respective refraction indices.

2. **Crystal anisotropy**

   Crystal anisotropy is equivalent to phase-matching condition as it leads to the same desirable results. As already mentioned, the polarization of the generated second harmonic wave is perpendicular to that of the incoming waves. In anisotropic materials, different directions have a different response. By orientating the crystal in a proper way, a suitable orientation can be achieved so as to make the incident and generated waves travel in the same phase velocity, i.e. both $\omega$ and $2\omega$ waves experience identical refractive indices.
3. Energy and momentum conservation

Energy and momentum conservation laws must hold for the incoming and outgoing photons, leaving the matter unchanged:

\[ \hbar \omega_1 + \hbar \omega_2 = \hbar \omega_3 \] (1.6)

So long as sum frequency generation satisfies energy conservation, it is called a ‘parametric process’. Let us note that in second harmonic generation, the two incident frequencies are equal: \( \omega_1 = \omega_2 = \omega \) and a \( 2\omega \)-frequency signal is generated.

As far as momentum conservation is concerned, it requires that the outgoing signal will be emitted in the direction that results by the sum of the wave vectors of the incident signals, while their lengths are taken into account (figure 1.4).

\[ \omega_1 + \omega_2 = \omega_3 \]

Figure 1.4: Momentum conservation in harmonic generation processes. In collinear second harmonic generation, both incident and generated second harmonic waves are in the same direction. In non-collinear second harmonic generation, the out-coming wave direction is located between the directions of the incoming waves. Lastly, the sum frequency generation can be a general case of adding integer multiples of the frequency \( \omega \). The third figure presents the sum of two \( \omega \) and \( 2\omega \) waves, resulting in a \( 3\omega \) field, the direction of which is dictated by the vector sum of the incoming waves.
1.3.2 The Kerr effect

More recently, the Kerr-lens passive mode-locking technique has been widely used. This is an effect which has been observed at solid state lasers and is related to non-linearity of the refractive index of a medium. It can be described as follows:

\[ n = n_0 + n_2 I \]  \hspace{1cm} (1.7)

where \( n_0 \) is the linear refractive index, \( n_2 \) is the non-linear refractive index (both depend on the medium) and \( I \) is the laser intensity.

The spatial shape of a laser beam’s intensity follows a Gaussian distribution. Due to this fact, the refractive index that different parts of the beam ‘feel’ varies among each other. More specifically, the non-linear refractive index is bigger on the Gaussian center of the beam, since it depends on the intensity. This leads to an ‘additional’ lens in the cavity and, consequently, to higher light intensity. This is a ‘new’ converging lens and it is known as the Kerr lens. Thus, the higher intensity parts will focus more strongly than the weaker parts. Although this phenomenon also occurs at lower intensities, it is conventionally said that the Kerr effect is observed only at high intensities given that, in this case, it is much more intense. The Gaussian shape of the beam, the intensity and the refractive index result to a self-focusing beam and smaller beam diameter.

Another consequence of the Kerr effect is the self-phase modulation. This is a phenomenon in which the time pulse duration is shortened, due to the intensity dependence of the refractive index which is higher in the center of the Gaussian pulse. Since the refractive index affects the phase of electric field through the wave vector \( k \) (equation 1.8), the nonlinearity that characterizes the material causes a phase shift (phase modulation) on the propagating wave. Plus, this variation in refractive index is time dependent, so the pulse phase experiences a temporal modification, widens its spectrum and leads to pulses with shorter duration.

\[ \phi = n \frac{2\pi}{\lambda} L = -(n_0 - n_2 I) \frac{2\pi}{\lambda} L \]  \hspace{1cm} (1.8)
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Figure 1.5: The Kerr effect. This figure presents the self-focusing beam after passing through the medium.

Figure 1.6: Self-phase modulation. The graph above shows the change of intensity over time. The second graph shows how the frequency changes with time.

White light generation is also an implication of the dependence of refractive index.
on light intensity. As a result of self-focusing and self-phase modulation, the spectrum of
a femtosecond pulse propagating in nonlinear medium is broadened and can cover some
hundreds of nanometers. This leads to white light supercontinuum generation of relatively
low intensity. However, white light generation is crucial for time-resolved spectroscopy
while supercontinuum pulses are used as probe light in pump-probe spectroscopy.
1.4 Ultrafast laser spectroscopy

Ultrafast processes refer to any procedures happening faster than within 1 ps. The field of science that studies these phenomena is known as *time-resolved (or ultrafast) spectroscopy*. In order to observe ultrafast events, one must investigate them using a component changing faster than the examined process. This could not be achieved by other means except from *laser ultrafast pulses*. They have been a key factor in studying and understanding ultrafast processes in novel material over the past decade, since they provide information about the carrier dynamics in photoexcited materials.

Ultrafast phenomena demand careful handling in order to investigate them even using light, fast as it may be. Therefore, light sources must be such that light and its parameters can be controlled in an especially precise manner. These sources could not be other than lasers. They were invented in 1960 and, since then, they enable scientists to control many properties of light such as:

- Intensity
- Wavelength
- Polarization
- Direction
- Phase
- Duration of pulse

Laser spectroscopy provides unprecedented degree of control over light and so it plays a crucial role in investigating ultrafast phenomena. Further, the general principles of the lasers for time-resolved spectroscopy will be discussed.
1.5 Generation of ultrashort pulses

1.5.1 Q-switched lasers

Q-switching is a technique used to obtain powerful laser pulses for nano-, microseconds or longer processes. Q-switched lasers mainly find applications in generation of nanosecond pulses of high energy and are also useful as energy sources (by pumping) other lasers, such as femtosecond lasers. The main principle of this method is switching the energy losses in the laser cavity, leading to different quality ($Q$) factor, hence the name Q-switch. Since the Q factor is inversely proportional to the bandwidth of the resonator, $Q = \frac{f_r}{BW}$ where $f_r$ is its center frequency, it seems that low Q factor indicates almost no resonance. In contrary, high Q factor signifies a lower rate of energy loss relative to the stored energy of the resonator; the oscillations die out more slowly.

The generation of Q-switched pulses can be described as follows: First, the resonator losses are kept at high levels. This ensures no lasing occurring under these circumstances, due to the accumulated energy of the gain medium, stored therein. This allows creating very strong population inversion, i.e. promoting almost all the atoms of the active medium into their metastable excited states. In this case, energy losses are only caused by spontaneous emission or even strong ASE. Subsequently, the losses are suddenly switched off, so the Q-factor of the cavity quickly increases. The laser starts lasing, initially in the form of noise and then is amplified extremely fast, because the active medium has stored a large amount of energy. In addition, it takes some hundreds or thousands of resonator round trips for the noise to be amplified to macroscopic power levels. The laser radiation also disappears evenly fast due to high intensity radiation produced which quickly re-inverses all the population inversion. In this way, high intensity pulses are produced which are also called as ‘giant pulses’. There are two main types of Q-switching: (i) active Q-switching and (ii) passive Q-switching.
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Active Q-switching

Here, the losses are modulated with an active control element (active Q switch), typically either an acousto-optic or electro-optic modulator. This may be a mechanical device such as a shutter, chopper wheel, or spinning mirror/prism placed inside the cavity. An advantage of this manner is that the switching time of the modulator can be even much longer than the pulse duration, just because it takes many resonator round trips for an intense pulse to be formed. However, this time must not be too long as there is a probability of double pulses or other instabilities to appear. The pulse repetition rate of an actively Q-switched laser can be controlled via the modulator. Modulators not only can achieve a faster transition from low to high Q factor and provide better control, but also can couple the rejected light out of the cavity which can be used elsewhere.

![Figure 1.7: Active Q-switching. Gain and losses in an actively Q-switched laser in respect with time. The Q-switch is activated at $t = 0$, but the power becomes high only after $\approx 0.2 \, \mu s$, rising exponentially.](image)

Passive Q-switching

The modulator used in passively Q-switched lasers is a saturable absorber and it is passive, since no external control is necessary. A saturable absorber is an optical medium
that absorbs laser radiation. It experiences high energy losses when most of its atoms are in their ground state and the medium absorbs the laser light, leading to low Q-factor inside the optical resonator. However, as long as most of the atoms become excited, so the laser power increases, it saturates the absorber and cavity losses immediately decrease, causing the absorber to become transparent (meaning high Q factor).

Figure 1.8: Passive Q-switching. Gain and losses in a passively Q-switched laser in respect with time. A short pulse is emitted only after $\approx 0.5 \, \mu s$ from the moment when laser gain exceeds the resonator losses. The power increases sharply as soon as the absorber begins to be saturated. By the time the gain is saturated to the level of the resonator losses, the power starts falling.
By way of explanation, as the absorber saturates, it allows light to travel through the cavity which is then partly reflected on the mirror. Due to this, the gain cavity energy rises, the laser pulse is then amplified by extracting energy and exits the optical cavity. In the meanwhile, the absorber recovers to its high-loss state before the gain recovers and the next pulse is delayed until the energy in the gain medium is fully replenished. Compared with active Q switching, passive Q switching is simple and cost-effective and is suitable for very high pulse repetition rates.

Figure 1.9: Laser cavities with different Q-switches. A: saturable absorber, B: acousto-optic modulator.
### 1.5.2 Mode-locking technique

Mode-locking technique is the foundation of the ultrafast pulses generation, since the key to produce light pulses with the durations of a few femtoseconds is the use of mode-locked lasers. To support this argument, let us explain what mode-locking actually is.

The wavelength produced by a laser depends on the gain profile of the active medium. The gain medium must have a broad bandwidth to allow a large number of longitudinal modes ($10^4 - 10^5$ modes). Random mode phases occur as a result of the different mode frequencies in the cavity that cause various modes to be generated at different times. Thus, the intensity of the electric field (which equals to the square of the sum of some such fields), is a random periodic function. First of all, in order to achieve a defined intensity function, all the modes with identical phases must be added. Hence, the resulting intensity will be a series of identical pulses. Subsequently, to generate a femtosecond laser pulse, we must add a sufficient number of different modes. The repetition frequency of the pulses (known as the laser repetition rate) is typically in the range of 80 MHz and given by the fraction $\Delta \nu = c/2L$, where $c$ refers to the speed of light and $2L$ is the distance the light needs to cover before reaching again the output. Therefore, the more different modes we add, the shorter the pulse will become. Finally, if these pulses maintain the same phase relation (phase-locked pulses), they will constructively interfere so as to obtain intense radiation, resulting in a single pulse circulating around the cavity. Every time the circulating pulse reaches the output coupler, part of it escapes the cavity and is emitted to the outer world. This would be a mode-locked laser.

The modes that remain in the cavity without constructively interfering will eventually experience further interference as they are traveling between the cavity mirrors. Then they will be added and produce an intense pulse while the intensity elsewhere will be nearly zero. In the end, all the pulses that exit from the laser output will last a few femtoseconds. This is a way in which the generation of ultrashort pulses can be achieved. In general, there are two ways of ultrafast pulses production using the mode-locking technique: the active mode locking, in which supplementary parts are placed into the laser cavity -such as a standing wave electro-optic modulator- and the passive mode
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Figure 1.10: Cavity modelocking. All the modes with identical phases constructively interfere at some point and destructively interfere elsewhere. The result is an ultrafast pulse that travels within the cavity at the speed of light.

locking, in which a signal external to the laser is not needed while the light in the cavity is rather used -such as a saturable absorber-. 
1.5.3 Titanium-sapphire laser

The titanium-doped sapphire (Ti:Al\textsubscript{2}O\textsubscript{3} or Ti:sapphire) laser is an active solid state medium which is used in lasers to produce pulses in the femtosecond time domain, as well as wavelength tunable lasers. Lasers based on Ti:sapphire were first constructed and invented in 1982 by Peter Moulton. Due to its many advantages, it had successfully replaced some of the most popular types of lasers that had being used before its invention e.g. the \textit{Q-switched lasers}, which produce low intensity light, as well as the \textit{Dye lasers} which were not especially attractive as lasing media. The last-mentioned generate very high intensity light which, on the other hand, diminishes fastly because of the degradation of the organic molecules. Additionally, some of them have even been found to be carcinogenic.

The greatest advantage of the Ti:Sapphire laser is its broader gain bandwidth, comparing to other materials, which allows wavelength tunability and light generation in the spectral range from 650 to 1100 nm. This range covers a large area of the electromagnetic spectrum thus it can easily be used in a wide variety of investigations. Furthermore, the emission spectrum and laser efficiency peak at around 800 nm whereas the peak of the absorption is located in the blue-green region of the spectrum, at around 500 nm, where powerful laser diodes are not available. In particular, the broad absorption band of the Ti:Sapphire allows it to be pumped by a variety of methods such as argon-ion lasers, frequency-doubled Nd:YAG lasers or flashlamps. Due to the fact that the absorption and emission bands do not mainly overlap, another important benefit is noted: losses due to reabsorption of the laser radiation are minimized.

Some of the further advantages that signalize the Ti:Al\textsubscript{2}O\textsubscript{3} are the following: Its excellent thermal conductivity allows experiments of high laser powers and intensities to be carried on, disregarding thermal effects. Moreover, the upper-state lifetime of Ti:Sapphire is as short as 3.2 \mu s and, together with the very high saturation power, these properties require high pump beam intensity and quality. Lastly, it is characterized by high repetition rate (70-100 MHz) and strong Kerr lens effect which will not be described here, as it is discussed in the corresponding section on page 18.
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1.5.4 CPA: Chirped Pulse Amplification

Chirped pulse amplification (CPA) is a technique employed to obtain higher pulse energies. The laser executing this technique is called regenerative amplifier. The chirp of an optical pulse can be considered as the time dependence of its instantaneous frequency.

The process which implements CPA is as follows: First, the duration of weak oscillator pulses is increased (the pulse is stretched in time) up to several hundreds of picoseconds. This reduces the peak power to a level where the detrimental effects in the gain medium are avoided, such as nonlinear pulse distortion or even destruction of the gain medium or of some other optical element. Then, one out of $\approx 80000$ pulses is injected into the amplifier cavity, with Ti:Sapphire crystal pumped by a Q-switched laser. The pulse is afterward amplified to several mJ by traveling within the cavity and exits from it. Eventually, the pulse is compressed (in time) back to several tens or hundreds of femtoseconds.

Stretching and compression are achieved with pairs of diffraction gratings to spread the pulse spectrum in space and organizing the beam path, in such a way that
lower frequency light travels a longer distance (in the stretcher) or shorter distance (in the compressor) than higher frequency light. Injection and ejection of pulses into the regenerative amplifier cavity is done using electronically controlled Pockels cells and reflective polarizers. At the end of a successful chirped pulse amplification, light parameters should approximately be as follows:

- Pulse repetition rate $\sim 1\text{kHz}$
- Duration $\sim 50\text{ fs}$
- Spectral width $\sim 30\text{ nm}$
- Pulse energy: 0.5-5 mJ

Figure 1.12: CPA: Chirped Pulse Amplification
1.6 Characterization of Ultrafast Pulses

Over the past decade, scientists have shown great interest in ultrafast pulses due to their importance for studying ultrafast processes such as molecular oscillations and atomic interactions which last a few femtoseconds. Nowadays, ultrafast lasers can introduce great improvements in the fields of medicine, dentistry, telecommunications and so on. However, high cost and complexity problems still need to be solved.

The most important parameters of ultrafast pulses that are of interest to the experimentalist are their frequency spectrum, duration and high peak power.

- **Broad frequency spectrum**

  The spectrum of a Gaussian pulse is also a Gaussian function and its spectral width is inversely proportional to the temporal duration:

  \[ \tau \cdot \sigma = 1 \]  

  (1.9)

  Moreover, according to Heisenberg’s uncertainty principle,

  \[ FWHM_\nu \cdot FWHM_t \approx 0.441 \]  

  (1.10)

  Both equations (1.9) and (1.10) show that the shorter the light pulse, the broader its frequency spectrum. Therefore, the preference in a wide frequency spectrum lies in the fact that the more different frequencies are present and also higher radiation can be achieved.

- **High peak power**

  Peak power \( P_p \) of a pulse with energy \( E_p \) and duration \( t_p \) is the rate of energy flow in every pulse. It is given by the equation:

  \[ P_p = \frac{E_p}{t_p} \]  

  (1.11)
which implies that short pulses require high power at the peak of the Gaussian pulse.

At high peak power, the electric field is high enough to cause multiple ionizations
or move electrons from their orbits. These processes take place so fast that, when a
specific threshold is exceeded, the sample is destroyed. This technique finds applica-
tions not only in medical treatments, dentistry and surgery but also in automotive
industry.
1.7 Applications of Ultrafast Pulses

Besides fundamental research, ultrafast lasers have also been employed for several practical and industrial applications, such as photomask repairs, ink nozzle drilling and medical stent fabrication. These lasers are now also used in the electronics industry for scribing, patterning and texturing of glass and semiconductors (e.g., photovoltaic cells and light emitting diode displays). Moreover, ultrafast lasers are used in industry for microelectronics devices. In medicine, ultrafast spectroscopy enables the manufacture of medical devices such as surgery needles and also can ‘photograph’ tissues.

The following diagram shows some of the properties and applications of ultrafast lasers.

Figure 1.13: Properties and applications of ultrafast pulses.
Chapter 2

Experimental techniques

2.1 Pump - Probe technique

In order to study and understand relaxation processes that occur in femtosecond timescale, suitable detectors with a fast enough response time must be available for use. Unfortunately, such detectors lack from industry. Only exception is streak cameras which have a time resolution of some hundreds of femtoseconds [3] (the time-resolution of the best optoelectronic streak cameras is around 180 femtoseconds [8]) and are quite costly.

Transient spectroscopy is a pump-probe technique that involves two laser pulses. This technique is ideal for studying relaxation processes in femtosecond timescale. The main idea of the method is that an ultrashort laser pulse is divided into two beams. Initially, a pump pulse stimulates the material interacting with the sample to excite it into a non-equilibrium state. This needs to be a high-intensity pulse in order to induct the dynamical process efficiently. Thenceforward, the system relaxes towards a new equilibrium state. Thereafter, the second pulse, known as the probe pulse, comes to measure the relaxation process and determine any changes in the transmission or reflection properties of the sample. In order to avoid perturbation of the sample’s properties, the probe pulse must have low intensity.
The two pulses follow a different optical path with respect to one another. The exact time of arrival of the probe pulse is accurately known and can be adjusted by a motorized translation stage of high accuracy (several micrometers). Thus, the probe pulse hits the sample with an alterable temporal delay $\Delta t$ in respect to the pump pulse. Since the incident pump beam modifies the sample properties, the initial probe beam changes as it interacts with the sample. Thus, these modifications can be observed by monitoring the probe signal as a function of the time delay to receive information about the carrier dynamics of the sample caused by the pump pulse.

Figure 2.1: A simplified illustration of a typical pump-probe technique. The incident ultrafast laser pulse is split to intense pump beam and weaker probe beam with a variable optical delay ($\Delta t$) in respect to each another. The pump beam photo-excites the sample whereas the probe beam detects the changes that pump beam has induced.
2.2 Experimental set-up

2.2.1 Generation of femtosecond pulses

Before analyzing the pump-probe experimental set-up, the system generating ultrafast laser pulses will be discussed. It comprises four main elements. The first laser used in the set-up is *Millenia*. It is a diode-pumped solid state laser producing green continuous-wave at 532nm. The light emitted by Millenia is afterwards absorbed by *Tsunami* via mode-locking technique. Tsunami is a femtosecond oscillator based on Titanium-Sapphire. It generates one pulse every 10 ns (i.e. repetition rate=100 MHz) which lasts as short as about 100 fs. The center wavelength of emission is around 800 nm (fundamental wavelength). However, the energy emitted is in the order of only 3-4 nJ per pulse (meaning $\sim 1$ Watt per $10^8$ pulses) which is not satisfactory enough for the needs of the experiment, hence the signal needs to be amplified. Consequently, the next part of the optical setup, *Spitfire*, plays the role of an amplifier, where CPA (see page 29) takes place. The 100 fs short pulse is temporarily broadened up to 100 ps by using a diffraction grating arrangement, so as to avoid optical damages caused by high energy peaks. The laser pulse is then amplified by *Empower Spectra Physics*, a Q-switched diode-pumped Nd:YLF laser operating at 527nm running at 1kHz repetition rate and 15 W of average power. The latter achieves change in the polarization state of light passing through it using Pockels cells which act as fast optical switches. In addition, 1000 per 100 000 pulses for every second are synchronized, due to Millenia and Tsunami repetition rate (1kHz and 100MHz) and hence amplified up to $\sim 10^6$ times as it circulates in the optical cavity for several times, gaining additional energy in each round trip, until saturation gain occurs. After amplification, the pulse is injected from the cavity is then temporally recompressed to its original duration of 100 fs by a grating pair, but now the beam’s diameter has increased from $1\mu$m to 1cm. Eventually, the resultant pulses reach energy of 1 mJ/pulse at 800 nm, with time duration of 100 fs and repetition rate at 1 kHz.
2.2.2 Pump-probe set-up

The typical pump-probe set-up follows the laser system. Therefore, the generated beam needs to be separated with a beam splitter into the pump and the probe beam. Pump passes through a $\lambda/2$ plate, which controls the intensity of transmitted beam before a polarizer. Hence it is directed through a BBO (Beta Barium Borate) crystal, where second harmonic generation (frequency doubling) takes place. In this manner, the pump beam acquires central wavelength of 400nm, from the 800nm fundamental, as needed for the purposes of this set up.

On the other hand, probe beam follows a completely different path. It is crucial that pump and probe beam travel in the same optical distance before hitting the sample so that a precise motorized transitional stage controls the alteration of the probe path length to achieve the delay between them. The translation stage has resolution of 1µm.
After probe is temporally delayed in respect with pump beam, a few $\mu$J of the probe beam are focused into a sapphire crystal using appropriate focus lens. Continuum white light is then generated, covering the spectral range between 400 nm to 1000 nm. However, the initial 800 nm component is $\sim 10^3$ times stronger than the rest components of white light. In consequence, a Notch filter is placed right after white light generation point, in order to reduce the intensity of 800 nm to balance it with the other components. This is an ideal solution, since such filter transmits most frequencies through it unaltered, but highly reflects those in a specific range (795-815 nm in this case, see Figure 2.3).

![Notch filter % transmission graph](image)

**Figure 2.3:** Notch filter (%) transmission graph. This filter highly reflects wavelengths between 795-815 nm while the transmission passbands, in which the average transmission exceeds 90%, range from 610 - 778 nm and 838 - 1060 nm. The center wavelength is at 808±2 nm.

Thereupon, the required probing wavelength must be selected and, for this reason, Bandpass filters are inserted in the probe path, thus several excitation states can be probed. Bandpass filters transmit a well-defined wavelength band of light, while rejecting
CHAPTER 2. EXPERIMENTAL TECHNIQUES

other unwanted radiation. They are the opposite of Notch filters. Their design consists of two reflecting stacks, separated by an even-order spacer layer. These reflecting stacks are constructed from alternating layers of high and low refractive index materials, which can have a reflectance in excess of 99.99%. By varying the thickness of the spacer layer and/or the number of reflecting layers, the central wavelength and bandwidth of the filter can be altered. Consequently, they allow the desirable wavelengths to pass and probe the sample. For instance, the transmission curve of a Bandpass filter with central wavelength of 450 nm is presented in Figure 2.4.

Figure 2.4: Bandpass filter (%) transmission graph. This filter transmits pulses centered at 450 ± 2 nm. FWHM equals to 10 ± 2 nm which is ideal for the 100 fs lasting probe pulse with 10 nm width. The blocking region of this filter ranges from 200 to 3000 nm.
Lastly, the pump and probe beams are focused on the same spatial point on the sample. In order to ensure that the probe beam detects a uniformly excited area, the pump pulse is spatially controlled to have a diameter at least twice the diameter of the probe beam. The probe beam experiences transmission and reflection changes caused by the pump beam. These modifications are measured using lock-in amplifiers with reference to an optical intensity modulator (an optical chopper) of the pump beam, so as to improve signal-to-noise ratio. Optical chopper is a plate with chopper blades rotating with frequency of 30 Hz which periodically interrupts a light beam. Thus, it synchronizes the signal which eventually reaches the lock-in amplifier. In this way, noise is limited and a higher percentage of the signal is amplified. A lock-in amplifier rejects noise signals, at frequencies other than the reference frequency, preventing the noise from affecting the measurement. The combination of lock-in amplifiers and optical chopper ensures the reduction of noise and the amplification of the actual signal. The signal exiting lock-in amplifiers is collected using a digital Labview based program which controls many experimental parameters including the translation stage movement.
2.2.3 Spectrometer set-up

The process described in the previous section is based on the selection of the preferable probe wavelength, using Bandpass filters, in order to investigate the changes caused by the pump laser. This however is a long process since one has to take measurements over broad range of the white light. Especially in a spectral range of 400-750 nm, which is the range of white light wavelengths consisting the probe pulse, even taking one measurement per 50 nm require a long time. In this work, a spectrometer system equipped with a fast CCD array to simultaneously make measurement over a broad range of wavelengths is set up. Here, a detailed description of the spectrometer system is to be presented.

In particular, Bandpass filters, detectors and lock-in amplifiers are replaced with
CHAPTER 2. EXPERIMENTAL TECHNIQUES

Figure 2.7: Spectrometer set-up

the spectrometer system. Another modification in this set-up is that an additional Short-pass Edgepass Filter is placed before the reflection/transmission beam enters the spectrometer system. These elements are used to isolate regions of a spectrum since they transmit wavelengths shorter than the cut-off wavelength of the filter, which range mainly between 400-750 nm instead of 400-1000 nm of the initial white light probe beam. In fact, a small part of longer wavelengths still remain but they are much weaker hence they are not taken into account. Wavelengths longer than 750 nm are blocked further in order to prevent the component of around 800 nm from reaching the CCD array, due to its very high sensitivity. Despite using Notch filter to reduce the high intensity of the 800 nm white light component, even lower intensities could still saturate CCD detectors. The transmission graph of such shortpass filters used in the present set-up is presented in Figure 2.8.

Moreover, a removable mirror is inserted into the reflection/transmission optical
CHAPTER 2. EXPERIMENTAL TECHNIQUES

Shortpass filter (%) Transmission graph

Figure 2.8: Shortpass filter (%) transmission graph. The shaded region in this graph denotes the spectral range over which this filter is mainly used. It transmits wavelengths ranging between 400-750 nm which are shorter than the 750 nm cut-off wavelength of the filter.

path, as shown in Figure 2.7. When it is present, it allows the reflection signal passing through it and finally reaching the spectrometer system. Otherwise, when it is magnetically rotated in a proper way, it allows the transmission signal to penetrate it and reach the spectrometer system. Furthermore, a focusing lens is used to direct either the transmission or reflection signal (which consist of white light ranged from 400-750 nm) into an optical fiber. Hence, white light is transmitted between the two ends of the fiber reaching the spectrometer system which is equipped with a diffraction grating monochromator. Thus, white light is refracted and projected onto a Charge Coupled Device (CCD). All the other components of this set-up remain the same as those of a typical pump-probe configuration, as described in section 2.6.

A Charge Coupled Device (CCD) is an integrated circuit consisting of an array
of 1024 pixels etched onto a silicon surface. Pixels are two-dimensional light sensitive elements of 3\(\mu \text{m}\) thickness, spaced less than 1\(\mu \text{m}\) apart. Each pixel functions as a photodiode and detects different wavelength while all of them operate at the same time, covering wide range of white light simultaneously. For this reason, each detector is calibrated so that the various wavelengths can be distinguished. As a result, photons incident on this surface generate charge that can be read by electronics and turned into a digital copy of the light patterns falling on the device.

Figure 2.9: A) The spectrometer system in detail, equipped with a diffraction grating monochromator and a CCD array. B) A simplified illustration of a CCD array. The actual CCD array used in this set-up consists of 1024 pixels.

Due to the large number of 1024 detectors, lock-in amplifiers are not a functional option and so the signal-to-noise ratio can not be improved. Also, CCD arrays are so sensitive that they can even detect a few photons. Therefore, it is crucial that noise be limited as much as possible. For this reason, a different technique is used to reduce noise: The optical chopper inserted into the pump optical path is now set to rotate at 500 Hz, i.e. half the frequency of the pump’s repetition rate which is 1 kHz. Furthermore, similarly to
the typical pump-probe set-up, the optical chopper is synchronized with the pump signal. In other words, half the pulses of the initial pump beam are allowed to penetrate the optical chopper and reach the sample, while this blockage is implemented alternately to each pulse. However, no modification is applied to the original probe beam, as described in section 2.6, which also has a repetition rate of 1 kHz. This implies that only every other probe pulse which hits the sample experiences the changes caused by the unblocked pump pulse. On the other hand, a probe pulse arriving on the sample while the pump pulse is blocked, does not ‘feel’ any changes and so remains the same as the initial probe pulse. Such probe pulses are considered as the background as they do not deliver any information about the carrier dynamics of the sample, but they just describe the initial condition of the system. On this account, the computer program is set to calculate the difference of two consecutive probe pulses (i.e. a pair of one modified and one unmodified pulse.)

Let us note that in a laser consisting of 1000 pulses/sec, no major changes occur amongst nearby pulses, especially between two consecutive ones which are almost identical, whereas distant pulses show bigger changes. The mechanism of noise reduction is based on this detail: we take into account that the difference of two successive pulses indicates almost the actual change of the probe beam. Thus, the program averages the difference of every pair of consecutive pulses. The system’s duration of measurements can be any number of seconds while the program controls the number of seconds for which it will calculate the average signal difference. For example, for this experiment we take measurements for 30 seconds while the averaging is repeated 500 times/second, since there are 500 pulse pairs per second. Therefore, the final result has been averaged 15,000 times.

With this method, the actual changes of the probe signal before and after hitting the sample are determined, while a significant amount of noise is removed. The mechanism of noise reduction is illustrated in Figure 2.10.
Figure 2.10: Noise reduction process using an optical chopper. A) Initial pump laser at 400 nm with 1 kHz repetition rate. B) Pump laser after the optical chopper is applied: every second pump pulse is blocked. C) Transmitted or reflected probe laser, white light with 1 kHz repetition rate. Every probe pulse which hits the sample while a pump pulse penetrates the optical chopper experiences the changes caused by the unblocked pump pulse. On the other hand, a probe pulse arriving on the sample while the pump pulse is blocked, does not ‘feel’ any changes and so remains unmodified. The computer program is set to calculate the difference of every two consecutive probe pulses, i.e. a pair of modified and unmodified pulses, as well as to average the differences.
Chapter 3

Data Analysis

In this chapter, the experimental data will be analyzed as a means to obtain information about ultrafast carrier dynamics of the sample, using the femtosecond pump-probe transient absorption spectrometer. The sample used in this experiment is a Polysilicon thin film of variable thickness (5 nm, 10 nm, 20 nm) evaporated on a quartz substrate. Polysilicon, also called Polycrystalline silicon or poly-Si, is a high purity, polycrystalline form of silicon, used as a raw material by the solar photovoltaic and electronics industry.

In order to proceed to analysis of these measurements, the effects of ‘state filling’ and ‘free carrier absorption’ detected in this experiment first need to be discussed. These are two main contributions due to changes in the dielectric functions causing changes to the measured reflectivity and transmission. The data are presented in 3D graphs of the intensity of transmission signal as a function of the various wavelengths of the probe beam and the temporal delay $\Delta t$. Positive or negative sign of the transmission change is assigned to ‘state filling’ or ‘free-carrier absorption’ effects respectively which are explained below.
3.1 ‘State filling’ and ‘free carrier absorption’ effects

‘State filling’ effect occurs when photo-generated carriers occupy energy states, resulting to a positive change in the probe transmission signal, meaning a negative change in the photo-induced absorption. If photon energy of the excitation (pump) pulse is longer than the band gap of the semiconducting material, pump pulse which hits the sample will generate carriers in the conduction band. At time delay very close to $\Delta t = 0$ ps the pump beam excites electrons from the valence band into the conduction band and, at the same time, so the probe beam tries to do with the remaining carriers in the valence band. Hence, the majority of free, photo-generated carriers are found in the conducting band at time delay $\Delta t \approx 0$ ps. The maximum change of the transmission signal occurs at probe wavelengths as near as possible to the excitation wavelength. Moreover, at $\Delta t > 0$ ps the number of occupied conduction states decreases since some carriers leave, hence it is more possible that the probe beam excites carriers as there are more available states in the conduction band. Similarly, at times $\Delta t >> 0$ ps even fewer carriers are found in the conduction band thus a larger number of carriers can be excited by the probe beam. On the other hand, at times $\Delta t < 0$ ps the probe beam arrives earlier than the pump beam, so there is no change induced in the transmission signal since no carriers have been excited yet. [3] The above-mentioned carrier evolution is illustrated in the following diagram.

On the contrary, a negative change of the transmission signal indicates the ‘free carrier absorption’ effect. It takes place when free carriers are excited from an already-excited probe state to another, unoccupied state of higher energy in the same band. The additional energy which free carriers acquire corresponds to low energy photons which were generated due to the probe beam. At positive time delays $\Delta t \approx 0$ ps, a large number of carriers is excited into the conduction band by the pump beam, while the probe beam causes secondary absorption of carriers at higher energy states. This implies positive change in absorption, hence negative change in the transmission signal. Moreover, at times $\Delta t > 0$ ps, less absorption caused by the probe beam is observed, since a number of carriers leave the probed states. Therefore, the transmission signal becomes less negative.
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Figure 3.1: Carrier evolution in semiconducting material and the state filling effect. (A) At time delay $\Delta t \approx 0$ ps the pump beam excites electrons from the valence band into the conduction band and so the probe beam tries to do with the remaining carriers in the valence band. (B) At time delay $\Delta t > 0$ ps the number of occupied conduction states decreases since some carriers leave, there are more available states in the conduction band and the probe beam is more possible to excite carriers. (C) At times $\Delta t >> 0$ ps even fewer carriers are found in the conduction band thus a larger number of carriers can be excited by the probe beam. [3]

At times $\Delta t >> 0$ ps, only a small number of carriers still exist in conduction band states so a small number of carriers or no carriers will be excited by the probe beam. In this case the absorption/transmission signal becomes zero. The following figure illustrates carrier evolution in semiconducting material describing free carrier absorption.

Both effects, ‘state filling’ and ‘free carrier absorption’ are competing effects and may occur at the same time. However, the sign is determined by the dominant effect. Normally, state filling dominates when photon energy of the excitation (pump) pulse is longer than the band gap of the semiconducting material, otherwise the dominant effect is free carrier absorption. This is due to the fact that in an ideal pure semiconductor, no energy states at energy levels below the band gap are available. Therefore, absorption of the probe pulse from the photoexcited carriers to higher energy states becomes significant [3].
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Figure 3.2: Carrier evolution in semiconducting material and the free carrier absorption effect. (A) At positive time delay $\Delta t \approx 0$, the probed states have a large number of carriers which will be excited into even higher states by absorbing photons from the probe beam. (B) At time delay $\Delta t > 0$ ps, fewer carriers are further excited by the probe beam due to a number of carriers leaving the conduction band states. (C) At times $\Delta t >> 0$ ps, only a few carriers are left in the detected states so the absorption/transmission signal becomes zero. [3]

3.2 Analysis of Time-Resolved Transmission Change Measurements

In the following section, data analysis and the experimental results are to be examined. In this work, we have obtained measurements of differential transmission of several thicknesses of Polysilicon thin films (5 nm, 10 nm and 20 nm) using the spectrometer set-up. Differential transmission $\Delta T$ is a non-dimensional quantity and is calculated as follows:
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\[ \Delta T = \frac{T - T_0}{T_0} \]  

(3.1)

where \( T_0 \) is the transmission signal measured without sample excitation caused by the pump pulse and \( T \) is the transmission signal measured in the presence of the pump pulse which excites the sample, as shown in Figure 2.10, page 37.

Transmission at 5 nm thickness of Polysilicon thin film

The differential transmission in the case of 5 nm thickness of the sample thickness is presented in a 3D graph in Figure 3.3 as a function of both the various wavelengths of the probe beam and the temporal delay \( \Delta t \). In general, it is observed that the transmission change is mainly negative at all wavelengths, especially at the shorter ones, whereas only a small part of the differential transmission is positive at 450 nm at times \( \Delta t \approx 0 \) ps.
Figure 3.3: Differential transmission of 5 nm thickness of Poly-Si thin film

In Figure 3.4, the differential transmission of several selected wavelengths depending on time delays $\Delta t$ between the pump and probe pulses is presented. As it can be observed, there is a negligible part of positive transmission change at 450 nm at times $\Delta t \approx 0$ ps caused by state filling which is not clearly distinguishable. Elsewhere, the differential transmission change is negative which is attributed to free carrier absorption. In particular, photo-excited carriers are further excited into higher energy states of the conduction band. This is accomplished since carriers absorb photons from the probe beam and, for this reason, the transmission signal decreases. Moreover, different wavelengths imply different energy states. As it can be seen, the transmission change is more negative at shorter probing wavelengths. This indicates that there is higher density of energy states at shorter wavelengths, hence the shorter the probing wavelength, the higher the excitation possibility. The amplitude of transmission depends on the coupling efficiency.
between these energy states and the number of carriers present in the lower coupled energy states. Therefore, at 450 nm we observe minimum (maximum) transmission (absorption) in contrast with 735 nm. In general, there is a sharp drop in transmission change at $\Delta t \approx 0$ ps. Furthermore, at times $\Delta t > 0$, transmission increases as a result of fewer carriers experiencing secondary excitation caused by the probe beam, while more and more carriers are leaving the conduction band as long as the probe pulse is being delayed. In particular, longer wavelengths show steeper increase in differential transmission than the shorter ones.

Comparing the two graphs above, it is clear that higher resolution can be achieved using the spectrometer system. In fact, by utilizing this set-up as well as the 3D graphs similar to Figure 3.3, one can simultaneously observe the carrier dynamics for a wide spectrum of wavelengths. On the contrary, this would not have been possible with a typical pump-probe technique since it would require specific bandpass filters for choosing
CHAPTER 3. DATA ANALYSIS

the probing wavelengths and the data would have been exported as 2D graphs, similar to Figure 3.4.

Subsequently, normalized differential transmission ($\Delta T$) dependence on temporal delay ($\Delta t$) when performing exponential fitting for the selected wavelengths of 500 nm and 700 nm is presented in Fig.3.5 and Fig.3.6 respectively. Best fitting was obtained using a tri-exponential decay function (eq. 3.4 at 5 nm thickness, a double exponential decay function as shown in eq. 3.3 at thickness of 10 nm, whereas at 20 nm of thickness a single exponential decay function (eq. 3.2) was selected for better results.

$$y = y_0 + A_1 e^{-x/t_1}$$  \hspace{1cm} (3.2)

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$$  \hspace{1cm} (3.3)

$$y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + A_3 e^{-x/t_3}$$  \hspace{1cm} (3.4)

where $A_i$ is the percentage of carriers with lifetime $t_i$. The parameter $y_0$ is set to zero so as to obtain information on how fast/slow the relaxation processes occur for each percentage ($A_i$) of carriers by extracting carrier lifetimes $t_i$. 

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Figure 3.5: Normalized transmission at 5 nm thickness, $\lambda=500$ nm

Figure 3.6: Normalized transmission at 5 nm thickness, $\lambda=700$ nm

Figure 3.7: Time resolved transient normalized transmission measurements of 5 nm thickness of Poly-Si thin film on quartz using 500 nm and 700 nm probing wavelengths. The scattered symbols represent the experimental data while the red curve corresponds to the 3-term exponential decay fitting.

The values of fitting parameters extracted from the experimental data are summarized in Table 3.1. The data in Figures 3.5 and 3.6 clearly show that free carrier absorption is the main contributing factor for a probing wavelength equal to 500 nm and 700 nm respectively. At 500 nm, $\sim 40\%$ of carriers experience fast relaxation time constant of 10 ps while a slower time of 77 ps corresponds to 30\% of the carrier population. Additionally, a much slower time of 836 ps is detected for another 30\%. Moreover, a similar procedure is observed at 700 nm of probing wavelength, where $\sim 40\%$ of carriers depict a fast relaxation (6 ps), $\sim 30\%$ a slower relaxation time of 35 ps and $\sim 30\%$ a much slower time of 513 ps. In both cases, the fast decay time component $t_1$ is attributed to larger number of surface states found in thinner material and causing faster relaxation. Also, $t_2$ corresponds to carrier recovery from the conduction band’s energy states while the lower times $t_3$ are linked with long decays.
Table 3.1: Fitting parameters from the experimental data acquired at probing wavelengths of 500 nm and 700 nm at 5 nm thickness of Poly-Si thin film

<table>
<thead>
<tr>
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<th>$\lambda = 500\text{nm}$</th>
<th></th>
<th>$\lambda = 700\text{nm}$</th>
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<tbody>
<tr>
<td>$A_1$ (%)</td>
<td>44.7 ± 2.2</td>
<td>$A_2$ (%)</td>
<td>29.7 ± 3.6</td>
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<tr>
<td>$A_3$ (%)</td>
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<td>$t_1$ (ps)</td>
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<td>$t_3$ (ps)</td>
<td>835.7 ± 302.4</td>
<td>$t_1$ (ps)</td>
<td>6.2 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_2$ (ps)</td>
<td>35.0 ± 6.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$t_3$ (ps)</td>
<td>512.6 ± 66.8</td>
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Transmission at 10 nm thickness of Polysilicon thin film

In this section, the case of 10 nm thickness of Poly-Si thin film is examined. Differential transmission $\Delta T$ is shown as a 3D graph depending on both the various wavelengths of the probe beam and the temporal delay $\Delta t$ in Figure 3.8. Also, the dependence of $\Delta T$ on the temporal delay $\Delta t$ for several wavelengths is presented in Figure 3.9 as a 2D graph. Similarly with the previous section of 5 nm sample thickness, the transmission change is mainly negative (and more negative at shorter probing wavelengths), which is attributed to free carrier absorption. Moreover, the state filling effect (positive transmission change) at times $\Delta t \approx 0$ is slightly more visible here than it is in the case of 5 nm of thickness. The most important difference comparing the two last-mentioned sample thicknesses is that carriers show slower relaxation on the thickest Poly-Si thin film which is an important observation discussed and explained further.
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Figure 3.8: Differential transmission of 10 nm thickness of Poly-Si thin film
Figure 3.9: Differential transmission of 10 nm thickness of Poly-Si thin film - 2D graph

The same fitting procedure at probing wavelengths of 500 nm and 700 nm is also applied in the case of 10 nm sample thickness. The following Figures 3.10 and 3.11 depict the normalized transmission measurements as well as the 3-term exponential decay fitting. Fitting parameters from the experimental data are summarized in Table 3.2.
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Figure 3.10: Normalized transmission at 10 nm thickness, \( \lambda = 500 \text{ nm} \)

Figure 3.11: Normalized transmission at 10 nm thickness, \( \lambda = 700 \text{ nm} \)

Figure 3.12: Time resolved transient normalized transmission measurements of 10 nm thickness of Poly-Si thin film on quartz using 500 nm and 700 nm probing wavelengths. The scattered symbols represent the experimental data while the red curve corresponds to the 3-term exponential decay fitting.

Table 3.2 summarizes the values of fitting parameters extracted from the experimental data. At 500 nm of probing wavelength, \( \sim 30\% \) of carriers decay within 66 ps while the rest \( \sim 70\% \) of them has a slower relaxation time of 766 ps. Similarly, at 700 nm we observe \( \sim 40\% \) of carriers with 83 ps lifetime and \( \sim 60\% \) decaying at 1180 ps. In the case of 10 nm thickness, relaxation times are even slower comparing to the thinner Poly-Si film, since surface states are now fewer and carriers mostly recover from the conduction band’s energy states.
Table 3.2: Fitting parameters from the experimental data acquired at probing wavelengths of 500 nm and 700 nm at 10 nm thickness of Poly-Si thin film

<table>
<thead>
<tr>
<th></th>
<th>( \lambda = 500\text{nm} )</th>
<th></th>
<th>( \lambda = 700\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1(%) )</td>
<td>33.2 ± 3.5</td>
<td>( A_1(%) )</td>
<td>43.9 ± 7.6</td>
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<td>( A_2(%) )</td>
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<td>( t_2(\text{ps}) )</td>
<td>765.6 ± 106.1</td>
<td>( t_2(\text{ps}) )</td>
<td>1181.9 ± 558.0</td>
</tr>
</tbody>
</table>

Transmission at 20 nm thickness of Polysilicon thin film

The last Poly-Si thin film thickness which is under examination in this experiment is of 20 nm. The corresponding information of transmission change at 20 nm thickness is further illustrated in 3D and 2D graphs (Figures 3.13 and 3.14). In particular, free carrier absorption still exists while it is more intense at shorter wavelengths, where transmission change is more negative, as is the case of 5 nm and 10 nm thickness. The most important observation is that the carrier relaxation is the slowest comparing to the thinner Polysilicon films since the differential transmission drops and then slightly increases in respect with the time delay \( \Delta t \). At the same time, state filling appears more significantly than it does in the other cases and this effect occurs at all probing wavelengths.
Figure 3.13: Differential transmission 20 nm thickness
Accordingly to the previous sections, the normalized differential transmission at 500 nm and 700 nm probing wavelengths follows in Fig.3.15 and Fig.3.16 in order to further investigate the relaxation dynamics in the polysilicon thin films on quartz substrate. Table 3.3 presents the estimation of relaxation times in from the experimental results as well as the respective percentages of carrier population.
Figure 3.15: Normalized transmission at 20 nm thickness, \( \lambda = 500 \) nm

Figure 3.16: Normalized transmission at 20 nm thickness, \( \lambda = 700 \) nm

Figure 3.17: Time resolved transient normalized transmission measurements of 20 nm thickness of Poly-Si thin film on quartz using 500 nm and 700 nm probing wavelengths. The scattered symbols represent the experimental data while the red curve corresponds to the 3-term exponential decay fitting.

The results from the experimental fitting at 20 nm thickness are presented in Table 3.3. As it can be seen, both in the case of \( \lambda = 500 \) nm and \( \lambda = 700 \) nm, \( \sim 100\% \) of carriers relax in 725 ps and 868 ps, respectively. In this case of 20 nm thickness, the slowest relaxation times are observed, since grain boundaries increase hence fewer surface states are found and the state filling effect is more intense.

Table 3.3: Fitting parameters from the experimental data acquired at probing wavelengths of 500 nm and 700 nm at 20 nm thickness of Poly-Si thin film.

<table>
<thead>
<tr>
<th>( \lambda = 500nm )</th>
<th>( \lambda = 700nm )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( t_1 )</td>
</tr>
<tr>
<td>103.5 ( \pm 5.0 )</td>
<td>725.3 ( \pm 14.6 )</td>
</tr>
</tbody>
</table>
Conclusions

Ultrafast pulsed lasers are widely used to generate excitation states in materials through light-matter interactions in order to investigate the dynamics processes as the system returns to its equilibrium. In a typical pump-probe technique, an ultrafast pulse is divided into the pump pulse used to excite the material and the probe pulse which is used to probe the changes induced by the pump. The probe beam is initially utilized to produce white light generation and in turn is directed on to the excitation region of the sample. Narrow band pass filters are then used to select the probing wavelength. This however is a long process since one has to take measurements over broad range of the white light.

In this work, a spectrometer system equipped with a fast CCD array is set up. The main feature of this system is its ability to simultaneously make measurement over a broad range of wavelengths. In comparison to a typical pump-probe technique, this system provides multiple benefits which are shown in this experiment. First of all, fast measurements were accomplished within a few hours or even minutes. In contrast, in a typical pump-probe technique, it takes up to days in order to repeat the measurements using different narrow band filters to cover a wide spectrum of desirable probing wavelengths. Moreover, using the spectrometer system, a whole spectral data can be obtained at the same time, whereas in a typical pump-probe technique only the available narrow-band filters can be used. For example, this laboratory is equipped with narrowband filters covering a range of wavelengths only per 50 nanometers. This would be a major problem in the case where it would be necessary to study carrier dynamics using a probing wavelength for which the corresponding filter would not be available.
CHAPTER 3. DATA ANALYSIS

Furthermore, measurements of the differential transmission dependence on the temporal delay $\Delta t$ of the probe beam with respect to the arrival time of the pump beam (i.e. time zero) were carried out, for probing wavelengths ranged from 400 to 750 nm. The sample was a Polysilicon thin film of various thicknesses of 5, 10 and 20 nm, evaporated on a quartz substrate. Through these measurements, ‘free-carrier absorption’ and ‘state filling’ effects occurred, which are assigned to negative or positive sign of the transmission change, respectively. A positive change in the transmission signal is the result of the occupation of energy states by photo-generated carriers which is what is known as state filling. On the other hand, a negative change is detected when free carrier absorption takes place, which is a consequence of the secondary excitation of free carriers by the probe beam from the probed states into higher energy states.

In addition, as a means to investigate the carrier dynamics of the sample, data analysis was applied which provided information on the carrier relaxation times after the excitation caused by the pump pulse. The conclusion that follows is that the larger the thickness of the Polysilicon thin film, the slower the relaxation which excited carriers experience. At thinner polysilicon films, surface states become more important which is the reason why carriers relax in shorter times comparing to thicker polysilicon films. Moreover, the smaller the thickness, the more difficult it is to observe the state filling effect. As a polysilicon material becomes thicker, grain boundaries decrease due to its polycrystalline structure. Hence, surface states become less important and the relaxation becomes slower. The state filling effect then starts to occur more, as thickness increases. All the above-mentioned are confirmed through the experimental results of this work.

To summarize, the carrier dynamics of Polysilicon thin films were investigated using the femtosecond pump-probe transient absorption spectrometer described in this work. In conclusion, it is shown that this set-up works efficiently and optimizes a typical pump-probe technique.
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