Chapter 2

Experimental

The use of in-situ, non-invasive techniques with time resolution is of primary importance for the analysis of the dynamics of ultrashort laser pulse induced processes. Among the different possible magnitudes whose time evolution can be accessed, the measurement of optical properties provide a specially powerful tool to follow the carrier dynamics and structural evolution of semiconductors under laser irradiation [Shv77], [Sie94], [Sok95], [Sha96], [Hua98]. In the present chapter, we will provide the details concerning the experimental methods for inducing structural transformation processes and analyzing their dynamics.

Transformations of the specimens under study have been induced under different laser irradiation conditions varying the pulse duration, fluence and wavelength. Sample parameters as thickness, structure and substrate have also been varied to modify conveniently the heat flow conditions upon pulsed laser irradiation. In addition, several pretreatment procedures - including furnace annealing and laser annealing - have been performed in order to modify the structural state of the specimen before laser exposure. The transformation dynamics upon laser irradiation has been followed in-situ by means of both, conventional (e.g. [Jel87]) real time reflectivity measurements with ns-resolution and by a novel set-up developed in this work. The latter provides real time reflectivity measurements in which ps-resolution is achieved for a single laser pulse exposure by means of a Streak Camera. Finally, post-irradiation analysis of the samples has been done by optical microscopy, in-situ static reflectivity measurements, Raman Spectroscopy and Second Harmonic Generation microscopy.

2.1 Irradiation with picosecond laser pulses
Surface melting and rapid solidification as well as structural relaxation has been induced in the specimens by an amplified dye laser system providing picosecond pulses. This laser system has been the most important experimental tool required for the present work. Most of the difficulties and advantages of the experimental work carried out to investigate the structural transformation dynamics in thin films under ps pulse irradiation are related to its specific characteristics. Thus a detailed description of the system follows, including the actual problems and characteristics. I hope that the information contained will help future researchers facing problems in similar experiments.

The laser system is composed of four main components (Argon-ion laser, dye laser, Nd:YAG laser and pulsed dye amplifier) and designed to produce ps laser pulses of high peak power in the visible spectral region. An schematic drawing of the system is given in Figure 2.1 where the system has been divided in an oscillator and an amplifier subsystem:

![Diagram of laser system](image)

**Figure 2.1:** Laser system for the generation of amplified dye laser ps pulses, including the characteristics of the components. The Ar⁺ laser and the dye laser form the oscillator subsystem and the Nd:YAG laser and the pulsed dye amplifier the amplifier subsystem.

**Oscillator subsystem:** Synchronously pumped dye laser
Chapter 2: Experimental

The oscillator subsystem is formed by a mode locked dye laser which is synchronously pumped by an Ar$^+$ laser. In such a system, an actively mode locked Ar$^+$ laser at $\lambda = 514.5$ nm (master oscillator) is used to pump a dye laser at $\lambda = 583$ nm whose cavity length is matched to that of the Ar$^+$ laser [Dem81], [Cha76]. The output of the Ar$^+$ laser consists of a 82 MHz pulse train with a pulse duration of $\approx 180$ ps. Each of the pump pulses generate a circulating dye laser pulse inside the dye laser cavity. The configuration of matched cavity lengths allows the generation of dye laser pulses much shorter than those of the Ar$^+$ laser, the working principle being schematically shown in Figure 2.2.

![Dye Laser Net Gain (Percent)](image1)

![Intensity (Watts)](image2)

**Figure 2.2.:** Pulse shortening in the synchronous pumping process. Taken from [Cha76].

---

* SPECTRA-PHYSICS Ar$^+$ laser, Model 2040E. Cavity length with prism 1.78 m, mode spacing 84 MHz, specified maximum output power: 25 W (cw, all lines), 10 W (cw, 514.5 nm), 5 W (mode locked, 514.5 nm). The laser is actively mode locked by amplitude modulation (AM-mode locking, see for instance reference [Fre95]) by means of an intracavity acousto-optic modulator. The latter operates at a frequency equivalent to twice the round trip time in the laser cavity, i.e. 41.06 MHz.

† SPECTRA-PHYSICS dye laser, Model 375B run with Rhodamine 6G, specified maximum output power: 780 mW in cw for cw-pumping at 4 W, or 300 mW mode locked power for mode locked-pumping with 1.4 W.

‡ This wavelength is chosen from the broad wavelength range of Rhodamine 6G (568 - 660 nm) in order to match the peak wavelength of the dye amplifier run with Kiton Red 620 (576 - 592 nm).

§ The cavity of the dye laser actually has to be slightly shorter than that of the Ar-laser in order to achieve maximum pulse compression. Tuning of the dye laser cavity length is performed mechanically by the user and allows the variation and optimization of the dye laser pulse duration.
Each time an argon pulse reaches the dye jet, the previously generated dye pulse which circulates in the dye laser cavity arrives there. Because of the large stimulated emission cross-section of the dye medium, the inverted population is rapidly depleted by the incoming dye laser pulse. Following this depletion, the remaining part of the pump pulse has insufficient energy to bring the dye laser medium back above the lasing threshold. Thus, the resulting dye pulses are much shorter (FWHM = 1 - 20 ps$^*$) than the Ar$^+$ laser pulses or the dye molecule decay time ($\approx$1 ns).

The pulse duration was continuously monitored by means of a scanning autocorrelator$^\dagger$ [Dem81], [Ipp70]. In the autocorrelator, the input beam is split into two replica pulses which travel different path lengths before they are recombined. The recombined signal is then focused into a phase matched second harmonic generation (SHG) crystal whose frequency-doubled output is detected by a photomultiplier tube. Since the efficiency of the SHG is proportional to the square of the instantaneous intensity, the signal is much higher when the two pulses overlap temporally than when they are separated. A scan of the delay between the two pulses over a range of about two pulse widths in each direction gives the nonlinear autocorrelation function, whose deduction is described elsewhere [Dem81]. The shape of this function is symmetric by definition and its width is related by a certain factor to the actual pulse width. The factor depends on the pulse shape as listed for common examples in Table 2.1. Figure 2.3 shows an experimental autocorrelation trace of the synchronously pumped dye laser. The pulse duration is 7 ps assuming a one-sided exponential pulse shape. This is consistent with the pulse duration of about 10 ps measured by the Streak Camera (see Figure 2.12).

The stable and optimum pulse duration of the oscillator used is 7 ps.

$^\dagger$ INRAD autocorrelator, Model 5-14BX, sweep range $\pm$ 60 ps, minimum input power $5 \times 10^{-4}$ W, compatible with pulse repetition rates of 1 Hz to 100 MHz.
Table 2.1.: Relationship between the laser pulse duration and the width of the autocorrelation function for representative pulse shapes. The factor listed has to be multiplied by the width of the autocorrelation function.

<table>
<thead>
<tr>
<th>Pulse shape</th>
<th>Autocorrelation Function</th>
<th>Shape factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>square</td>
<td>square</td>
<td>1.0</td>
</tr>
<tr>
<td>Gaussian</td>
<td>Gaussian</td>
<td>0.707</td>
</tr>
<tr>
<td>Lorentzian</td>
<td>Lorentzian</td>
<td>0.5</td>
</tr>
<tr>
<td>one-sided exponential</td>
<td>two-sided exponential</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Amplifier subsystem: Nd:YAG laser pumped dye amplifier

The output pulse train of the oscillator subsystem is used to seed a pulsed dye amplifier*, whose layout is schematically drawn in Figure 2.4.

Figure 2.4.: Layout of the final component of the high energy ps laser pulse system, the pulsed dye amplifier (PDA-1).

The amplifier consists of three amplification stages (dye cells) which are pumped by a frequency-doubled Nd:YAG laser† working at low repetition rates (from 10 Hz to single pulse

---

* SPECTRA-PHYSICS / QUANTA RAY pulsed dye amplifier, Model PDA-1, run with Kiton Red 620 at 583 nm. Specifications: Amplified pulse energy 0.5 mJ, pulse duration broadening by a factor of 2, ratio between pulse energy and amplified spontaneous emission (a.s.e.) energy 2%, energy fluctuations ± 25%.

† SPECTRA-PHYSICS / QUANTA RAY pulsed Nd:YAG laser, Model GCR-11, in Q-switched short pulse mode 2.5 ns pulse duration, 150 mJ maximum pulse energy at 532 nm, gaussian spatial mode.
operation). The Nd:YAG pulses are split into three components and each of them excites the dye in the three amplification cells. The pump beam path is designed in such a way that all three excitation stages can be depleted synchronously by a single ps pulse traversing all cells just in the moment of maximum excitation. This synchronization between the ps pulse train and the Nd:YAG laser is done by an electronic synchronizing module.

Fundamental requirements for a reasonable performance

- **Extremely clean pulse shape of the ps pulse train.** Small post-pulses would be preferentially selected for amplification because they are usually much longer than the main pulse (even if they have peak intensities as low as 5% with respect to the main pulse). The result would be a much broader pulse (hundreds of ps) or even two pulses. Such an unclean pulse shape with small post pulses appears typically:
  
a) when the Ar laser current is too high. The excess of intracavity power causes the appearance of small leaks in the intracavity-AOM optics leading to the formation of broad (≈ 500 ps), low intense post pulses about 1.4 ns after the main pulse. This temporal structure is reproduced in the dye laser oscillator output and the broad post pulses are preferentially amplified.

b) when the dye laser cavity is too short with respect to the cavity length of the Ar laser. This leads to the formation of a relatively narrow post pulse (≈ 100 ps) about 400 ps after the main pulse.

- **Low jitter of all components.** This is an indispensable condition for effective amplification. Otherwise, the ps seed pulse and the ns pump pulse would show different and varying arrival times at the dye cells of the amplifier. As a consequence, the output pulse energy would suffer large fluctuations, or the pulse amplification would be suppressed completely producing a large amplified spontaneous emission (a.s.e.).

Once all these problems are under control a high-energy and low-jitter pulse of about 30 ps is produced by the system. Nevertheless, fluctuations in the pulse energy of up to ±25% and in the pulse duration from 15 - 60 ps are observed. Direct measurements of the amplified pulse have been performed with the Streak Camera and a typical result can be seen in Figure 2.13., section 2.2.

---

*SPECTRA-PHYSICS / QUANTA RAY* synchronizer module, Model SM-1. This unit delays the trigger pulse for the Q-switch of the Nd:YAG from 1 - 15 ns. This range is sufficient to be able to select only one of the ps pulses to be amplified since they are separated ≈ 12 ns (inverse of the repetition frequency 82 MHz). The synchronization of the Nd:YAG pulse with the ps pulse train is done via a reference signal from the mode locker of the Ar laser. An additional electronic output (sync out) provides a low-jitter TTL signal which occurs early enough to provide a suitable trigger for the Streak Camera.
Fluence determination and calibration

The amplified beam emitted by the laser system is regulated in energy, spatially filtered and focused onto the sample surface, as schematically drawn in Figure 2.5. A $\lambda/2$-waveplate in combination with a polarizing beam splitter cube are used in order to allow a precise adjustment* of the transmitted energy. The spatial filter† consists of two lenses with a focal length of 100 mm each, separated by 200 mm and a circular pinhole‡ of 100 $\mu$m diameter in-between. The spatial profile of the ps pulsed laser beam after the spatial filter is gaussian elliptical with a relation of the vertical to the horizontal diameter of $\approx 4:3$. The beam is then focused onto the sample by a lens with a focal length of 250 mm. Translating the lens over a range of 25 mm allows a variation of the illuminated area at the sample site between approximately $1 \cdot 10^{-3}$ cm$^2$ and $4 \cdot 10^{-3}$ cm$^2$.

![Figure 2.5: Beam path of the ps laser pulse after the pulsed dye amplifier.](image)

The pulse energy is obtained by calibrating the response of a reference detector that measures a reflection of the incoming pulse at a thin glass plate with the response of a detector at the sample site. For the calibration of the energy density at the sample site (energy/illuminated area), denominated fluence $F$, the illuminated area has been measured as a function of pulse energy for several positions of the focusing lens. For this purpose a thin amorphous film has been irradiated at various locations with increasing pulse energies inducing crystallization. The film used was a 50 nm thick a-GeSb film on a glass substrate due to its very low and precise crystallization

---

* The working principle of this energy regulation is the rotation of the polarization (initially vertical) by an angle $2\theta$ as a result of rotating the waveplate by an angle of $\theta$. Such a rotation causes a variation of the transmission through the polarizing beam splitter, since the latter is set up to let pass only vertical polarization.

† The principle of such a spatial filter is that an inhomogeneous incident intensity distribution is converted at the focal point of the first lens into its fourier-transformed intensity distribution. If at this point a pinhole is set to limit the beam in such a way that only the central maximum of this fourier-transformed intensity distribution can pass, then the re-transformation of this maximum after the second lens gives a spatially gaussian intensity distribution. The mathematical deduction of the principle is based on the Fraunhofer approximation to the theory of diffraction [Men73].

‡ The pinhole has to stand high intensities and is made of a gold-plated copper disc especially designed to reflect most of the light and diffuse rapidly the remaining absorbed heat.
threshold and the large optical contrast between amorphous and crystalline state of the material. The latter makes it easy to determine the extension of the crystallized region by optical microscopy. The square of the horizontal and vertical diameters \(d_x\) and \(d_y\) of the crystallized areas are then plotted as in Figure 2.6 as a function of the logarithm of the pulse energy \(E\). This way of plotting is due to the expected gaussian intensity profile \(I(d)\) of the laser pulse. The following calculation is done for the case of the horizontal diameter \(d_x\).

\[
E(d_x) = E_0 \cdot e^{-b_x \cdot d_x^2} \quad \Rightarrow \quad d_x^2(E) = b_x \cdot (\ln E)
\]

(2.1)

The slope of the left plot in Figure 2.6 corresponds to the area factor \(b_x\) and \(b_y\). The latter are related to the gaussian 1/e semiaxis \(r_x\) and \(r_y\) of the intensity distribution, which enables the calculation of the area \(A = \pi r_x r_y\) of the elliptical spot the following way:

\[
r_x = \frac{d_x}{2} = \frac{\sqrt{b_x}}{2} \quad \Rightarrow \quad A = \frac{\pi \cdot \sqrt{b_x \cdot b_y}}{4}
\]

(2.2)

The fluence at the maximum of this distribution is given by \(F = E/A\). A series of irradiations at increasing fluences have been performed at four different positions of the focusing lens. The corresponding spot areas \(A\) have been calculated following equations 2.1, 2.2 and the obtained values are shown in the right plot of Figure 2.6. The linear dependency allows to extrapolate the spot area for any \(z\)-position of the focusing lens.

![Figure 2.6: Calibration of the spot area upon irradiation with ps laser pulses.](image)

**Left plot:** Square of the vertical and horizontal spot diameter \(d_x\) and \(d_y\) versus \(\ln E\) for a given \(z\)-position.

**Right plot:** Spot area \(A\) for different \(z\)-positions of the focusing lens deduced from equations 2.1 and 2.2.
Chapter 2: Experimental

The maximum fluences at the sample site are ≈ 600 mJ/cm². Although the cumulative effect of the several errors (energy calibration, deviation from a gaussian profile, etc.) makes the absolute fluence determination to be within 10%, the large dynamic range and linearity of the monitor detectors makes the relative fluence determination of two different pulses to have an accuracy close to 2%.

2.2 In-situ real time optical measurements

The evolution of the optical properties of the studied materials upon irradiation with laser pulses has been measured in several configurations. Real time measurements of the sample reflectivity at the air/film interface and at the substrate/film interface (through the substrate) have been performed, together with real time transmission measurements. This has been done using a detection system with ns resolution. In addition, reflectivity measurements with ps resolution have been essential to obtain information about the early stages of the measured processes and to determine the influence of the rise time of the detection system on the results.

Experimental set-up

The experimental set-up for real time optical measurements upon irradiation with ps pump laser pulses is schematically drawn in Figure 2.7. The sample itself is mounted on a three-axis translation stage with a movement precision of 10 µm. The pump pulse passes through several optical components (described in Figure 2.5) and impinges at the sample surface. A probe beam laser is focused onto the center of this spot and the reflected light is sent to a fast detector passing several optical components. Both, the probe beam and the detector used depend on whether the measurements are done with ns- or ps-resolution. The details of both set-ups and their components in addition to the synchronization between pump laser, probe laser and detector are described in detail in the following.
Figure 2.7: Experimental set up for real time reflectivity measurements upon irradiation with a ps pump pulse. The inset near the sample shows the approximate relation of pump and probe spot sizes.
Real time optical measurements with \textit{ns-resolution}

\textbf{• Probe laser}

The evolution of the sample reflectivity upon irradiation is measured in real time by a means of a HeNe probe laser beam (632.8 nm, cw power $\approx 3$ mW). The HeNe laser beam is temporally pulsed by means of an acousto-optic modulator\(^\ast\) (AOM), controlled by a pulse delay generator. This allows the probe beam to be only present at the sample site when the pulse generator provides a pulsed signal. The generated probe pulse has a duration of 1-3 $\mu$s, which is sufficiently long to follow accurately the transient change of the optical properties of the sample induced by the pump pulse and short enough to avoid any significant heating or annealing effects on the sample [Afo90]. The temperature increase caused by the probe beam for the case of 3 $\mu$s pulses with 1 mW\(^\dagger\) average peak power at the sample site has been estimated to be $\approx 5$ K for an absorption of 50 % [Sol91].

The probe beam is then focused to a spot size of about 50 $\mu$m at the center of the sample region irradiated by the pump pulse which guarantees that the reflectivity is measured over a homogeneously irradiated region. This is of major importance because otherwise the observed reflectivity changes would be an average over regions unevenly illuminated and therefore at a different temperature or even thermodynamic state. Such an averaging would affect not only the measured reflectivity values corresponding to a single phase but also the dynamics; for instance by smearing out a fast process occurring in the center by averaging it with a slow process occurring at the outer regions of the probed region. The angle of incidence is very small (5\%) in order to keep the probe spot size as small as possible. The reflected probe beam is then re-collimated by a lens and aligned through a dispersion prism. This is important in order to separate the probe pulse from the scattered light from the pump pulse making use of the different refraction angles of the prism for different wavelengths. After passing the prism, the probe pulse is focused on a fast detection system, whose characteristics are described later on.

\textbf{• Synchronization}

The timing signal that allows the synchronization of the pump and probe pulses is provided by the internal clock of the Nd:YAG laser. This signal is produced before the trigger of the Q-switch in the Nd:YAG laser cavity and is generated early enough to trigger the delay generator, which itself controls the AOM. This configuration allows to adjust precisely the time of arrival and duration of the probe pulse. In a typical situation, the probe pulse arrives about 400 ns before the

\footnote{An AOM acts like a periodic diffraction grating. The working principle is described for instance in reference [Hun95].}

\footnote{This value is realistic because the 3 mW laser output experiences losses traversing the AOM (60% efficiency) and other optical components (mirrors, lenses).}

57
pump pulse. This ensures that already a constant reflectivity level has been reached\(^*\) which corresponds to the optical constants of the sample before irradiation.

### Signal Detection

The detection of the pump pulse induced reflectivity changes is performed by means of a fast amplified photodiode\(^†\). The signal measured by this diode is then filtered with a narrow-band notch filter in order to suppress the 500 MHz = (2 ns)\(^-1\) modulation produced by mode competition in the HeNe laser [Jel86], [Sol90]. The filtered signal is finally recorded by means of a Transient Digitizer\(^‡\). Although in some aspects similar to an oscilloscope (vertically deflected signal, horizontally deflected time base), the core element of a Digitizer is a scan converter tube instead of the cathodic ray tube (CRT) of an oscilloscope. Whereas in an oscilloscope the waveform is displayed as a trace on the phosphor screen, in a Digitizer it is written on a silicon diode matrix and read there as in a vidicon TV camera. This principle together with the enormous charge gain in the converter tube allows to deflect the writing beam at high speeds while the readout is performed slower, resulting in a nominal maximum time resolution of 10 ps/pixel. The actual time resolution is nevertheless limited by the corresponding risetimes and bandwidths of the photodiode, the vertical amplification unit and the horizontal sweep unit to a value of about 1 ns. The Digitizer is remote controlled by a PC and a fast detector is used to trigger the Digitizer by the pump pulse itself (see Figure 2.7). The temporal position of the measured signal is then determined within 0.1 ns (jitter of the digitizer) with respect to the irradiation pulse.

A typical signal of the HeNe probe pulse entering the detection system can be seen in Figure 2.8. On top of the 1μs probe pulse of constant reflectivity \(R_0\) one can see a typical pump laser induced change of the sample reflectivity which will be denominated thereafter reflectivity transient. Depending on the duration of this transient, the time window of the Digitizer has to be properly selected. In most cases, a time window of 200 ns turned out to be sufficient, which is a good compromise between still a reasonable temporal resolution\(^\S\) and wide enough to follow the complete reflectivity evolution.

---

\(^*\) Taking into account the rise time of the AOM which is in the order of 100 ns.

\(^†\) OPTO-ELECTRONICS INC. amplified photodetector, Model AD-110-01, rise time 430 ps.

\(^‡\) TEKTRONIX programmable digitizer, Model 7912AD. Bandwidth 500 MHz, fastest sweep range 500 ps/division, rise time 0.8 ns, time resolution 10 ps/pixel, 0.1 ns jitter.

\(^\S\) More about the real temporal resolution of this detection system will be said when the obtained results are compared to the measurements performed with the Streak Camera.
Chapter 2: Experimental

Figure 2.8.: Typical signal of the 1 µs probe pulse reflected at the sample and measured by the fast photodiode. The shaded area indicates the time window selected by the digitizer containing the transient reflectivity changes induced by the pump pulse (arrow). The amplitude $R_0$ is proportional to the sample reflectivity before irradiation with the pump pulse.

• **Alternative set-ups**

Small modifications to the previously described set-up allow to measure the time evolution of the optical transmittance and the reflectivity at the film/substrate interface, provided that a transparent substrate is used. Figure 2.9 shows the three configurations used, designated as FSR* (Front Side Reflectivity), FST (Front Side Transmission) and BSR (Back Side Reflectivity). The use of the three configurations provides complementary information in time and depth about the melting and solidification processes we want to study.

Figure 2.9.: Experimental configurations used to measure the time evolution of the Front Side Reflectivity (FSR), Front Side Transmission (FST) and Back Side Reflectivity (BSR) upon laser irradiation of the samples.

* This configuration is the same as the one shown in Figure 2.7.
Real time optical measurements with **ps-resolution**

An improvement of the time resolution of optical measurements is commonly done by pump and probe measurements in which an ultrashort (mostly fs) laser pulse is splitted in two parts with different intensities [Dem81], [Sha96]. The high intensity pulse serves as the pump pulse and the low intensity pulse is used as a probe pulse which is delayed temporally by means of an optical delay line. Such a system has an extremely high time resolution (given by the pulse duration) but requires the performance of many irradiations at different delays in order to reconstruct the time evolution in the time window of interest. This drawback is especially important in the time window 50 ps - 5 ns in which pump and probe measurements require many irradiations and large delay lines and in which real time measurements using photodiodes and oscilloscopes normally have not sufficient resolution. The novel set-up developed in this work involving a Streak Camera combines the advantages of the other techniques, since it resolves events occurring in that time window and provides results in a **single-pulse irradiation experiment**.

The experimental setup is conceptually very similar to that described in the previous section, but using a Streak Camera as the light detection system. This configuration allows us to determine the time evolution of the optical properties with picosecond resolution. A Streak Camera is a light detector much faster than any fast photodiode, because it is based on a different principle. In order to understand the experimental problems that arise when working with a Streak Camera, it is necessary to describe the working principle more in detail which is schematically drawn in Figure 2.10.

- **Working principle of a Streak Camera**

![Figure 2.10: Principle of a streak camera. Dark (light) circles of the electron density distribution correspond to a high (low) number of electrons which induce a bright (low) light intensity at the phosphor screen.](image)
Chapter 2: Experimental

The light signal to be measured is focused to a small spot at the entrance slit* of the streak camera. Internal optical components form an image of the slit on the photocathode of the streak tube. The photocathode converts the time-dependent light intensity distribution into a time-dependent electron density distribution. The number of generated photoelectrons per time unit is proportional to the instantaneous intensity of the incident light. The photoelectrons are then extracted by a low voltage field towards a vertical high voltage field produced by a pair of deflection plates. A high-speed, high-level voltage sweep (ramp) synchronized to the incident light signal is applied to the deflection plates in such a way that those electrons which arrive first experience a weak electric field, while those electrons which arrive later are exposed to a stronger field. As a consequence, the time-dependent electron density distribution is swept in the direction from top to the bottom. Provided a linear voltage ramp, a linear conversion into a space-dependent (vertical) electron density distribution is obtained. Then, this electron distribution reaches a Micro Channel Plate (MCP) where each electron is multiplied by a gain factor, independently of its spatial position. The amplified electron distribution finally hits a phosphor screen where it is converted back into a space-dependent light distribution. This phosphor screen is imaged by a cooled CCD camera that reads out the light distribution allowing quantitative measurements.

- Non-linearities of a Streak Camera and their correction

In order to provide a conversion of the time scale into a spatial scale, all conversion steps have to be linear, i.e.:

a) The response of the photocathode must be linear, i.e. the number of electrons produced must be proportional to the number of incident photons.

b) The voltage ramp has to be linear in order to permit a linear conversion of time in space.

c) The amplification in the MCP has to be linear in order to maintain the intensity distribution of the original signal.

d) The phosphor screen has to produce a fluorescence intensity proportional to the number of incident electrons.

e) The CCD must provide a linear read-out of the intensity of the phosphor screen.

* The entrance slit is variable from a few µm to a few mm. Since a wide slit would reduce the time resolution we worked with a slit width of 30 µm that provides a reasonable compromise between high time resolution and sufficiently large light input.
These five fundamental requirements for linearity impose a serious problem to the production of high quality Streak Cameras as the one we use, fabricated by HAMAMATSU. Looking in detail to the situation, it turns out that the only step involving the temporal resolution is step b which is related to the linearity of the voltage sweep. HAMAMATSU provides an implemented correction of the sweep nonlinearities in the form of a polynomial fit to the sweep ramp, correcting well these nonlinearities. The fit formula is then programmed in the software which automatically performs the correction, displaying the signal with the corrected time scale. Nevertheless, the precise and linear performance of all the other steps defines the linearity of the sensitivity and has the same importance for high resolution measurements.

The conversion from a time-dependent into a space-dependent light distribution such as that performed by the Streak Camera can be thought of as an imaging process. However, any imaging system presents an input-output transfer function due to inhomogeneities in its spatial profile. These non-uniformities in the sensitivity of the whole imaging system are globally designated as “shading effects” which have to be corrected for high resolution measurements. A helpful tool to correct these shading effects is the so-called “shading correction” provided by HAMAMATSU. The principle idea is to illuminate the streak camera with a spatially and temporally homogeneous light source (a broad spot of a cw lamp emitting white light). The image is stored and any deviation from a constant value of this image must therefore be caused by imperfections in the imaging system. The software provides a tool to remove such imperfections in the real signal image by using this shading image. Unfortunately, the acquisition of these shading images is time consuming because the image differs for each time scale of the Streak Camera and depends also on the amplification factor of the MCP. A light source which is absolutely homogeneous in time and space is neither easily available which makes this correction method to depend on the illumination. Therefore, only a few of the transients obtained with the Streak Camera and presented in this thesis have been treated by “shading correction”. In order to correct the inhomogeneities of the imaging system we have divided the reflectivity transients by those obtained blocking the pump pulse before the specimen. This procedure has turned out to provide reasonable and reliable results and is much less time consuming.

• Streak image analysis

Due to the final readout element of the Streak Camera (the CCD camera), a measured signal appears as a 3D-image consisting of the two spatial dimensions of the screen and the pixel colour (or brightness) as the third dimension.

HAMAMATSU universal streak camera, Model C5680, input optics transmittance 200 - 1600 nm, streak tube transmittance 200 - 850 nm, MCP Gain 3000. Synchroscan unit, Model M5675, working frequency 82.16 MHz, 4 time windows (2, 1.4, 0.8, 0.2 ns), time resolution in the 200 ps window: 1.4 ps. Single sweep unit, Model M5676, single pulse operation, 8 time windows (50, 20, 10, 5, 2, 1, 0.5, 0.2 ns), time resolution in the 200 ps window: 1.44 ps.

consisting of the two spatial dimensions of the screen and the pixel colour (or brightness) as the third dimension.
trace which corresponds to the time and intensity evolution of the probe beam. The image is stored and treated by two means. First, the background caused by the dark current of the CCD camera is removed, by taking a further image with the shutter closed and subtracting it from the stored data-image. Then, the image is shading corrected as described before. For the case of reflectivity measurements following the set-up in Figure 2.7, the resulting image is a data array of 1024×1024 pixels containing a vertical signal trace (probe beam) about 5 pixels broad (FWHM). Out of the whole array, a sub-array of about 1024×20 pixels containing the signal trace is selected*, as shown in Figure 2.11. This sub-array is horizontally averaged to provide a one-dimensional intensity profile. The vertical pixel scale is converted by means of the calibration curves of the Streak Camera sweep into a time scale.

* Even if the signal trace is only 5 pixels broad, we select a width of 20 pixels to account for a eventual tilt of the CCD camera. A comparison to profiles taken from narrower areas showed no effect on the signal-to-noise ratio or the time resolution.

Figure 2.11.: Left: Streak camera image of the probe laser pulse consisting of a 1024×1024 pixel array. The inner array of 20×1024 pixels contains the signal and is used to calculate a vertical profile. Black and white have been inverted for printing purposes. Right: The resulting vertical profile already converted from a pixel scale into a time scale.

- Spatial dimension of a Streak Camera

Another important aspect of a Streak Camera, not mentioned before, is the use of the third dimension of the Streak image; the x-dimension along the entrance slit of the streak camera. This third axis opens the possibility of measuring two or more signals at the same time, by focusing them at different horizontal locations at the slit. The most important application of Streak Cameras is indeed time-resolved spectroscopy. Here, the light signal is spectrally dispersed into its wavelength components by means of a spectrograph. The output of the spectrograph is a
horizontally dispersed broad light spot which enters the slit of the Streak Camera. The resulting Streak image as detected by the CCD camera will then be a 3D-image, the vertical dimension (y) giving the temporal evolution of the light intensity (z-coordinate (pixel intensity)) at a certain wavelength (x-coordinate).

This application is ideal for temporally and spectrally resolved fluorescence measurements. As an example, Figure 2.12 displays such an image of the fluorescence of a laser dye (DASPI) that we have measured* with the Streak Camera. The colors have been inverted in this case for printing purposes so that dark areas mean high pixel intensity and bright ones low intensity. Vertical and horizontal intensity profiles taken from the image along the dashed lines are plotted at the right hand side and at the bottom. The vertical profiles along $\lambda_0$ and $\lambda_1$ give the temporal evolution of the fluorescence at these two wavelengths and the horizontal profiles along $t_0$ and $t_1$ represent the fluorescence spectrum at these times.

![Streak image of the time-resolved spectrum of the fluorescence of the laser dye DASPI. The profiles at the borders are taken along the dashed lines at the wavelengths $\lambda_0$ and $\lambda_1$ and the times $t_0$ and $t_1$.](image)

* in collaboration with the group of Dr. Paul French at the Imperial College in London.
• **Pulse duration measurements**

There are two operation modes of the Streak Camera. In *synchroscan mode* the voltage sweep is applied repetitively at a high frequency (82MHz) allowing the continuous acquisition of a signal that is periodically present at that frequency. These signals are accumulated and averaged. In *single sweep mode* only one transient signal event is detected. Naturally, we use the single sweep mode when acquiring optical transients upon irradiation by ps laser pulses because we are not interested in averaging the transients. Nevertheless, the synchroscan option has turned out to be a powerful tool to control the dye laser oscillator because it reveals better than a diode or an autocorrelator* the presence of small post-pulses which may experience unwanted amplification in the dye amplifier, thus broadening and worsening the temporal profile of the pump pulse.

The dye laser pulses from the oscillator (non-amplified) have been measured both in synchroscan mode and single sweep modes and the results are shown in Figure 2.13. This comparison demonstrates clearly the averaging effect of the synchroscan mode which measures a much broader pulse (35 ps) than the single sweep mode. This effect is due to the temporal jitter† of the 82 MHz pulse train over a measurement time of about 100 ms. The value of 10 ps given by the jitter-free single sweep measurements is consistent with the value provided by the autocorrelator (7 ps, see Figure 2.3). In addition, Figure 2.13 supports the assumption of a one-side exponential decaying pulse shape for the conversion of the autocorrelation trace into a pulse duration.

* Notice that the maximum time window of a scanning autocorrelator is typically no more than 100 ps. Thus, a postpulse further delayed will never be detected but can be strongly amplified.

† Such a jitter is inherent to actively mode-locked laser systems whereas passively mode-locked systems like solid-state femtosecond lasers (Ti:Sapphire) are jitter-free [Fre95].

![Graph showing pulse duration measurements](image-url)

*Figure 2.13.: Streak Camera measurement of the dye laser pulses (non-amplified) in synchroscan mode (broad pulse) and single sweep mode (narrow pulse).*

---

Chapter 2: Experimental
Chapter 2: Experimental

Figure 2.14 shows a Streak Camera measurement of a typical amplified ps pulse as it is used for irradiation of the samples. It can be clearly seen that the main amount of energy is deposited within ≈ 30 ps.

![Streak Camera measurement of an amplified dye laser pulse in single sweep mode.](image)

- **Limitations of the experimental set-up**

  An intrinsic problem of the optical measurements we perform with the Streak Camera is the fact that we measure deviations from a constant reflectivity level, namely that of the sample before the arrival of the pump pulse. This forces us to use a relatively long probe pulse, with a pulse intensity as high as possible in order to have a high signal-to-noise ratio. Unfortunately, the use of long pulses (above some tens of ns) generates enormous problems for Streak Camera measurements. The most important of them (apart from the fact that cw-like illumination reduces the lifetime of the photocathode) are the so-called “space charge effects”. These effects occur when a long and relatively intense light pulse reaches the photocathode where the incident photons generate continuously a large number of electrons. In such a situation, the applied electric field is not able to remove all photoelectrons sufficiently fast from the photocathode and a local charge cloud is formed at it. The cloud may reach a considerable extension, much larger than the light spot, and may shield the extraction potential. This will affect notably both the time and the space resolution as well as the linearity of the intensity distribution. As a consequence, if working with a long light pulse, its intensity has to be kept always below the threshold for space charge formation.

\[ \text{The threshold light intensity for space charge formation is relatively easy to determine because it manifests by a non-proportional spatial broadening of a signal when the intensity is increased.} \]
This reduction of the incident light intensity leads to an additional problem since the actual number of the photons/time-unit is decreased. The number of photons is proportional to the time scale as can be seen in Figure 2.15, where the area below the reflectivity transient corresponds to the number of photons for different time windows. While for large time windows, many photons contribute to the signal, only a small amount of photons are effective when going to short time scales as can clearly be seen.

![Figure 2.15.](image)

Figure 2.15.: Influence of the time scale chosen at the Streak camera (ranging between 50 ns and 0.2 ns) and the number of photons which contribute to the signal. The transient has been taken as an example from Figure 2.8.

In short time windows, these few effective electrons are distributed along the whole y-axis of the CCD screen which provides a low signal. In order to compensate the low signal, the MCP gain of the streak camera and the gain of the CCD camera must be increased which elevates considerably the noise level. In conclusion, a compromise has always to be achieved: The incident intensity must be low enough to prevent space charge formation but high enough to obtain a reasonable signal-to-noise ratio.

- **Probe laser**

The probe laser pulse has turned out to be the most problematic element of the whole set-up. A simple explanation for that is the difficulty to obtain a pulse intensity which is temporally constant in the small time window in which we are interested to measure (tens of nanoseconds with picosecond resolution). As it was already mentioned in the description of the detection system with ns-resolution, the HeNe laser presented intensity fluctuations due to competition of different laser modes. Using a faster detection system such as the Streak Camera, these intensity fluctuations are temporally resolved and we face a situation in which the intensity fluctuates...
arbitrarily between zero and a maximum value. These fluctuations, together with the low power of the HeNe laser, prevented the attainment of a reasonable signal-to-noise ratio for Streak Camera measurements and obliged us to use a single mode Ar\(^+\) laser\(^*\) working at the green line (514.5 nm). Single mode operation was achieved by introducing an intracavity etalon, whose principle of operation is schematically drawn in Figure 2.16.

![Figure 2.16.: Gain profile, resonator modes and spectral transmission of an etalon which is tuned for single-mode operation.](image)

Without an etalon, all laser modes within the gain curve of the Ar\(^+\) laser which are above the lasing threshold are able to contribute to the lasing process and a competition between them leads to the observed intensity fluctuations. Introducing an etalon and optimizing its narrow resonance transmission to be at the mode of main intensity \(\lambda_L\), all other modes can effectively be suppressed. Since the gain profile of the Ar\(^+\) laser has a spectral width \((\lambda_2-\lambda_1)\) of about 8 GHz, the free spectral width of the etalon must be larger (10 GHz) to achieve single mode operation [Dem81].

One of the consequences of introducing the etalon is that the intensity of the output beam is reduced considerably due to the single-mode operation in addition to some losses. Nevertheless, the power turned out to be still sufficient to provide a sufficiently intense probe beam for the Streak Camera measurements. The improvement achieved with the single-mode operation can be seen in Figure 2.17 showing a Streak Camera measurement of the probe laser intensity with and without etalon. Whereas the intensity without etalon is fluctuating strongly (multimode operation generating mode competition), the trace recorded with etalon is temporally much more stable\(^†\) in a time scale of 2 ns.

\* SPECTRA-PHYSICS Ar\(^+\) laser, Model 165-07. specified maximum output power: 3 W (cw, all lines), 1.2 W (cw, 514.5 nm), with intra-cavity etalon (measured): 450 mW (single mode cw, 514.5 nm).

\† The slight curvature of the trace (decreasing to both ends) is caused by shading.
• **Synchronization**

The synchronization scheme in the experiments performed with the Streak Camera has to solve additional problems to those found when using the Transient Digitizer and the photodiode. First, the times of arrival of the pump and the probe pulse at the sample surface have to be synchronized. Secondly, the Streak Camera sweep has to be synchronized with the time of the arrival of the signal at the entrance slit of the Streak Camera. The first synchronization is done using the same scheme already described for the case of the Digitizer. Also here, the probe pulse duration (1 μs) is much longer than the largest time window of the Streak Camera (50 ns) which implies that the jitter of this signal is not relevant. In contrast, for the second synchronization a nearly jitter-free trigger signal is essential to synchronize the streak sweep and the temporal position of the pump pulse. It is worth to notice that there is a specific delay ranging from 20 - 70 ns (depending on the time window) between the arrival of the trigger signal and the moment at which the actual sweep is produced in the Streak Camera. Therefore, the trigger signal has to occur well before the ps pump pulse is released by the dye amplifier. An apparently obvious possibility would be the use of an optical delay line for the pump pulse, using a fraction of the pump pulse taken before the delay line as an *optical trigger* signal for the Streak Camera. If such a delay line is mounted in air, its length should be of no less than 30 m which would generate severe problems in terms of alignment, stability and beam divergence. The use a single mode optical fiber delay line is impossible since the fiber core should stand power densities in the order of 100 Terawatt/cm². Therefore, an *electronic trigger* signal was chosen, provided by the synchronizer module\(^*\) which couples the Nd:YAG laser (10 Hz clock), the Q-switch and the dye laser oscillator clock (82 MHz). This signal permits to trigger the streak camera sufficiently early and with a relatively small jitter (500 ps).

\(^*\) Described in detail in section 2.1.
2.3 Samples and their treatment

This section is dedicated to the description of the samples used in this work. First, the synthesis process of the specimens in addition to their optical characterization is described briefly. Secondly, the pretreatment techniques used to modify the initial state of the specimens before irradiation are explained.

Synthesis and characterization

As outlined in Chapter 1, the properties of amorphous semiconductor films do depend both on the deposition technique and on the particular deposition parameters. Spectroscopic ellipsometry in combination with an effective medium modeling is a suitable means to determine the optical properties and the void concentration of a film [Pil87], [Yan87]. A comparative study between a-Ge films produced by different deposition techniques revealed that laser-deposited and dc-sputtered films are denser than electron-beam-deposited films [San92]. The low void fraction can be explained by the high kinetic energy of the species reaching the substrate [Mul87]. It was demonstrated that the stability of the amorphous Ge films and the constancy of their optical properties is related to a low void content [Asp82], [San92].

The samples used in this study are amorphous Ge and Ge$_{0.07}$Sb$_{0.93}$ films grown by dc-sputtering as well as single crystal wafers. The films were grown from (99.999%) Ge and Sb targets using an Ar operating pressure of $4 \times 10^{-3}$ Torr in a vacuum system with a residual pressure of $3 \times 10^{-6}$ Torr. The deposition rate has been 0.25 nm/s. The substrates are glass and Si <100> wafers covered by their native oxide and held at room temperature during the deposition. The ellipsometric parameters of our films have been measured by means of a commercial SOPRA spectroscopic rotating polarizer ellipsometer. The void fraction of the films is estimated to be below 4 % and relatively constant over depth for film thicknesses between 50 and 200 nm [San92]. The wafers are 0.3 mm thick <111> c-Ge, cleaned with organic solvents. No attempt has been done to remove the native oxide layer which has a thickness of about 2-3 nm [Veg93b]. Tables 2.2 and 2.3 give the sample description and the optical constants of the involved materials and their phases at the wavelengths of interest for this work.

* As for example the one proposed by Bruggeman [Bru35].
† The optical constants of a-Ge have been measured [San92], those of l-Ge are taken from the work of Jellison and Lowndes [Jel87] and the ones of c-Ge and c-Si from reference [Pal85]. The values for l-Ge at 193 nm could not be taken from reference [Jel87] being limited to the visible range (< 4eV). The optical constants of a-Ge$_{0.07}$Sb$_{0.93}$ films have been measured [San97]. The optical constants of glass can be considered constant in the visible and completely absorbing in the ultraviolet (the transmission drops to zero at 280 nm).
## Chapter 2: Experimental

<table>
<thead>
<tr>
<th>sample</th>
<th>film thickness (nm)</th>
<th>state before irradiation (history)</th>
<th>substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Ge</td>
<td>50</td>
<td>as-grown</td>
<td>glass (1 mm)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>thermally annealed</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>ps laser pulse pre-irradiated</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>ns laser pulse pre-irradiated</td>
<td></td>
</tr>
<tr>
<td>a-Ge</td>
<td>50</td>
<td>as-grown</td>
<td>Si wafer (0.3 mm)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-Ge</td>
<td>300,000</td>
<td>wafer</td>
<td>—</td>
</tr>
<tr>
<td>a-Ge0.07Sb0.93</td>
<td>25</td>
<td>as-grown</td>
<td>glass (1 mm)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a-Ge0.07Sb0.93</td>
<td>25</td>
<td>as-grown</td>
<td>Si wafer (1 mm)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2.: The samples used in this work indicating structure (a- or c-indicating amorphous or crystalline, respectively), film thickness, state before irradiation and substrate type.

<table>
<thead>
<tr>
<th>wavelength</th>
<th>HeNe = 633 nm</th>
<th>Dye = 583 nm</th>
<th>Ar+ = 514 nm</th>
<th>ArF = 193 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>optical constant</td>
<td>n</td>
<td>k</td>
<td>1/α (nm)</td>
<td>n</td>
</tr>
<tr>
<td>a-Ge</td>
<td>4.7</td>
<td>1.8</td>
<td>28</td>
<td>4.53</td>
</tr>
<tr>
<td>c-Ge</td>
<td>5.5</td>
<td>0.66</td>
<td>76</td>
<td>5.55</td>
</tr>
<tr>
<td>l-Ge</td>
<td>3.26</td>
<td>5.92</td>
<td>8.5</td>
<td>2.77</td>
</tr>
<tr>
<td>glass</td>
<td>1.5</td>
<td>0</td>
<td>&gt;10m</td>
<td>1.5</td>
</tr>
<tr>
<td>c-Si</td>
<td>3.87</td>
<td>0.02</td>
<td>2520</td>
<td>4.00</td>
</tr>
<tr>
<td>a-Ge0.07Sb0.93</td>
<td>3.88</td>
<td>2.81</td>
<td>18</td>
<td>3.60</td>
</tr>
</tbody>
</table>

Table 2.3.: Refractive index and optical penetration depth (1/α = λ/4πk) of the film and substrate materials and their phases at the laser wavelengths λ used in this work. Taken from Refs. [San92], [San97], [Pal85] and [Jel87].
Chapter 2: Experimental

Pretreatment techniques

• **Furnace annealing**

  In some cases the samples have thermally annealed in a furnace under vacuum conditions \((10^5 \text{ mbar})\). Due to the simplicity of the technique, its description is done by the annealing parameters such as annealing temperature and time, which will be given when presenting the experimental results.

• **Laser annealing**

  In addition, pretreatment of the specimens has been done by laser annealing before measuring in real time the reflectivity upon ps laser pulse irradiation. Three different types of laser pulses with different fluences have been applied for this purpose, as described in the following.

1. **Nanosecond excimer laser pulses**

   Nanosecond laser pulses in the ultraviolet are provided by an excimer laser. The laser is filled with an ArF gas mixture which enables the generation of laser pulses at a wavelength of 193 nm and 12 ns duration. The pulse energy is stable within 10%. The temporal shape of these pulses can be seen in Figure 2.18.

   ![Figure 2.18.: Temporal profile of an excimer laser pulse giving a FWHM value of 12 ns.](image)

   The use of a beam homogenizer leads to a homogeneously illuminated, rectangular spot of \(\approx 4\times4 \text{ mm}\) at the sample site. The spatial profile has been measured with a detector which was placed behind a pinhole. This pinhole was located at the sample site and displaced in discrete
steps scanning an area of 6×6 mm registering the intensity at each position. Figure 2.19 shows a contour plot of this scan in which the lines indicate a level of the same intensity.

![Contour plot](image)

*Figure 2.19.: Contour plot of the spatial top-hat profile of the excimer laser pulses after the beam homogenizer at the sample site. The central area of 2×2.5 mm is homogeneously flat within 10%.*

The difference in intensity between two neighbor lines is 10%. The upper plane corresponds therefore to a very flat intensity distribution from 90 - 100%. This fact assures that the central area of 2×2.5 mm is exposed to a intensity distribution which is homogenous better than 10%. This is especially important for structural relaxation experiments where the samples are pre-irradiated with an excimer ns laser pulse and subsequently irradiated at various locations of the central area with ps laser pulses, assuming that the material has experienced the same local fluence of the excimer laser over the whole region. As in the case of the ps laser pulse system, the pulse energy is obtained by measuring a calibrated reference energy. The fluence range accessible with excimer laser pulses at the central region of the sample amounts to 0-350 mJ/cm². The absolute error in fluence calibration is determined basically by the spatial intensity distribution and therefore within 2-10%, whereas the relative fluence determination has an accuracy close to 2%.

### 2. Nanosecond dye laser pulses

The amplified dye laser system described in section 2.1 permits also the generation of nanosecond laser pulses at a wavelength of 583 nm and 2.5 ns duration. This operation mode is possible when switching of the mode locker of the Ar⁺ laser resulting in a cw laser output of the latter. The oscillator subsystem then operates as a cw dye laser working at 583 nm. Traversing the dye amplifier the pump pulses of the Nd:YAG laser amplify a short temporal section of that cw-laser light. Thus, both the pulse duration and shape of the output dye pulses are very similar to the ones of the Nd:YAG laser. The ns dye laser pulses are used to pre-irradiate the material at a
certain fluence. Subsequently, the reflectivity changes induced upon further irradiation with ps laser pulses at the same location are measured.

3. Picosecond dye laser pulses

These pulses are provided by the amplified dye laser system itself and thus at a wavelength of 583 nm and 30 ps duration, as described in section 2.1.

2.4 Optical simulations

The performance of numerical simulations of the optical reflectivity changes upon phase transformations turned out to be an essential tool for the understanding of the experimental results. The details about the applicability of the program used, allowing a manifold of different simulation scenarios, will be explained in the following.

Optical simulations of the induced reflectivity changes were performed, taking into account the wavelength of the probe laser, the angle of incidence and the optical constants of the substrate and the involved phases of the film or bulk material (α-, c-, l-Ge and GeSb). This has been done by means of a direct calculation of the reflectivity evolution for a monochromatic electromagnetic wave interacting with a multilayered system formed by α-, c-, l-material and a substrate when the thickness of one layer increases at the expense of the other or converts into another phase. This kind of reflectivity calculations is based on the use of Fresnel formulae, as described in many reference books on classical optics [Bor65]. The core computer program was developed by Dr. R. Serna and extended by Dr. J.M. Ballesteros in order to allow the simulation of more complex scenarios. With the latter version, all three different types of melting/solidification scenarios introduced in section 1.5 (Figure 1.8) can be simulated: Interfacial solidification, bulk solidification and explosive crystallization.

For the simulation of interfacial solidification, the program transforms layer by layer (step = 1 nm) the optical constants* of the initial film material (α-Ge or c-Ge) into the constants of the different phases involved in the process (α-, c-, l-Ge) and calculates the reflectivity of the whole system at the monitoring wavelength as a function of the transformation depth. In the case of bulk solidification, an accurate representation of the process should involve the conversion of the molten volume into crystallites distributed within an amorphous matrix as a function of the crystalline fraction. A good model is provided by effective-medium theories such as the one developed by Bruggemann [Bru35] which is used here. In this case, the program calculates the reflectivity of a solidified Ge film as a function of the crystalline fraction. In the case of explosive crystallization, the reflectivity evolution is calculated as a thin liquid buried layer with constant

---

* The values for each phase and the substrate at the wavelength used are listed in Table 2.3, section 2.3.
Chapter 2: Experimental

thickness propagates in depth. The program also allows the resolidified upper layer to be crystalline or amorphous.

2.5 Ex-situ measurements of structural changes

Several techniques have been used to characterize the actual state of the Ge specimens after irradiation. In addition to optical microscopy which is mainly sensitive to ablation phenomena, Raman spectroscopy and SHG microscopy has been applied ex-situ to determine state of the specimen after irradiation.

Raman Spectroscopy

• Theory and applicability for the study of Ge films

Raman Spectroscopy is a relatively simple way to determine whether the actual state of the Ge films under investigation is amorphous or crystalline. For centrosymmetrical semiconductors as c-Ge the momentum conservation rule allows only scattering by zone center (q = 0) photons [Hay78]. The first order Raman spectrum of c-Ge presents a narrow optic phonon band Ge at 298 cm\(^{-1}\) with an intrinsic line width of about 3 cm\(^{-1}\) at 300 K [Gon85]. For amorphous Ge, the momentum conservation rule does not apply due to the translational symmetry breakdown and other phonons can participate in the Raman scattering. This results in an asymmetrical broadening - the characteristic broad transverse optic (TO) phonon band - and redshift of the peak frequency towards a value of 270 cm\(^{-1}\) [Lan85], [Tsu85].

In c-Ge, Raman spectroscopy measurements provide the phonon correlation length (L) which is a measure for the average distance between defects (in the case of structural damage) or of the particle size (in the case of nanocrystals). It can be used to determine the average size of the polycrystalline material induced upon rapid solidification. Several studies have demonstrated that this way of estimation of the average crystallite size provides values which are in reasonably good agreement with the values obtained by other techniques such as transmission electron microscopy [Bot96], [Dut96], [Gon85], [Fuj91]. The phonon correlation length in the crystalline material was determined from the experimental Raman spectra using the ratio \(\Gamma_a/\Gamma_b\), where \(\Gamma_a\) and \(\Gamma_b\) are respectively the half widths of the optical phonon band of c-Ge at the low and the high frequency sides of the spectrum. The actual relation between \(L\) and the ratio \(\Gamma_a/\Gamma_b\) we use here was determined by J. Gonzalez-Hernandez et al. assuming a gaussian spatial correlation model [Gon85]. The ratio \(\Gamma_a/\Gamma_b\) is independent on the apparatus correction function and therefore an accurate correlation length can be obtained in a simple way.

In addition, the Raman spectrum should reproduce the phonon density of states [Shu70]. In the case of the amorphous phase this results in a broad spectrum at 270 cm\(^{-1}\) related to TO phonons and other broad bands at lower frequencies associated with longitudinal optic (LO) and acoustic phonons. This fact enables the use of Raman spectroscopy to obtain direct information
Chapter 2: Experimental

on structural relaxation. In addition, this method has the enormous advantage that it is insensitive to impurities. Structural relaxation can be appreciated in the following features of the Raman spectrum, as already demonstrated on a-Ge [Yeh83], [Tsu84], [For88], [Veg94] and a-Si [Bee85], [Tsu83], [Tsu84], [Tsu85].

1. The ratio of the transverse optic (TO) and the transverse acoustic (TA) peak intensities increases upon relaxation.
2. The position of the TO peak shifts towards higher wavenumbers.
3. The width of the TO peak decreases.

The last feature, the narrowing of the TO peak, reflects directly a narrowing of the distribution of stretching vibrational frequencies and can be related quantitatively to the relaxation process through the average bond angle distortion $D_q$. Equation 2.3 provides an approximately linear relation between the half width of the TO peak ($\Gamma/2$) and $D_q$.

$$\Delta \theta_b \approx \sqrt{\left(\frac{\Gamma/2}{2.65}\right)^2 - 9^2}$$

(2.3)

$\Gamma/2$ is measured at the high-wavenumber side to avoid influences of the nearby acoustic phonons and the LO peak. The (strain) energy stored in an amorphous network due to the bond-angle distortions is proportional to the square of the bond-angle distortion, i.e. $U_b \sim (\Delta \theta_b)^2$ [Tsu85], [For88].

Although most authors agree on the qualitative relation between the Raman spectrum and the energy and structure of the amorphous network, there is no agreement on the absolute numbers involved. Equation 2.3 is empirical and based on experimental data provided by Cerdeira et al. [Cer72], Tsu et al. [Tsu85], and on calculations by Martin [Mar70]. In any case, there is a general agreement in the consideration that $\Delta \theta_b$ can only vary within a finite interval in which the extreme values correspond to the maximally relaxed or de-relaxed states of the amorphous material. The full range of bond-angle distortions according to their estimates are for Ge $6^\circ - 8.5^\circ$ and for Si $7^\circ - 10^\circ$ (also reported by Refs. [Won86], [Sai82]). Other estimates provide the range for Si to be $7.7^\circ - 10.5^\circ$ [Bee85]. Please note, that the excessive range in Ge reported by Fortner ($9.2^\circ - 12^\circ$) [For88] is based on the full width $\Gamma$ and therefore influenced by other bands. In this work, the relation expressed above (equation 2.3) will be used. More information about the different models relating the Raman linewidth and the bond angle distortion can be found elsewhere [Sin88].

* A more refined expression is given in Ref. [Tsu85].
• **Experimental set-up**

All Ge samples used in the present work have been inspected by optical microscopy and their structure characterized before and after irradiation by means of Raman spectroscopy in Micro-Raman configuration [Tan86], [Jim93]. This configuration allows the measurement of the relatively small irradiated areas at their very center, i.e. the same location where the probing laser hits the surface, as schematically drawn in Figure 2.20.

![Figure 2.20.: Set-up for Micro-Raman spectroscopy.](image)

The Raman measurements have been carried out using a DILOR XY Raman spectrometer attached to a metallographic microscope for excitation and scattered light collection. The excitation beam was delivered by an Ar⁺ laser at 514.5 nm. In order to avoid the presence of both spectral broadening and/or annealing of the surface due to laser induced heating, the power of the excitation beam is kept low enough (a few mW) and the beam is slightly defocused leading to a spatial resolution of a few µm. The samples were mounted on a XY translation stage allowing the selection of different areas of the specimen with a high spatial accuracy (10 µm). The detection of the Raman scattered light was made with an intensified silicon photodiode array. The Micro-Raman signal for α-Ge is very weak, thus requiring long integration times and a tedious spectra acquisition.

---

* The Raman measurements have been performed at the Dto. de Física de la Materia Condensada, Cristalográfía y Mineralogía, Facultad de Ciencias, Universidad de Valladolid - Spain in collaboration with Prof. Dr. Juan Jiménez, Dr. Carlos García and Oscar Martínez Sacristán.
Chapter 2: Experimental

Second Harmonic Generation (SHG) microscopy

- **Theory and applicability for the study of Ge films**

  In addition to the previously described techniques, Second Harmonic Generation microscopy has been tested as a possible method to measure the state of relaxation in the films. SHG microscopy provides information about the material structure because SHG is related to the second order non-linear susceptibility tensor which is a measure for the lattice symmetry [Tom83], [Sha83b], [Sok95]. Semiconductor crystals possessing inversion symmetry as Ge and Si are known to have a rather weak second-order nonlinearity of the quadrupole type [Gov83], since the electric dipole contribution is forbidden by symmetry. Nevertheless, anomalously highly efficient SHG in reflection has been reported in ion-implanted pulsed laser annealed c-Si <111> [Gov89]. The authors attributed the origin of this increase to the presence of mechanical stress in the surface layer. This observation leads to the expectation that for amorphous semiconductors, where the lattice symmetry breakdown causes also a strain field, SHG could be sensitive to the state of relaxation.

  The generated SH in centro-symmetric crystals may consist of three components (generated at the surface, at buried interfaces and in the bulk). The attribution of a certain change in the entire signal upon relaxation to a certain component would require a more detailed mathematical analysis which is been beyond the scope of the present work. Although these problems limit the interpretability of the results, the observed contrast of the measurements upon relaxation and crystallization is astonishing this being the reason why preliminary results are included in the Appendix B. To the best of our knowledge, this is the first time that this technique is applied to measure structural changes in thin amorphous semiconductor films.

- **Experimental set-up**

  The experimental set-up for measuring the SHG in the sample is similar to the one used for Micro-Raman measurements shown in Figure 2.11. Femtosecond laser pulses (FWHM = 25 fs) from a Ti:Sapphire laser (instead of a cw Ar$^+$-laser) are reflected by a dichroic mirror (instead of a beam splitter) and pass through a microscope which focuses the pulses down to a spot size of 1 $\mu$m at the sample surface. Both the specular reflected light and the generated SH signal are recollimated by the same microscope and separated by the dichroic mirror into its two

---

1. The measurements have been performed at Institut für Experimentalphysik, Freie Universität Berlin - Germany, in collaboration with Prof. Dr. Eckart Matthias and Dr. Uwe Conrad.
2. Remind that the electric dipole contribution, dominant in non-centro-symmetric crystals, is forbidden.
3. The dichroic mirror has an optimum reflectance at the peak laser wavelength of $\lambda = 800$ nm and a optimum transmission at the SH ($\lambda = 400$ nm).
wavelength components, the fundamental being reflected and the SH being transmitted. The SH signal is then detected by a photomultiplier connected to a lock-in-amplifier in order to improve the signal-to-noise ratio. The samples were mounted on a motorized X-Y translation stage allowing the performance of 2-dimensional scans of the areas of interest with a spatial resolution of a few \( \mu \text{m} \). The laser fluences used for the SHG-measurements were in the order of 20\( \mu \text{J/cm}^2 \) at a wavelength of 800 nm. The use of such low pulse fluences (about 3 orders of magnitude below the melt threshold) ensured that no structural transformation was induced by the fs pulses.