Thin Film Cavity Ringdown Spectroscopy (tf-CRDS)
a direct and ultra-sensitive absorption technique
for defect measurements on a-Si:H thin films

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Abstract

We have further explored the applicability of cavity ringdown spectroscopy, an ultra-sensitive gas phase absorption technique, with respect to measure defect related absorptions in thin films. This report focuses on a thorough investigation of several issues arising from the insertion of a sample into a high finesse optical cavity and on the application of the technique, called thin film cavity ringdown spectroscopy (tf-CRDS), on a-Si:H thin films of different thickness. The stability and mode formation of an optical cavity containing a sample has been studied by means of a 2D finite element analysis. The build-up time of the cavity and the changes in the cavity output signal due to the insertion of the sample have also been investigated and revealed that no significant change is observed as long as the reflectivity of the sample is lower than the reflectivity of the cavity's mirrors. The losses caused by the surface roughness of the sample have been estimated from scalar surface scattering theory employing surface morphology data from atomic force microscopy experiments. It is shown that this will eventually limit the absorption sensitivity of the technique, which is calculated to be as low as $10^{-7}$ per pass. Absorption measurements have been performed on several thin a-Si:H films of varying thickness (3.5-1031 nm) in a broad spectral range (0.7-1.7 eV) using an optical parametric oscillator (OPO) laser system and show good agreement with conventional transmission spectroscopy and photothermal deflection spectroscopy. Necessary correction for interference in the a-Si:H thin films have been modeled in a straightforward but complete way by an ab initio electric field intensity calculation for a thin film placed in an optical cavity. Material properties such as the averaged defect density, the surface and bulk defect density and the Urbach energy can be determined from the optical absorption spectrum. The high sensitivity of tf-CRDS allowed us to determine the optical absorption spectrum of a 3.5 nm a-Si:H film revealing a different spectral behavior in the sub-gap of a surface dominated (3.5 nm) and bulk dominated (1031 nm) a-Si:H film. This difference is possibly caused by a different dominant type of defect present in the surface compared to the bulk. From the above it can be concluded that tf-CRDS is a direct ultra-sensitive absorption technique which can be used during light soaking experiments and in situ detection of defects during real-time film growth in order to reveal the a-Si:H growth mechanism.
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1. Introduction: optical absorption spectroscopy and a-Si:H

1.1 Technology assessment

Hydrogenated amorphous silicon (a-Si:H) has become an important candidate for use in the next-generation flexible thin solar cells. In this type of solar cells, the a-Si:H is used as the intrinsic active material which converts photon energy into free electron-hole pairs. In comparison to crystalline silicon (c-Si), which is presently most commonly used in solar cells, a-Si:H has a higher photo-absorption coefficient and therefore a-Si:H films can have a much smaller thickness compared to c-Si films in e.g. solar cells, to achieve a similar level of light absorption. Apart from application in solar cells, a-Si:H is also used in thin film transistors (TFT), light emitting diodes (LEDs), light sensing detectors and imaging devices. It can be stated that a-Si:H is an important material in present and future technology.

The amorphous nature of a-Si:H gives rise to a considerable amount of defect states in the a-Si:H band gap. These defects, a free bond on a Si-atom in the a-Si:H matrix, or dangling bond as depicted in Fig. 1.1, can act as a recombination site for photo-generated electron-hole pairs, thereby for example limiting the efficiency of a-Si:H solar cells. Therefore the number of defects will highly determine the a-Si:H quality.

![Figure 1.1 Schematic representation of the a-Si:H matrix with dangling bonds present in the bulk and at the surface.](image)

A concern in the technological application of a-Si:H is the photo-induced degradation of a-Si:H, the so-called Staebler-Wronski effect [2]. The Staebler-Wronski effect is an important issue for the a-Si:H solar cell technology because it causes the solar cell
efficiency to drop 20-30% after prolonged light illumination. The degradation arises from the creation of additional dangling bonds during light illumination.

A-Si:H films are commonly produced by plasma enhanced chemical vapor deposition (PECVD) using radio frequency (rf) driven parallel plate reactors to create a silane (SiH₄) plasma. During growth dangling bonds at the surface are supposed to act as important growth sites for adsorption of the reactive species generated in the plasma. As already mentioned the amorphous matrix leads to the existence of dangling bonds, most likely created during growth. A direct detection technique for dangling bond detection during growth would therefore greatly improve the insight into the growth mechanism of a-Si:H.

In this report an ultra-sensitive direct absorption technique, based on cavity ringdown spectroscopy (CRDS), is further developed for ex situ defect density measurements on as-deposited a-Si:H films in preparation for in situ detection to study the a-Si:H growth mechanism.

In this chapter, after a detailed analysis of the optical absorptions in a-Si:H, commonly used defect detection techniques will be discussed. Finally, after a short introduction into CRDS, an extensive motivation of the research will be given.

1.2 Analysis of the optical absorption of a-Si:H

Optical measurements are among the most powerful methods of material characterization. These methods can be used for fast and nondestructive monitoring of the material properties.

One of the most commonly investigated quantities in optical measurements is the absorption coefficient α, which is defined as the intensity loss per unit length (cm⁻¹) according to the Lambert-Beer law [5]:

\[ I(\lambda, d) = I_0 e^{(-\alpha d)} \]

with \( I_0 \) the incident power and \( d \) the thickness of the absorbing medium. The absorptance, \( \alpha d \), and consequently the absorption coefficient can be obtained straightforwardly by:

\[ \ln\left(\frac{I}{I_0}\right) = -\alpha d \]  

The optical absorption spectrum, the absorption coefficient versus the photon energy, of a-Si:H is widely studied to determine i.e. the electronic density of states in the bulk of a-Si:H. The general accepted model of the electronic density of states (DOS) of a-Si:H is proposed by Street et al. [6] and is shown in Fig. 1.2 (a). The DOS of a-Si:H consist of a valence and conduction band with their characteristic exponential tails with slopes \( E_{0v} \) and \( E_{0c} \), respectively, arising from the amorphous nature of a-Si:H. Furthermore dangling bond states exist in the mid-gap region in the form of two peaks which can be attributed to the neutral defect \( D^0 \) and negatively charged defect \( D^- \). Moreover, in Figure 1.2 (a) also
the possible optical transitions in a-Si:H are shown. These transitions can be divided into three groups and are related to the (typical) optical absorption spectrum of a-Si:H as depicted in Fig. 1.2 (b).

Region C in Fig. 1.2 (b) is associated with transitions from the valence band to the conduction band (transitions T_1 in Fig. 1.2). In solar cells these transitions are mainly responsible for the creation of electron-hole pairs by photons. In region C the optical absorption coefficient of a-Si:H is significantly higher than for c-Si.

Region B in Fig. 1.2 (b) is associated to transitions from the exponentially decreasing DOS in the valence band and transitions to the exponential decreasing DOS of the conduction band (transitions T_2 and T_3 in Fig. 1.2 (a)) leading to an exponential decreasing $\alpha$. This region can therefore be characterized by the so-called Urbach energy $E_u$ [7]:

$$\alpha(E) \sim \exp\left(\frac{E}{E_u}\right), \quad (1.3)$$

with $E$ the photon energy.

Region A corresponds to transition from the extended valence band to the defect states (T_4 in Fig. 1.2) and from defect states to the extended conduction band (T_5 in Fig. 1.2). This part of the optical absorption spectrum is the so-called sub-gap absorption region. This absorption is assumed to be related to the dangling bonds in a-Si:H. From integrating the absorption in the sub-gap region the defect density ($N_d$) of a-Si:H can be obtained, which gives a good indication of the material quality.

There is abundant evidence from optical data that the Urbach slope $E_u$ and the defect density $N_d$ are correlated. Figure 1.3 shows that most of the published data for $E_u$
and defect density fall in the shaded region in the defect density versus $E_u$ diagram. Therefore the Urbach energy can also be used for a rough indication of the material quality.

![Figure 1.3 Correlation between the Urbach slope $E_u$ and the defect density. Published data for doped and undoped a-Si:H prepared under a variety of deposition conditions fall within the shaded area.][23]

Due to the low density of sub-gap states, the probability for transitions from and to defect states is extremely low, resulting in a low absorption in region A of Fig. 1.2 (b). But knowledge of region A is essential for determining the quality of a-Si:H. Therefore an extremely sensitive absorption technique that directly can determine the absorption coefficient in a broad spectral range is needed. Preferential this absorption technique is also applicable in situ, thereby allowing to monitor the defect density during growth, to such that insight can be gathered into the growth mechanism of a-Si:H.

In the next section, some commonly used techniques for optical absorption measurement will be discussed. The main focus will be on techniques capable of determining the optical absorption in region A and B as shown in Fig. 1.3.

### 1.3 Optical absorption techniques

Transmission reflection spectroscopy (discussed in more detail in section 4.1) is one of the most straightforward ways to determine the optical absorption spectrum of a-Si:H films. By measuring at the same time the incident, reflected and transmitted intensity of an electromagnetic wave that is impinged on a sample, the intensity loss due to absorption in the film can be determined and can be related to the optical absorption spectrum of the thin film. The sensitivity of this method is limited by the stability of the
light source used and the precision of intensity detection. Transmission reflection spectroscopy (TR) is capable of determining absorptions down to $1 \times 10^{-3}$ per pass and therefore is not capable of determining the absorption coefficient in the defect related part of the spectrum (region A). Consequently TR is not suitable to study the a-Si:H quality in terms of defects. Several (indirect) techniques have been developed, specifically for determining the absorption spectrum in the defect related part of the spectrum.

Two commonly used techniques for sub-gap absorption measurements, i.e., constant photocurrent (CPM) [8] and dual beam photocurrent (DBP) [9], are based on measuring the photocurrent generated under illumination of the sample in order to determine the absorption coefficient. Both CPM and DBP measure only transitions contributing to free electrons to the conduction band, therefore transition $T_4$ in Fig. 1.2 is not taken into account and thereby underestimating the defect density. To obtain absolute values for the absorption coefficient, the photocurrent methods need to be calibrated by TR. The photocurrent is measured by ohmic contacts. Therefore this technique cannot be used during growth of a-Si:H films.

Other commonly used techniques used for determining the sub-gap absorption of a-Si:H are photothermal deflection spectroscopy (PDS, discussed in more detail in chapter 5) [10] and the related technique of photo acoustic spectroscopy (PAS) [11]. These two techniques are based on measuring the heat generation caused by the non-radiative recombination of the photo-carriers, which are created by periodically illuminating the sample. PDS measures the deflection of a probe laser beam, which arises from the temperature-induced variation of the refractive index of the surrounding medium. The deflection of this probe laser beam is proportional to the absorbed heat in the sample. In PAS the heating of a gas volume by the sample is detected as sound with a microphone. The measured sound amplitude is proportional to the absorbed heat. Both PDS and PAS measure all the optical transitions depicted in Fig. 1.2, thereby assuming that all the created electron-hole pairs will recombine non-radiatively. The most accurate way to extract absolute values from PDS and PAS is to calibrate the signal to TR measurements in the high-energy range (1.8 eV, around the optical band-gap). These techniques cannot be applied in situ during growth, due to the necessary media for detecting the heat generation in the film.

Although CPM, DBP, PDS and PAS yield accurate information about region A in Fig. 1.3, they all still have a number of drawbacks. As indicated these (indirect) techniques need to be calibrated by TR measurements to obtain the most accurate absolute $\alpha$ values. The methods based on detecting photocurrent, CPM and DBP, do not measure all the defect related transitions, therefore underestimating the defect density. Furthermore all the techniques cannot be applied in situ during growth to study the role of defects during growth. Therefore a new direct technique is needed that measures all the transitions as depicted in Fig. 1.2 (a) and can be applied in situ. In the next section a ultra-sensitive direct technique, based on cavity ringdown spectroscopy, will be introduced that also can be applied in situ.
1.4 Cavity ring down spectroscopy

A very successful technique for obtaining absorption spectra in the gas phase is cavity ringdown spectroscopy (CRDS), introduced in 1988 by O'Keefe and Deacon [1]. This highly sensitive (capable of detecting absorptions as low as $5 \times 10^{-13}$ per pass close to the shot noise limit [12]) and direct technique is insensitive to incident intensity variation and can be applied in situ. CRDS in the gas phase is e.g. used for detecting SiH$_3$ radicals in a remote Ar-H$_2$-SiH$_4$ plasma [13] and for detecting CH radicals in an expanding argon/acetylene plasma [14]. Extension of CRDS to the solid state could yield an extremely sensitive direct spectral absorption technique, which in principle can be applied in situ. In the next section CRDS and the first attempts of CRDS on thin films will be discussed.

1.4.1 Principle of cavity ringdown spectroscopy

A general CRDS setup consists of two plano-concave mirrors, as depicted in Fig. 1.4. A mono-chromatic light pulse is coupled into the cavity. Because the reflectivity of the mirrors is not equal to 100% some of the light leaks out of the cavity and is detected by the detector behind the cavity. The optical field in the cavity will decay exponentially in time, and can be expressed by a characteristic time constant $\tau$, known as the ringdown time. The ringdown time can be expressed in the following equation [5]:

$$\tau(\omega) = \frac{t_r}{\sum_i L_i(\omega)}, \quad (1.4)$$

where $t_r$ is the roundtrip time for the light in the optical cavity and the denominator contains the sum of all the losses $L_i(\omega)$ inside the optical cavity. As can be seen from Eq. (1.4) the ringdown time is unaffected by intensity fluctuations of the light source.
Figure 1.4 Schematic representation of an optical cavity consisting of two highly reflective mirrors.

For a cavity without an absorbing medium, an empty cavity, the ringdown time is mainly determined by the mirrors reflectivity. The loss $L_0$ in an empty cavity is than approximately equal to $1-R$, with $R$ the mirrors reflectivity. So by determining the ringdown time of the empty cavity one can obtain the reflectivity of the mirrors used. In this report the typically used cavity mirrors have a reflectivity of approximately $R=0.9998$, resulting in a ringdown time of 5 µs for an empty cavity of 0.3 m length.

For an optical cavity $t_r$ is known ($t_r=L/c$, c the speed of light and $L$ the cavity length). By measuring the ringdown time, the sum of all the losses inside the cavity can be calculated by Eq. (1.4). By performing a differential measurement i.e. by determining the ringdown time with and without an absorbing medium, the additional cavity losses $L_{add}$ can be obtained straightforwardly:

$$L_{add}(\omega) = t_r\left(\frac{1}{\tau_2(\omega)} - \frac{1}{\tau_1(\omega)}\right),$$

(1.5)

with $\tau_1$ and $\tau_2$ the ringdown time of the cavity without absorbing medium and the ringdown time of the cavity with the absorbing medium, respectively, as depicted in Fig. 1.5. The intrinsic loss of the cavity can be defined as the loss determined by Eq. (1.4) for $\tau_1$ i.e., the loss of the cavity without additional absorbing medium. For gas phase measurements $L_{add}=\alpha d$ and $\alpha$ can straightforwardly be obtained from the additional cavity loss.
Figure 1.5 Exponential decay of an cavity with ($\tau_2$) and without ($\tau_1$) absorbing species.

Because the transitions $T_4$ and $T_5$ in Fig. 1.2 (a) can only be observed if the absorption technique is sensitive enough, an estimate of the sensitivity of CRDS has to be made. The sensitivity of CRDS was first derived by Zalicki et al. [15] and the minimal detectable additional cavity loss, $L_{add}$, is given by the product of the intrinsic loss $L_0$ of the empty cavity i.e. without absorbing medium that is to be measured and the relative uncertainty in the determination of the ringdown time:

$$L_{min} = L_0 \left| \frac{\Delta \tau}{\tau} \right|,$$

(1.6)

The intrinsic losses of the system should be as low as possible and the ringdown time should be determined as accurately as possible to achieve the highest sensitivity. Therefore if an intrinsic loss of $1 \times 10^{-4}$ can be achieved, which is possible as will be shown, and the ringdown time can be determined accurately enough, it is feasible to expand CRDS to the solid state. To determine an $\alpha \sim 1$ cm$^{-1}$ for a 10 nm film, an absorption, $\alpha \Delta \tau \sim 1 \times 10^{-6}$ has to be determined. In the next section extension of CRDS to the solid state will be discussed briefly.

1.4.2 Thin-film cavity ring down spectroscopy (tf-CRDS)

A straightforward way to extend CRDS from the gas phase to the solid state is to put a thin solid film on an optically transparent substrate inside the optical cavity parallel to the cavity mirrors, as depicted in Fig. 1.6. However the presence of the additional substrate in the optical cavity gives rise to numerous issues. The stability of the optical cavity after insertion of thin solid film is not necessarily guaranteed. The build up time of the optical field and the change in roundtrip time in the optical cavity can influence the detected signal. Surface and bulk scattering will possibly give rise to additional cavity losses.
From Eq. (1.4) it can be seen that not \( \alpha \) is measured in CRDS, but the additional cavity loss. In contrary to the gas phase, an extensive analysis is needed to relate \( L_{\text{add}} \) to the absorption coefficient \( \alpha \) for tf-CRDS. All these issues will be addressed in detail in Chapter 3 and 4 for thin film cavity ringdown spectroscopy (tf-CRDS).

![Figure 1.3 Schematic representation of a solid sample in an optical cavity. Sample is placed parallel to the cavity mirrors in the optical cavity.](image)

Already some approaches were made to extend CRDS to the solid state. Engeln et al. [16] were the first to perform CRDS on the solid state. They placed a glass substrate with a thin (10-30 nm) \( \text{C}_{60} \) film under normal incidence in an optical cavity to probe the fundamental IR lines of \( \text{C}_{60} \). The results obtained by tf-CRDS agreed well with conventional Fourier transform infrared (FTIR) measurements. Logunov [17] used tf-CRDS to probe thin (2-20 \( \mu \)m) polymer film samples in the telecommunication wavelength ranges of 1200-1650 nm, to study the properties of thin films compared to thick bulk films. Smets et al. [18] were the first to perform cavity ringdown on a-Si:H thereby using single wavelength cavity ringdown to probe the sub-gap (1.17 eV) of a-Si:H. In this report the single wavelength study performed by Smets et al. will be extended to a spectral study.

The studies of Engeln et al., Logunov, and Smets et al. used the sample positioning as depicted in Fig. 1.7. Other cavity designs were proposed by Kleine et al. [19], Marcus et al. [20] and Pipino [21,22]. Kleine et al. used the cavity mirrors as a substrate, thereby avoiding cavity stability issues due to insertion of an additional element. Marcus et al. proposed to put the solid sample under Brewster angle geometry to exclude sample reflectivity. Recently Pipino proposed a total internal reflection (TIR) resonator for detecting species by the exponential decaying evanescent electric field. The losses by total internal reflection are only determined by scatter losses at the interface and absorption losses in the TIR resonator. In future work this design will be applied \textit{in situ} to study the growth mechanism of a-Si:H.

In Table 1.1 the literature on tf-CRDS is summarized. Several of the issues concerning tf-CRDS are not yet addressed in literature. None of the authors [16-22] makes an attempt to relate cavity loss to the absorption coefficient. Most of the authors [16-18,20] do not discuss stability issues concerning an optical cavity containing a substrate. Influence of reflection of the inserted sample is ignored [16-18] or cancelled [19] by the Brewster-angle geometry. Most of the authors [16-20] disregard scatter
losses, or make no attempt to separate scatter losses from absorption losses. All authors [16-22] address the increase in intrinsic loss of the cavity due to substrate absorption.

All the above studies indicate that it looks quite promising to extend CRDS to the solid state, but as mentioned there are numerous of issues that still need to be resolved. In this report several issues concerning tf-CRDS will be discussed.

Table 1.1: Overview of the literature on tf-CRDS and the issues addressed.

<table>
<thead>
<tr>
<th>Authors:</th>
<th>Wavelength Range:</th>
<th>Issues addressed:</th>
<th>Probed medium:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engeln et al. [16]</td>
<td>8-9 µm</td>
<td>Substrate absorption Sample reflection ignored</td>
<td>C₆₀, fundamental IR lines.</td>
</tr>
<tr>
<td>Logunov [17]</td>
<td>1260-1330 nm 1480-1650 nm</td>
<td>Substrate absorption Alignment of sample determines accuracy measurement</td>
<td>2-20 µm polymer films</td>
</tr>
<tr>
<td>Marcus et al. [20]</td>
<td>5.5-6.5 µm</td>
<td>Reflection losses Substrate absorption Sensitivity increased by transients distribution</td>
<td>C₆₀ fundamental IR lines</td>
</tr>
<tr>
<td>Kleine et al. [19]</td>
<td>5.8-6.2 µm</td>
<td>Mirror as substrate</td>
<td>Molecular thin layers of iodine</td>
</tr>
<tr>
<td>Smets et al. [18]</td>
<td>1064 nm</td>
<td>Substrate absorption Build-up time optical field</td>
<td>10-3000 nm a-Si:H</td>
</tr>
<tr>
<td>Pipino [21,22]</td>
<td></td>
<td>Scatter losses Mode structure Mode matching Probing via evanescent wave Applicable in situ Polarization effect Limit intrinsic loss</td>
<td>NO₃ radical</td>
</tr>
</tbody>
</table>
1.5 Motivation and goal of this report

As mentioned above the amorphous nature of a-Si:H leads to defects states in the band-gap. These defects play a major role in the applicability of a-Si:H films in e.g. solar cells. Defects are also expected to play a major role during growth of a-Si:H films in plasma deposition. To improve insight into the role and evolution of defects in a-Si:H, a diagnostic technique is needed to study the defects during and after a-Si:H deposition.

Cavity ringdown spectroscopy has shown to be a useful technique for gas phase analysis. Although CRDS on the solid state has been reported in literature, it is still not a common technique for thin film characterization. Several issues concerning tf-CRDS such as: cavity stability, mode formation in an optical cavity, scattering by substrate/sample, sample reflectivity, substrate absorption and to correcting additional cavity loss for interference still need to be resolved. This report will show that tf-CRDS is a powerful tool for thin film characterization. Many important issues and questions, that need to be resolved for application of tf-CRDS, will be discussed in detail.

As proof of principle tf-CRDS will be applied ex situ on thin a-Si:H films to probe the sub-gap absorption of a-Si:H. Tf-CRDS will be compared to commonly used absorption techniques, such as transmission spectroscopy and photothermal deflection spectroscopy. It will be shown that it is possible to determine the Urbach energy, the defect distribution and the spectral signature of bulk and surface defects in thin a-Si:H films by tf-CRDS.

The report starts off with the experimental setup of the tf-CRDS setup (Chapter 2). The laser system, the mirrors, the alignment procedure and the data-acquisition system will be discussed in detail. Also mode formation in an optical cavity, by a 2 dimensional finite element method, and the influence of ambient water absorption will be discussed. Next a substrate will be introduced into the cavity (Chapter 3). Issues concerning: cavity stability, scattering, sample reflectivity and substrate absorption will be discussed. In Chapter 4 the electric field intensity profile in a thin film placed in an optical cavity will be derived, necessary to relate the measured additional cavity loss due to a thin a-Si:H films to the optical absorption coefficient of the a-Si:H films. In Chapter 5 the results obtained by tf-CRDS will be compared to absorption spectrum obtained by PDS and transmission spectroscopy. In Chapter 6 the results obtained by tf-CRDS on thin a-Si:H films will be discussed and material properties, such as the Urbach edge, defect density, defect distribution and spectral signatures of the bulk and surface defects will be derived. Finally, the conclusions and recommendations from this report will be presented in Chapter 7.
2. Experimental setup, intrinsic losses and mode formation of an optical cavity

To give the reader more insight in the main principles of CRDS, an extensive overview of the CRDS setup will be given. The focus will be on the tunable laser source, the cavity mirrors, the near infrared detectors, alignment of the cavity, purging of the cavity, mode formation and stability requirements. Finally the intrinsic losses of the cavity will be presented.

2.1 Experimental details of the tf-CRDS setup

The CRDS setup as depicted in Fig. 2.1 can be divided into four systems, the laser system, the optical cavity, the detectors and the data acquisition system. The four systems will be discussed in detail in the following sections.

![Figure 2.1 Experimental setup for CRDS.](image)

2.1.1 Nd:YAG and OPO laser system

The Nd:YAG laser (Spectra Physics GCR-230) produces light pulses (8-9 ns) with a fundamental wavelength of 1064 nm at a repetition rate of 30 Hertz. To narrow the bandwidth of the Nd:YAG laser, the optical cavity of the laser is seeded by a diode laser operating at 1064 nm. The fundamental output of the Nd:YAG is doubled to a
wavelength of 532 nm by a KDP (Potassium di-Hydrogen Phosphate) crystal. A successive KDP crystal mixes the 532 nm light with the original 1064 nm beam, resulting in a wavelength of 355 nm. The 355 nm light is separated from the 1064 and 532 nm light by two dichroic mirrors [24]. The 1064 nm and 532 nm beams are led into a beam dump and the 355 nm light is used as a pump beam for the optical parametric oscillator (OPO) system (Spectra Physics MOPO 710). The typical output power of the 355 nm pump beam of the Nd:YAG laser system is 8-10 W (267-333 mJ per pulse).

The heart of the OPO system is a parametric gain medium, BBO (β-BaB₂O₄) crystal, transferring the energy of the pump photon to two other photons $\omega_s$ (the “signal” photon) and $\omega_i$ (the “idler” photon). The OPO laser system is tunable from 1.80-3.02 eV (410-690 nm “signal” range) and from 0.56-1.70 eV (730-2200 nm “idler” range) and is horizontally polarized. The typical output energy of the OPO system is shown in Fig. 2.2 (a).

![Energy mJ vs Wavelength nm](a)

![Linewidth cm⁻¹ vs Wavelength nm](b)

Figure 2.2 Specifications of the Spectra Physics MOPO-710 system a) typical output energy of the idler range b) linewidths (cm⁻¹) of signal and idler output range [25].
A characteristic of the OPO system is the relatively high linewidth (>10 cm\(^{-1}\)) of the output laser beam. The bandwidth of the OPO for the “signal” and “idler” output range is shown in Fig. 2.2 (b). The large bandwidth of the OPO laser system is e.g. apparent in the coherence length of the OPO output laser light. The coherence length of a light source can be expressed in the following equation [26]:

\[ l_c = \frac{\lambda^2}{\Delta \lambda}, \]

(2.1)

with \( \lambda \) the laser wavelength and \( \Delta \lambda \) the bandwidth of the laser. For the OPO system the coherence length, according to Eq. (2.1), is typically 1 mm.

The OPO laser system requires the pump laser to be operating at optimal conditions, therefore the Nd:YAG needs to be warmed up for approximately 20 minutes prior to coupling the 355 nm output of the Nd:YAG into the OPO system.

### 2.1.2 Highly reflective mirrors

The optical cavity (\( L=0.4 \) m) is created by two highly reflective (R>0.9998) dielectric mirrors, which have a wavelength operation range of \( \pm \) 15\% of the designed center wavelength. Dielectric mirrors consist of a stack of \( \lambda/4-\lambda/4 \) double-layer films with high refractive contrast of the layers. In Table 2.1 the specifications of the high reflecting mirrors are shown.

<table>
<thead>
<tr>
<th>Energy range (eV)</th>
<th>Center energy (eV)</th>
<th>Model nr. Newport</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.43-1.63 (761-869 nm)</td>
<td>1.53 (810 nm)</td>
<td>10CV00SR.40F</td>
</tr>
<tr>
<td>1.09-1.24 (996-1134 nm)</td>
<td>1.17 (1060 nm)</td>
<td>10CV00SR.50F</td>
</tr>
<tr>
<td>0.88-1.01 (1231-1412 nm)</td>
<td>0.94 (1320 nm)</td>
<td>10CV00SR.60F</td>
</tr>
<tr>
<td>0.75-0.85 (1457-1659 nm)</td>
<td>0.80 (1550 nm)</td>
<td>10CV00SR.70F</td>
</tr>
</tbody>
</table>

With the mirrors in Table 2.1 it is possible to cover most part of the 0.7-1.7 eV energy range, allowing to probe a large part of the sub-gap absorption of a-Si:H. The reflectivity of these mirrors will be determined in Section 2.3.

### 2.1.3 Near infrared detectors

To cover the total energy range of interest two types of near infrared detectors have to be used. For the energy range of 1.12-1.70 eV (700-1100 nm) a photo multiplier tube (PMT Hamamatsu R5108) with a typical rise time of 5 ns is used. The quantum efficiency (number of emitted electrons per incident photon) as a function of the photon energy of the PMT detector is shown in Fig. 2.3 (a). The PMT can be used from visible down to 1.12 eV (1100 nm) for detecting the exponential decaying field in the optical cavity. For
photon energies lower than 1.12 eV, the quantum efficiency of the PMT is insufficient for CRDS measurements.

Figure 2.3 Quantum efficiency (left) of the Hamamatsu R5108 photomultiplier tube as a function of the photon energy (300-1200 nm) [27]. Relative sensitivity of the New Focus 1811 FS photodiode (right) as a function of the photon energy (900-1650 nm) [28].

For the energy range of 0.75-1.02 eV (1200-1660 nm) a 125 MHz photo diode detector (New Focus 1811) was used with a typical rise time of 3 ns. The sensitivity of the photodiode as a function of the photon energy is shown in the right of Fig. 2.3.

By the use of the OPO laser system, the highly reflecting mirrors and the 2 types of near-infrared detectors, it possible to perform CRDS in the 0.75-1.7 eV range.

2.1.4 Data acquisition system and Labview program

The signal of the detector i.e. PMT or photodiode is fed into a home-built data acquisition system (TUeDACS), which is triggered by the Nd:YAG. The TUeDACS system consists of a 12-bit analog/digital converter (Transient Recorder) with a sampling rate of 100 MHz. The TUeDACS has an input range of −1 to 1 V. Because the PMT has a maximal output voltage of −300 mV during the measurements, the output of the PMT is matched to the input of the TUeDACS by a home-build transimpedance amplifier with a bandwidth of ~17 MHz [29]. The transients are sent “real time” to a PC where the ringdown time is determined by a weighted least-square fit of the logarithm of the transient [30]. A typical transient for a photon energy of 1.17 eV and a cavity length of 0.17 m is shown in Fig. 2.4, the resulting ringdown time equals $\tau = 2.633 \times 10^{-6}$ s.
Figure 2.4 Exponential decay of an empty optical cavity with a length of 0.17 m for a photon energy of 1.17 eV. The resulting ringdown time, obtained from the weighted least-square fit of the logarithm of the exponential decay, equals $\tau = 2.633 \times 10^{-6}$ s.

Normally an average of 400 separate ringdown times is taken to determine the ringdown time. A typical ringdown time distribution for an empty cavity is shown in Fig. 2.5. The average ringdown time equals $\tau = 8.005 \times 10^{-6}$ s with an $\sigma_\tau = 14 \times 10^{-9}$ s. From Fig. 2.5 also the sensitivity of the setup can be determined according to Eq. (1.5), the sensitivity for this photon energy and cavity length equals $1.4 \times 10^{-8}$ when 400 averages are used. In the remaining of this report it will be assumed that the ringdown time can be determined with an accuracy of at least 1 %.

Figure 2.5 Distribution of ringdown times for an empty cavity ($L = 0.381$ m) for a photon energy of 1.18 eV. The determined average ringdown time is $8.005 \times 10^{-6}$ s with a $\sigma_\tau = 14 \times 10^{-9}$ s. The intrinsic loss, determined by Eq. (1.3) equals $1.6 \times 10^{-4}$ s.
2.1.5 Alignment and purging of the optical cavity

A slight misalignment of the cavity will result in additional cavity losses and therefore a wrong ringdown time. To improve reproducibility, essential for differential measurements, a straightforward alignment procedure is needed and will be discussed below.

Before aligning the optical cavity, as depicted in Fig. 2.1, first the optical axis has to be defined:

1. Remove the two mirrors, and replace mirror 1 by a diaphragm (diaphragm 2) at the same height as the diaphragm (diaphragm 1) behind prism 2.
2. By iteratively aligning the laser spot (visible at 1.7 eV) at the diaphragm 1 by prism 1 and at diaphragm 2 by prism 2, the optical axis is defined.

The optical axis is now defined, next the optical cavity can be aligned:

1. Replace diaphragm 2 by mirror 1, and make sure the laser beam is reflecting exactly from the middle of the mirror.
2. The reflection of mirror 1 has to coincide with the middle of diaphragm 1, and check if the laser beam is still reflecting exactly from the middle of the mirror. Mirror 1 is now exactly perpendicular to the optical axis.
3. Put mirror 2 at its final position and make sure that the back reflection from mirror 2 is exactly from the middle of the mirror, and coinciding with the middle of diaphragm 1. Mirror 2 is parallel to mirror 1 and perpendicular to the optical axis.
4. Optimize the ringdown time in the Labview program, by adjusting the mirrors position via the microscrews.

To reduce the influence of dust and water absorption (see also Section 2.2), part of the set-up, as indicated in Fig. 2.1, is covered with a dry nitrogen purged box.

Figure 2.6 Change in ringdown time due to purging of the cavity. The intrinsic loss is reduced from $3.2 \times 10^4$ to $2.8 \times 10^4$ per pass at 1.01 eV.
The change in ringdown time due to purging is shown in Fig. 2.6. It is seen that the intrinsic loss of the cavity can be reduced from $3.2 \times 10^{-4}$ to $2.8 \times 10^{-4}$ at 1.01 eV by purging, thereby improving the sensitivity of CRDS. The ringdown saturates after approximately 30 minutes, therefore the cavity is purged for 30 minutes before each measurement. Therefore the day-to-day variations in the humidity will not affect the measurement, thereby improving the reproducibility of the method.

A straightforward alignment procedure and purging of the optical cavity improve the reproducibility of CRDS. Next a theoretical description of stability and mode formation in an optical cavity will be discussed, needed for treatment of the optical cavity containing a substrate in Chapter 3.

### 2.2 Stability and mode formation in an optical cavity

The stability of an optical cavity can be defined such that a paraxial ray is refocused within the cavity after reflections from the mirrors, such that the optical energy is contained or trapped inside the cavity. In short it can be stated that an optical cavity consisting of two mirrors will be stable when [5]:

$$0 \leq g_1 g_2 \leq 1,$$

where:

$$g_1 = 1 + \frac{L}{R_1},$$

$$g_2 = 1 + \frac{L}{R_2},$$

with $R_1$ and $R_2$ the radii of curvature of the high reflecting mirrors and $L$ the cavity length. For example for a cavity of $L=0.4$ m and cavity mirrors with a radius of curvature $R_1=R_2=-1$ m, the factor $g_1 g_2=0.36$, and according to Eq. (2.2) this optical cavity will be stable.

Only well defined electromagnetic cavity modes can be stored inside the optical cavity. Following Bush and Bush [5], using Laguerre-Gaussian waves for describing an optical cavity with cylindrical symmetry, the cavity resonance frequencies can be written down as follows:

$$\nu_{pqr} = \frac{c}{2L} (p + q + r + 1) \frac{\cos^{-1}(\pm \sqrt{g_1 g_2})}{\pi},$$

(2.5)
with $c$ the speed of light, $\nu=c/\lambda$ the frequency, $\lambda$ the wavelength, $L$ the length of the cavity, $p$ the longitudinal index and $q$ and $r$ the two transverse mode indices of the cavity. It can be seen from Eq. (2.5) that the longitudinal mode spacing is equal to:

$$\Delta \nu_{\text{longitudinal}} = \frac{c}{2L}, \quad (2.6)$$

and the transverse mode spacing equal to:

$$\Delta \nu_{\text{transverse}} = \frac{c}{2L} \left[ \cos^{-1} \left( \pm \sqrt{\frac{g_1 g_2}{\pi}} \right) \right]. \quad (2.7)$$

For a cavity consisting of two mirrors with a radius of curvature of $R=-1$ m and a length of $L=0.4$ m, normally used in the tf-CRDS experiments, the resulting longitudinal mode spacing is 375 MHz and the transverse mode spacing is 144 MHz using Eq. (2.6) and Eq. (2.7). The bandwidth of the OPO laser system is approximately 300 GHz ($10^{-1}$ cm$^{-1}$), resulting in approximately 1000 longitudinal modes in the optical cavity.

The mode structure of an optical cavity can also be examined by solving the Maxwell equations. By using Maxwell-Ampere's law [31]:

$$\nabla \times H = \sigma E + \frac{\partial E}{\partial t}, \quad (2.8)$$

and Maxwell-Faraday's law:

$$\nabla \times E = -\mu \frac{\partial H}{\partial t}, \quad (2.9)$$

and by writing the electro-magnetic fields in a time-harmonic form:

$$H(x,y,z,t) = H(x,y,z)e^{i\omega t}, \quad (2.10)$$

$$E(x,y,z,t) = E(x,y,z)e^{i\omega t}, \quad (2.11)$$

the following eigenvalue problem can be defined:

$$\nabla \times \left( \frac{1}{\mu} \nabla \times E \right) = \omega^2 \varepsilon E, \quad (2.12)$$

with $\varepsilon$ the permittivity of the medium, $\mu$ the permeability of the medium, $\omega = 2\pi c/\lambda$, $E$ the electric field, $H$ the magnetic field and $\sigma$ the conductivity.

The partial differential equation (2.12) can be solved by a 2-dimensional finite element method, FEMLAB [32]. The cavity design is shown in the left of Fig. 2.7.
Equation (2.12) will be solved in the mode where the electric field only has a component in the $z$ direction. The boundary conditions are defined such that the electric field in the $z$ direction ($E_z$) equals zero at the mirrors.

The solution is obtained by dividing the optical cavity in a finite number of elements and the partial differential equation is linearized for each of these elements. The resulting solution for $E_z(x,y)$ is linear for each element and continuous over all the finite number of elements. It is well known that a finite element treatment of a physical problem not always delivers physical solutions. For a stable optical cavity the optical energy has to be confined in the optical cavity, as depicted schematically in the right of Fig. 2.7, solutions that violate the optical energy confinement are ignored.

The finite element method will only give physical solutions if the problem can be divided in sufficient elements. Therefore the frequency range is chosen to be $\{4.8-5.6 \times 10^9$ Hz$\}$ and the diameter of the mirrors is chosen to be 0.6 m, this will not influence the validity of the obtained eigenmodes.

In Fig. 2.8 the results are shown for Eq. (2.12) in an optical cavity consisting of two mirrors with radius of curvature of $R=1$ m and a separation of 0.4 m. In the left of Fig. (2.8) the lowest order transverse electromagnetic (TEM) mode is shown. The cross-sectional profile of the lowest order TEM mode is Gaussian. In the right of Fig. 2.8 the ninth TEM mode is shown, the cross sectional intensity profile is broken up in an array of sub beams.
Figure 2.8: Femlab eigenmode calculation of an 2-D optical cavity \((L=0.4 \text{ m})\) consisting of two perfectly conducting mirrors \(R_1\) and \(R_2\) with a radius of curvature of \(-1\text{ m}\). Left the fundamental TEM is shown and right the ninth transverse TEM mode is shown. Green indicates \(E_z=0\) and blue and red indicates \(E_z\) is negative and positive, respectively.

In Fig. 2.9 the mode spectrum of an optical cavity consisting of two mirrors with radius of curvature of \(R=-1\text{ m}\) and a separation of 0.4 m is shown. For clarity only the 12\(^{th}\) and 13\(^{th}\) longitudinal modes are shown. In Fig. 2.9 it can clearly be seen that the longitudinal mode spacing is larger than the transverse mode spacing for this cavity geometry. The transverse mode spacing (144 MHz) and longitudinal mode spacing (375 MHz) determined by FEMLAB agree with the values obtained by Eq. (2.7) and Eq. (2.6).

Figure 2.9: Femlab eigenmode calculation of a 2-D optical cavity \((L=0.4 \text{ m})\) consisting of two mirrors \(R_1\) and \(R_2\) with a radius of curvature of \(-1\text{ m}\). The modes are indicated by \((p,q)\) with, \(p\) the longitudinal mode number (also indicated by the color of the bar) and \(q\) the transverse mode number (also indicated by the height of the bar). Note that the transverse mode spacing is smaller than the longitudinal mode spacing.
It is shown that stability and mode formation of an optical cavity can be treated with a 2-D finite element method. The extensive treatment of the mode structure of an optical cavity is needed for analyzing the implications when placing a substrate in an optical cavity in Chapter 3. In the next section the intrinsic losses of an empty optical cavity will be determined.

2.3 Intrinsic losses empty cavity

As discussed in section 2.1.2, 4 sets of mirrors are used to cover the energy range of interest (0.7-1.7 eV). In the left of Fig. 2.10 the intrinsic loss of the empty cavity is shown as a function of the photon energy, unfortunately the 0.7-1.7 eV range is not completely covered by these 4 mirror sets. For clarity, also the absorption by gas-phase water in the 0.7-1.7 eV range is shown in the right of Figure 2.10. The intrinsic loss of the empty cavity is mainly determined by the reflectivity of the mirrors, in some energy regions water absorption causes additional losses in the cavity.

From the right of Fig. 2.10 it can be concluded that the intrinsic loss of the empty cavity is still influenced by absorption of water in the gas phase. The OH vibrational related absorption peaks of water around 1.1 eV and 0.9 eV are mainly determining the intrinsic loss of the empty cavity, even after 30 minutes purging with dry nitrogen, thereby limiting the sensitivity and reproducibility of the CRDS measurements in these energy regions.

The small increase in intrinsic loss at 1.55 eV in the left of Fig. 2.10 is probably due to a combination mode of OH stretching and SiO$_4$ vibrational mode present in the substrate material of the dielectric mirror [33]. This will be discussed in detail in Section 3.3.1. From Fig. 2.10 (a) it can also be seen that the intrinsic losses of the empty cavity are well below $2 \times 10^{-4}$ per pass for most of the energy range used. If the ringdown time can be determined with a $\sigma_r/r=0.01$ and when 400 averages are used, the sensitivity (by using Eq. (1.5)) of the setup is well below $1 \times 10^{-7}$ per pass for most wavelengths. The intrinsic losses of the empty cavity, without influence of water, are equal to the losses at the mirrors. So by determining the intrinsic loss of an empty cavity the reflectivity of
high reflecting mirrors can very accurately be determined. From the right of Fig. 2.10 it can be seen that the reflectivity of the mirrors is typically well above $R=0.9998$ for the 0.7-1.7 eV range.

### 2.4 Conclusions

In conclusion, it is shown by using the Nd:YAG-OPO system, 4 sets of dielectric mirrors and 2 types of near-infrared photo detectors, it is possible to perform CRDS in the 0.75-1.7 eV range.

The reproducibility of the CRDS measurements is improved by a straightforward alignment procedure and by purging the setup with dry nitrogen.

It is shown that the eigenmodes of an optical cavity can be determined by a 2-D finite element method, needed for describing the optical containing a substrate in Chapter 3.

The intrinsic losses of the empty optical cavity are determined and found to be below $2\times10^{-4}$ per pass for most of the energy range used.
3. Introduction of a substrate in an optical cavity

In chapter 2 the experimental details of the CRDS setup have been introduced and stability and mode formation of an optical cavity are discussed. Next a substrate will be placed into the optical cavity. The insertion of the substrate can affect the optical cavity in several ways. First the stability of the optical cavity is examined by using 2-D finite element analysis, and the influence of misalignment of the cavity will be discussed. The change in roundtrip time in the optical cavity and the build-up effect caused by the substrate could influence the detected exponential decay of the light intensity inside the optical cavity and therefore affect the tf-CRDS measurement. Roughness of the substrate could induce additional cavity losses via surface scattering, thereby overestimating the absorption losses. The absorption of the substrate material will determine the intrinsic losses of the system and consequently the sensitivity. Therefore the optical absorption spectrum of synthetic quartz will be discussed and problems due to an inhomogeneous OH concentration in the synthetic quartz will be addressed.

3.1 Stability of the optical cavity containing a substrate

In Section 2.1.6 the stability of the empty optical cavity is discussed. The stability of an optical cavity containing a substrate can be treated analogous to the stability of a two-mirror cavity. If the substrate is plano-parallel, equivalent to a radius of curvature of infinity, the two element optical cavity is stable when the substrate is placed within the radius of curvature of the mirror as depicted in the left of Fig. 3.1. For the three element optical cavity, the substrate has to be placed within the radius of curvature of both mirrors for the cavity to be stable, as depicted in the left of Fig. 3.1. The stability of the cavity can also be determined by using Eq. (2.2), $g=1$ can be assigned to the substrate and Eq. (2.2) can be applied for the combination of both mirror 1 and mirror 2 with the substrate.

![Figure 3.1 Schematic presentation of stability of optical cavity with plano-concave mirrors and a plano-parallel substrate.](image)
The stability of an optical cavity containing a substrate can also be examined by solving the eigenvalue problem for $E_z(x,y)$ stated in Eq. (2.12) for the cavity design depicted in Fig. 3.2. The insertion of the substrate in the optical cavity is apparent in the function $\varepsilon(x,y)$, which is not constant for the cavity design depicted in Fig. 3.2. For the substrate $\varepsilon(x,y)=2.25$ and $\varepsilon(x,y)=1$ outside the substrate. The finite element method will only give physical solutions if the problem can be divided in sufficient elements. Therefore the thickness of the sample was chosen to be $d=0.02$ m with a cavity length $L=0.3$ m and the examined frequency range was chosen to be $\nu=\{1.46-1.52 \times 10^{10}$ Hz\}

![Figure 3.2 Schematic representation of the geometry used for the eigenmode calculations for an optical cavity containing a substrate. The cavity mirrors with a radius of curvature of $R=-1$ m have a spacing of 0.3 m.](image)

In the left of Fig. 3.3 the fundamental mode is shown for the cavity design depicted in Fig. 3.2. In the right of Fig. 3.3 the second TEM mode is shown, higher order TEM modes are also stable in the optical cavity containing a substrate.
Figure 3.3 Femlab eigenmode calculation of an optical cavity ($L=0.3$ m) consisting of two mirrors $R_1$ and $R_2$ with a radius of curvature of $R=-0.5$ m, containing a substrate of $d=0.02$ m and with a refractive index of $n=1.5$. In the left the fundamental mode is shown and in the right the second TEM mode is shown. Blue and red indicates zero and positive absolute $E_x$, respectively.

In Fig. 3.3 the eigenmode spectra for an empty cavity (left) and a cavity containing a substrate (right) are shown. The most obvious difference between the eigenmode spectrum of an empty cavity and the eigenmode spectrum of a cavity containing a substrate is the absence of the highest order transverse modes in the cavity containing a substrate. For this cavity design and frequency range TEM modes with an transverse mode index >6 are not stable in an optical cavity containing a substrate. The higher order transverse modes travel a different optical path in the optical cavity and are more easily distorted by the inserted substrate. Therefore higher order transverse modes are not stable in an optical cavity containing a substrate, resulting in a less dense mode structure compared to the empty cavity.

Figure 3.4 Femlab eigenmode calculation of an optical cavity ($L=0.3$ m) consisting of two mirrors $R_1$ and $R_2$ with a radius of curvature of $R=-0.5$ m. Left for an empty cavity and right for the cavity containing a 0.02 m sample of $n=1.5$. The modes are indicated by $(p,q)$ with, $p$ the relative longitudinal mode number (also indicated by the bar color) and $q$ the transverse mode number (also indicated by the bar height). Note the decrease in higher order transverse modes due to the insertion of the substrate.
The eigenmode calculations by the finite element method show that the mode spectrum is less dense for an optical cavity containing a substrate, but there are still ample of stable eigenmodes. Therefore the tf-CRDS measurements will not be affected.

Misalignment of the substrate in the optical cavity, however, will lead to a non-single exponential decay due to extra loss mechanisms (e.g. reflection losses). This is shown in Fig. 3.5. In the left of Fig 3.5 a misaligned optical cavity is shown, the decay is clearly not single exponential, contrary to the decay presented in the right of Fig. 3.5, where the decay is single exponential for a aligned substrate. Therefore the exponential decay of the optical cavity is always monitored during sample alignment.

![Figure 3.5 Exponential decay of an optical cavity containing a misaligned substrate (left) and an aligned substrate (right) for a photon energy of 1.23 eV.](image)

### 3.2 Additional influences of substrate on a stable optical cavity

Formation of a stable optical cavity containing a substrate is still possible as shown in the previous section. Higher order transverse modes will not be stable, but there are still enough cavity modes for light coupling in the optical cavity and therefore the ringdown is not affected. Nevertheless the inserted substrate will affect the optical cavity in several ways. The roundtrip time of the light in the optical cavity will change and the reflectivity of the sample could induce build up effects, thereby changing the detected exponential decay of the light intensity in the optical cavity. Interference in the substrate could alter the cavity losses and roughness of the sample can influence the cavity loss. These effects will be treated in detail in this section.

#### 3.2.1 Influence substrate on roundtrip time of the optical cavity

The roundtrip time in the optical cavity will be changed, due to the different refractive index of the substrate. The refractive index of the used substrate material, synthetic quartz, is \( n = 1.5 \) therefore the roundtrip time will be enhanced compared to an empty cavity in air. The additional cavity loss is calculated by using Eq. (1.4), and is affected by
an altered roundtrip time. Therefore the additional cavity loss due to insertion of the substrate is underestimated if the change in roundtrip time is not taken into account. In the tf-CRDS measurements this will result in an underestimation of the additional cavity losses of 0.2%, as can easily be calculated using Eq. (1.4). Therefore it is concluded that the change in roundtrip time induced by the insertion of the substrate does not significantly affect the additional cavity loss measurements and therefore this effect will be neglected.

3.2.2 Build-up effect due to the substrates reflectivity

The reflectivity of the inserted substrate could induce a non-uniform electric field energy distribution in the optical cavity, thereby distorting the detected exponential decay. Smets [4] calculated the influence of insertion of an infinitesimal thin non-absorbing substrate in the middle of the cavity. It is found that, apart from a small build up effect, there is no effect of the sample’s reflectivity on the resulting exponential decay.

![Figure 3.6 Influence of sample reflectivity (R={0.01, 0.5, 0.9, 0.98, 0.988}) on the exponential decay of the cavity with mirrors with an reflectivity of 0.99.](image)

The build up effect is noticeable, as shown in Fig. 3.6, if the sample’s reflectivity is comparable to the mirror’s reflectivity. If the ringdown time is determined after the initial build up effect, e.g. starting from 300 ns for R=0.988, there is no influence of the sample’s reflectivity on the determined exponential decay time. If only the quartz substrate is present in the optical cavity, R~0.04. Therefore the build-up effect is not observed in an optical cavity only containing a substrate. In Chapter 4 a substrate containing a thin a-Si:H film will be placed into the cavity, the reflectivity of the substrate-film will change as a function of the thickness and wavelength due to
interference in the thin film. Therefore, it is always made sure that the exponential decay
time is determined after the build-up effect during measurements on thin a-Si:H films.

3.2.3 Surface scattering from the substrate

The substrate can also induce additional cavity losses due to scatter losses from a rough
surface. An first estimate of the additional losses due to surface scattering is made by the
commonly used surface scattering theory of Beckman [34]. Beckman derived a model
using scalar theory describing surface scattering from a random rough surface in 2
dimensions. The intensity of the scattered wave, for normal incidence, can be expressed
as:

\[ I(\lambda, \sigma, T, \theta_z) = e^{-\pi} \left( \rho_0 + \frac{\pi T^2}{X} \sum_{m=1}^{\infty} \frac{g^m}{m! m} e^{-\frac{\lambda^2}{4m}} \right), \quad (3.1) \]

\[ \sqrt{g} = 2\pi \frac{\sigma}{\lambda} (1 + \cos \theta_z), \quad (3.2) \]

\[ \rho_0 = \frac{\sin(v_x X)}{v_x X}, \quad (3.3) \]

\[ v_x = \frac{2\pi}{\lambda} (-\sin \theta_z), \quad (3.4) \]

with \( \lambda \) the wavelength of light, \( \sigma \) the RMS surface roughness, \( X \) the spot size, \( T \) the
correlation length of the surface roughness and \( \theta_z \) the angle of the scattered light
compared to the normal in the \( x \) direction. \( \rho_0 \) describes the specular reflection, the light
reflected in accordance with the law of reflection. The terms in the sum of Eq. (3.1)
describe the diffuse (isotropic) scattering from a rough surface. The transition from
totally specular reflection to diffuse reflection depends on the \( g \) parameter (roughness
compared to the wavelength) as depicted in Fig. 3.7.

![Image](image.png)

Figure 3.7 Transition from specular to diffuse scattering. The surfaces are (a) flat, (b) slightly rough,
(c) moderately rough and (d) very rough compared to the light wavelength [34].

The surface roughness of the a-Si:H samples used in the tf-CRDS experiments is
investigated by means of atomic force microscopy (AFM). The RMS surface roughness
of the a-Si:H films is determined to be below 0.7 nm for the 8 a-Si:H films (as shown for
the 1031 nm sample in Fig. 3.8).
For an estimation of the scatter losses the RMS roughness is taken to be 1 nm with a correlation length for thicker a-Si:H of approximately 150 nm [4]. The used wavelength range is 700-1700 nm, so \( g \ll 1 \) and the reflection will be mostly in the specular direction as depicted schematically in Fig. 3.7 (b).

In Fig. 3.9 the angular distribution of the scattered intensity is shown for a surface roughness of 1 nm and a correlation length of 150 nm. Most of the light is scattered around 0 rad, in the same direction as the normally reflected light. The scattered intensity decreases rapidly as a function of the scattered angle. It can also be seen that the diffuse scatter level is about \( 1\times10^{-15} \) and independent of the reflected angle.
Figure 3.9 Angular intensity distribution from a rough surface with correlation length of $150 \times 10^{-9}$ m and a RMS roughness of 1 nm.

In CRDS, light scattered under a small angle will be captured by the plano-concave mirrors, as depicted schematically in Fig. 3.10. For the cavity used in the tf-CRDS, light that is scattered under an angle less than 0.08 rad is not considered lost in the tf-CRDS experiments. The scatter loss in the tf-CRDS experiments is determined by the fraction of the light that is scattered over an angle of $>0.08$ rad as depicted schematically in Fig. 3.10. The scatter losses are estimated to be in the order of $1 \times 10^{-10}$ per pass for $\lambda=1000$ nm. Surface scattering is therefore not limiting the sensitivity of tf-CRDS and therefore can be ignored.

Figure 3.10 Schematic representation of scattered light captured by plano-concave mirrors.
3.2.4 Additional losses due to bulk scattering

Another scatter mechanism that could induce additional cavity losses is the scattering of light at micro voids in the bulk of the substrate or film. If the micro voids are assumed spherical, the scattering can be described by the theory of Rayleigh. For a Rayleigh scatterer, the fraction of energy which is scattered isotropically, can be expressed as [35]:

\[ Q_{sca} = \frac{128\pi^4}{3} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left( \frac{n}{\lambda} \right)^4 r^6, \tag{3.5} \]

with \( n \) the refractive index, \( \lambda \) the wavelength and \( r \) the radius of the micro-voids. Because Rayleigh scattering is isotropic, the cavity mirrors capture an insignificant portion of the bulk-scattered light and all the bulk-scattered light is assumed to be lost.

Optical absorption measurements on 1050 m synthetic quartz optical fibers [33] show that the bulk scattering is in the order of \( 5 \times 10^{-6} \) cm\(^{-1}\) for 1.03 eV, therefore it can be estimated that the bulk scatter losses will be below \( 5 \times 10^{-6} \) per pass for a 1.59 mm synthetic quartz substrate in the 0.7-1.7 eV range. Furthermore bulk scattering of the quartz substrate will cancel out in the differential measurements of the thin a-Si:H film in Chapter 4. For a-Si:H films bulk scattering could be important for the thicker a-Si:H films (>100 nm), but the spectral dependence of \( 1/\lambda^4 \) is not observed as will be shown in Chapter 6. Therefore bulk scattering can be disregarded for the measurements on thin a-Si:H films.

3.2.5 Interference in the substrate

As already mentioned in Section 2.1.1, one of the characteristics of the OPO system is the relative short coherence length of the laser light. The coherence length of the OPO is typically 1 mm, and therefore interference is not expected in a 1.59 mm quartz substrate and can therefore be ignored when only the substrate is present in the optical cavity. For a thin (<1µm) a-Si:H film on a quartz substrate, interference will affect the additional cavity loss. This will be treated extensively in Chapter 4.

In this section it is concluded that the change in roundtrip time, the build-up effect, and bulk scattering are not affecting the tf-CRDS measurement. Bulk scattering and interference can affect the tf-CRDS measurements, but can be ignored when only a substrate is placed into the cavity. Therefore the determined additional cavity loss can be related to absorption in the substrate material. In the next section the cavity losses due to substrate absorption will be discussed.
3.3 Additional cavity loss induced by substrate absorption

The optical absorption of the light inside the substrate will induce additional intrinsic cavity losses. From Eq. (1.5) it can be seen that for the best sensitivity, the intrinsic losses of the system have to be as low as possible i.e. the absorption of the substrate material has to be as low as possible in the desired energy range (0.7-1.7 eV).

In the previous experiments on a-Si:H performed by Smets et al. [18] Corning 7059 glass (C7059) is used as the substrate material. In Fig. 3.11 the typical absorption spectrum of C7059 is shown in the range of 1.12-1.28 eV.

![Absorption loss caused by a 0.5 mm Corning 7059 sample.](image)

The absorption is well above $1 \times 10^{-3}$ for the energy range 1.12-1.28 eV. The use of C7059 as a substrate material will limit the sensitivity of tf-CRDS, with a $\sigma/\tau=0.01$ using Eq. (1.5), to $1 \times 10^{-6}$ per pass, when 400 averages are used, in the energy range of 1.12-1.28 eV. For determining an absorption coefficient $\alpha=1$ cm$^{-1}$ for a 10 nm a-Si:H film, a sensitivity of $1 \times 10^{-6}$ needed. Also the absorption loss per pass is not constant over the C7059 substrate, therefore high quality synthetic quartz (Louwers, comparable with Suprasil) is chosen as a substrate material. By using synthetic quartz the absorption loss in the 0.7-1.7 eV energy range will be limited, and thereby the sensitivity of tf-CRDS will be increased.

3.3.1 Optical absorption spectrum of synthetic quartz

In Fig. 3.12 the additional cavity loss is shown for a 1.59 mm thick synthetic quartz substrate. In Fig. 3.12 it can clearly be seen that the OH related absorptions are dominating the optical absorption spectrum of synthetic quartz. Fundamental OH ($\nu_3$) vibration modes as well as combination modes of SiO$_4$ tetrahedron vibration ($\nu_1$) and the
OH vibration modes are observed in the additional cavity loss spectrum in Fig. 3.12. The peak positions and relative intensities are summarized in Table 1 [33]. For example the $2v_3$ OH vibrational overtone (the first overtone of the fundamental OH vibration) is limiting the sensitivity of tf-CRDS around 0.9 eV, and consequently the 0.88-0.92 eV energy will not be measured for the thin films deposited on synthetic quartz substrates. From Fig. 3.12 it can be seen that, by choosing synthetic quartz as the substrate material, the intrinsic loss of the substrate material is well below $1 \times 10^{-4}$ per pass for most of the 0.7-1.7 eV range, consequently the sensitivity is well below $1 \times 10^{-7}$ per pass, when 400 averages are used, by using Eq. (1.5) if the ringdown time can be determined within 1 %. The sensitivity of the tf-CRDS method is e.g. prominent by determining the $3v_3+2v_1$ overtone around 1.55 eV an increase in absorption of $1 \times 10^{-5}$ is easily determined by tf-CRDS.

Figure 3.12 Additional losses caused by a 1.59 mm synthetic quartz substrate in an optical cavity.

Table 1: OH vibrational modes and combination modes with SiO$_4$ tetrahedron vibration in synthetic quartz according to Humbach et al. [33].

<table>
<thead>
<tr>
<th>OH band identification</th>
<th>Energy (eV)</th>
<th>Relative $\alpha$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_3+2v_1$</td>
<td>0.66</td>
<td>0.84</td>
</tr>
<tr>
<td>$2v_3$</td>
<td>0.90</td>
<td>62.7</td>
</tr>
<tr>
<td>$2v_3+v_1$</td>
<td>1.00</td>
<td>2.7</td>
</tr>
<tr>
<td>$2v_3+2v_1$</td>
<td>1.09</td>
<td>0.07</td>
</tr>
<tr>
<td>$3v_3$</td>
<td>1.31</td>
<td>1.6</td>
</tr>
<tr>
<td>$3v_3+v_1$</td>
<td>1.41</td>
<td>0.08</td>
</tr>
<tr>
<td>$3v_3+2v_1$</td>
<td>1.50</td>
<td>0.0038</td>
</tr>
<tr>
<td>$4v_3$</td>
<td>1.71</td>
<td>0.078</td>
</tr>
</tbody>
</table>

Unfortunately inhomogeneity of the synthetic quartz substrate samples is observed during the absorption measurements. This inhomogeneity is observed for the different quartz
substrates as well as for different positions on the quartz substrates. The inhomogeneity is recognizable at the energy regions of the OH related absorption features; the cause of the inhomogeneity is a slightly different OH content in the synthetic quartz substrates. Because the quartz absorption spectrum is dominated by the OH related absorption peaks, scaling with the OH content, the inhomogeneity can easily be corrected for by scaling the OH concentration. In Fig. 3.13 the additional cavity loss which is cavity loss of substrate subtracted from the cavity loss of substrate and film, is shown for a 100 nm a-Si:H film deposited on a synthetic quartz substrate. In Fig. 3.13 it can clearly be seen that the uncorrected additional cavity loss shows features, especially in the 0.7-1.1 eV region, likely related to a differing OH content in the substrate material. As shown in Fig. 3.13 the additional cavity loss of the 100 nm a-Si:H film can be corrected for the spectral features of the OH in the substrate material by scaling the OH content of the substrate material. The variation in OH content is typically 10-40 % for the substrates used in the tf-CRDS experiments.

![Graph showing additional cavity loss with photon energy](image)

Figure 3.13 Correction for OH inhomogeneity of the additional cavity loss of a 100 nm a-Si:H film on a 1.59 mm synthetic quartz substrate, by scaling the OH content in the substrate material.
3.4 Conclusions

In conclusion it is shown that an optical cavity containing a substrate is still stable and cavity modes can develop.

The substrate influences the cavity by increasing the roundtrip time and the reflectivity of the substrate causes a build up effect. As shown these effects do not significantly influence the ringdown time in the tf-CRDS measurements. The roughness of the substrate does not influence the additional losses, because the scatter losses are much lower than the minimal detectable absorptions by tf-CRDS. Interference in the substrate can be ignored due to the small coherence length of the OPO laser system. The substrate absorption, together with the reflectivity of the mirrors, determines the intrinsic loss of tf-CRDS. By performing a differential measurement, these intrinsic losses are cancelled out. Unfortunately the intrinsic loss is affected by OH concentration variations in the synthetic quartz, but correction for the OH inhomogeneity is straightforward.

In the next chapter a model will be derived to extract the $\alpha d$ values from the additional cavity losses determined by tf-CRDS. This model will be applied to extract the $\alpha$ values for 8 thin (5-1000 nm) a-Si:H films.
4. Extracting absorption coefficient $\alpha$ from tf-CRDS measurements

The goal of this chapter is to obtain the absorption spectra of thin (3.5-1031 nm) a-Si:H films from tf-CRDS measurements.

To relate the additional cavity loss to $\alpha d$ of a-Si:H, an \textit{ab initio} model is developed that describes interference in a thin layer. To give the reader insight into interference effects, a short introduction will be given in Section 4.1 that deals with straightforward transmission-reflection measurements. In Section 4.2 a model will be developed, describing the electric field intensity profile in a thin film placed in an optical cavity. Finally the electric field intensity distribution will be used to correct the tf-CRDS measurements on thin a-Si:H for interference to obtain the optical absorption spectrum, $\alpha(E)$.

4.1 Transmission reflection measurements on thin films

First transmission reflection will be discussed theoretically to give insight in interference. In Section 4.1.2 transmission spectroscopy will be performed on 8 a-Si:H films to determine the thickness and refractive index.

4.1.1 Transmission reflection

When an electromagnetic wave with amplitude $E_0$ traveling in a medium with refractive index $n_1$ encounters a medium with a refractive index $n_2$, part of the incident electric field will be reflected and part of the electric field will be transmitted, as depicted schematically in Fig. 4.1.

![Figure 4.1 Schematic representation of transmission and reflection at an interface.](image-url)
Using the Maxwell equations, the transmitted and reflected electric field amplitudes $E_t$ and $E_r$ can be expressed in the following form for the electric field impinging under normal incidence [31]:

$$\frac{E_t}{E_0} = t_{12} = \frac{2n_1}{n_1 + n_2}, \quad (4.1)$$

$$\frac{E_r}{E_0} = r_{12} = \frac{n_2 - n_1}{n_1 + n_2}, \quad (4.2)$$

with $r_{12}$ and $t_{12}$ the well known Fresnel coefficients and 1 and 2 refer to medium 1 and 2, respectively, as indicated in Fig. 4.1. By using the relation between irradiance $I$ and electric field amplitude $E$:

$$I_E \sim n|E|^2. \quad (4.3)$$

the transmitted and reflected intensities, the transmittance $T$ and reflectance $R$, compared to the incident intensity $I_0$ can be written down in the following form:

$$\frac{I_T}{I_0} = R_{12} = r_{12}E_{12}, \quad (4.4)$$

$$\frac{I_T}{I_0} = T_{12} = \frac{n_2}{n_1}t_{12}E_{12}. \quad (4.5)$$

The sum of the transmittance and reflectance equals the incident intensity $n_1E_0^2$ indicating conservation of energy. For example for an electric field impinging on an air-quartz interface, 4% of the incident intensity is reflected, and 96% of the incident intensity is transmitted.

In a thin film, as depicted in Fig. 4.2, multiple reflections occur at the two interfaces, the air-film and the film-substrate interface. The resulting reflected and transmitted electric fields will be determined by adding up the several contributions as depicted in Fig. 4.2.
In transmission-reflection (TR) measurements the transmittance and reflectance are measured. The transmittance and reflectance can be calculated in the incoherence limit and in the coherence limit.

In the incoherence limit (coherence length light source $<< d$), the intensities of the multiple reflections have to be added to calculate the resulting transmittance and reflectance of the thin film, therefore the transmittance and reflectance will be wavelength independent (when disregarding the wavelength dependence of the refractive index).

In the coherence limit (coherence length light source $>> d$), the resulting transmittance and reflectance is determined by adding up the electric fields arising from the multiple reflections in the thin film and by taking phase differences due to different optical path lengths into account. The phase of the electric field can be defined by writing the electric field in one dimension in the following form:

$$E(\lambda, x, t) = E_0 e^{i k x - i \omega t}, \quad (4.6)$$

with $k = 2 \pi n / \lambda$, $n$ the refractive index, $\lambda$ the wavelength in vacuum, $x$ the position of the wave, $\omega = 2 \pi c / \lambda$ and $c$ the speed of light. From Eq. (4.6) it can be seen that the phase of the electric field is determined by the position $x$ and time $t$. To calculate the transmitted and reflected electric field the time dependency of Eq. (4.6) can be ignored.

The transmitted electric field can be expressed by:

$$E_T = t_{12} t_{23} E_0 + ... + t_{12} t_{23} r_{23}^{p-1} r_{21}^{p-1} E_0 e^{(-i 2kd(p-1))} + ... = \sum_{p=0}^{\infty} t_{12} t_{23} r_{23}^{p} r_{21}^{p} E_0 e^{(-i 2kd(p))}, \quad (4.7)$$
with \( d \) the film thickness and \( E_0 \) the incident electric field amplitude. The first three terms of the infinite sum of Eq. (4.7) are shown in Fig. 4.2. The infinite sum of Eq. (4.7) converges to the following expression:

\[
E_t = \sum_{p=0}^{\infty} t_{12} t_{23} r_{21}^p E_0 e^{(-2\pi lp)} = \frac{E_0 t_{12} t_{23}}{1 - r_{21} r_{23} e^{-2\pi d}}.
\]  (4.8)

From Eq. (4.8) it can be seen that the transmitted electric field of a thin film with thickness \( d \) will show modulation as a function of the wavelength. However in TR measurements only intensities are measured, therefore the transmittance has to be calculated.

The transmittance of the thin film can be calculated by applying Eq. (4.3) with the transmitted electric field calculated in Eq. (4.8). If one takes into account that the refractive index of the thin film is a complex function of the wavelength, the transmittance can be written down in the form presented by Ritter and Weiser [36]:

\[
T = \frac{(1 - R_{21})(1 - R_{23})(1 + \text{Im}(n)^2 / \text{Re}(n)^2)}{\exp(ad) + R_{21} R_{23} \exp(-ad) - 2\sqrt{R_{21} R_{23}} \cos(2kd - \delta_{21} - \delta_{23})},
\]  (4.9)

where the imaginary part of the refractive index, the so-called extinction coefficient, is related to the absorption coefficient via \( \text{Im}(n) = \lambda \alpha / 4\pi \) and \( \delta_{23} \) and \( \delta_{23} \) are the phases of the Fresnel coefficients arising from the complex refractive index of the thin film.

It can be seen from Eq. (4.9) that also the transmittance will show modulation as a function of the wavelength due to the cosine term in the denominator. In Fig. 4.3 the transmission as a function of the photon energy is shown for a 289 nm a-Si:H film on a 1.59 mm quartz substrate as measured by a spectroscopic ellipsometer (Woollam Co. M-2000) in transmission mode. By fitting the transmission as a function of the photon energy by Eq. (4.9), the transmission measurement yields the refractive index, absorption coefficient both as a function of the photon energy and the thickness of the a-Si:H film.

---

1 Normally the extinction coefficient is denoted as \( k \), but for clarity reasons it is denoted as the imaginary part of the refractive index in this report.
The reflectance of a thin film can be determined analogous to the transmittance. The reflected electric field can be expressed in the following infinite sum:

\[ E_R = r_{12}E_0 + \sum_{p=1}^{\infty} t_{12}t_{21}r_{23}^{-p}r_{21}^{p-1}E_0e^{-(i2kp\delta)}. \]  

(4.10)

In Fig. (4.2) the first three terms (excluding the phase of the electric field) of this sum are shown. The reflectance can be expressed in the following form presented by Ritter-Weiser [36]:

\[ R = \frac{R_{21}\exp(\alpha d) + R_{23}\exp(-\alpha d) - 2\sqrt{R_{21}R_{23}}\cos(2kd + \delta_{21} - \delta_{23})}{\exp(\alpha d) + R_{21}R_{23}\exp(-\alpha d) - 2\sqrt{R_{21}R_{23}}\cos(2kd - \delta_{21} - \delta_{23})}. \]  

(4.11)

From Eq. (4.9) and Eq. (4.11) it is also apparent that the absorption in the thin film is affecting the transmittance and reflectance.

The absorption loss of a TR measurement is defined as \( A = 1 - T - R \). Combining Eq. (4.9) and Eq. (4.11) and ignoring the phases differences arising from the complex Fresnel coefficients, Ritter and Weiser show that \( \alpha d \) can be expressed as a function of the absorption and the transmittance [36]:

\[ \alpha d = \ln\left[\frac{1}{2}\left((1 - R_{21})\left(1 + \frac{A}{T}\right) + \sqrt{(1 - R_{21})^2\left(1 + \frac{A}{T}\right)^2 + 4R_{21}}\right)\right]. \]  

(4.12)
Equation (4.12) indicates that the absorption determined during TR measurements is not straightforwardly related to an absorption coefficient. The absorption is also affected by interference and shows a similar modulation as the transmittance.

For transmission-reflection measurements it is trivial that absorption and transmission are determined in the same experiment, allowing the use of Eq. (4.12) to correct for interference. Equation (4.12) is also used in the so-called “absolute” CPM method by Fejfar et al. [37]: by measuring the photocurrent and transmission at the same time the CPM signal can be corrected for interference.

### 4.1.2 Transmission measurements on thin a-Si:H films

To investigate the optical absorption spectrum of a-Si:H by tf-CRDS, 8 a-Si:H films with varying thickness have been deposited in two deposition series at the AMOR set up in Delft. The a-Si:H films are deposited by a rf-plasma at 250 °C. Deposition series 1 is deposited in September 2002 and deposition series 2 in November 2002. Transmission spectroscopy is performed on all 8 a-Si:H films deposited on 1.59 mm synthetic quartz substrates and fitted by a Eq. (4.9) to yield the refractive index and absorption coefficient as a function of the photon energy as well as the thickness of the film. The thickness and deposition series is summarized in Table 4.1.

**Table 4.1 Thickness obtained by transmission, for the 8 rf-plasma deposited a-Si:H films on a 1.59 mm synthetic quartz substrate. The a-Si:H have been deposited at the AMOR set up in Delft.**

<table>
<thead>
<tr>
<th>Sample Thickness (nm)</th>
<th>Deposition series</th>
</tr>
</thead>
<tbody>
<tr>
<td>1031</td>
<td>2</td>
</tr>
<tr>
<td>312</td>
<td>2</td>
</tr>
<tr>
<td>289</td>
<td>1</td>
</tr>
<tr>
<td>177</td>
<td>2</td>
</tr>
<tr>
<td>98</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>9.1</td>
<td>1</td>
</tr>
<tr>
<td>3.5</td>
<td>2</td>
</tr>
</tbody>
</table>

The refractive index of the a-Si:H films is shown in Fig. 4.4 and is between 3.5 and 4.1 in the 0.7-1.7 eV range used in the tf-CRDS measurements. The refractive index did not significantly vary between the a-Si:H films.

The absorption coefficient determined by transmission spectroscopy will be compared to the absorption coefficient determined by tf-CRDS in Section 5.1.
Figure 4.4 Refractive index of the a-Si:H films.

As shown in Section 4.1.1, the measured quantities in e.g. transmission reflection are not straightforwardly related to an optical absorption coefficient. In tf-CRDS the measured quantity, the additional cavity loss, will also be affected by interference. The additional cavity loss is the only measured quantity in tf-CRDS, therefore correction by another measured quantity is not possible. Therefore the electric field intensity profile in the optical cavity has to be calculated. In the next section an \textit{ab initio} calculation of the electric field intensity profile in a thin film in an optical cavity will be presented, and used for correcting the additional cavity losses determined by tf-CRDS for interference.

4.2 \textbf{Determining \alpha d from additional cavity loss}

In Fig. 4.5 the additional cavity loss is shown for a 1031 nm a-Si:H film on a 1.59 mm quartz substrate. It can clearly be seen that the additional cavity loss observes the expected modulation due to interference in the thin film.
Figure 4.5 Additional cavity loss of a 250 °C rf-plasma deposited 1031 nm a-Si:H film on a 1.59 mm synthetic quartz substrate.

To correct for interference in a thin film placed inside an optical cavity first the electric field intensity profile $I(x, \lambda)$ in the thin film has to be determined. The refractive indices of all the media are assumed to be real; consequently the extinction coefficient is zero and the Fresnel coefficients are real.

The coherence length of the OPO laser system is approximately 1 mm, therefore interference in the 1.59 mm quartz substrate can be disregarded. For clarity first the electric field intensity profile will be calculated for an electric field impinging only on the air-film interface, as depicted in Fig. 4.6.

Figure 4.6 Schematic representation of the electric field at position $x$ in the film when an electric field with amplitude $E_0$ is impinging on the air-film interface.
In the thin film interference will occur, therefore the electric field in the thin film is determined by adding up all the contributions arising from the multiple reflections at the air-film and film-substrate interface and taking phase differences arising from different path lengths into account, as depicted in Fig. 4.6.

The electric field in the thin film \( E(\lambda, d, x) \) is calculated analogous to the transmitted and reflected electric fields in Section 4.1:

\[
E(\lambda, d, x) = t_{12} E_0 (e^{-i(x/k)} + r_{23} e^{-i(2d-x)/k} + r_{23}^2 e^{-i(2d+2x)/k} + r_{23}^2 r_{21} e^{-i(4d-x)/k} + \ldots) = \\
\sum_{p=0}^{\infty} t_{12} r_{23}^p r_{21}^p e^{-i(2pd-x)/k} E_0 + \sum_{p=1}^{\infty} t_{12} r_{23}^p r_{21}^{p-1} e^{-i(2pd-x)/k} E_0,
\]

with \( d \) the thickness of the film and \( x \) the position in the film, as depicted in Fig. (4.6).

Equation (4.13) gives the electric field in the thin film; by using Eq. (4.3) the electric field intensity profile in the thin film can be calculated:

\[
I(\lambda, d, x) = I_0 \frac{n_2^2 t_{12}^2}{n_1} \frac{1 + r_{23}^2 + 2r_{23} \cos[k(d-x)]}{1 + r_{21}^2 r_{23}^2 - 2r_{21} r_{23} \cos(kd)},
\]

where \( n_1 \) and \( n_2 \) are the refractive indices of medium 1 and 2, respectively, and \( I_0 \) is the incident intensity \( n_1 E_0^2 \).

![Figure 4.7: Electric field intensity profile as a function of position in the film for a wavelength of 1000 nm (1.24 eV) for a 30 nm a-Si:H film (left) and a 100 nm a-Si:H film (right) on a synthetic quartz substrate when the electric field with intensity \( I_0 \) is impinging on the air-film interface.](image)

In Fig. 4.7 the electric field intensity as a function of the position in the film is plotted for a 30 nm and a 100 nm a-Si:H film on a quartz substrate using Eq. (4.14) for a photon energy of 1.24 eV. It can clearly be seen that the electric field intensity is not constant over the position in the film. In the left of Fig. 4.7 also can be seen that the electric field intensity in a thin film can be larger than the incident electric field intensity. This is explained by the small phase difference between the several reflected electric waves.
In the tf-CRDS experiment the electric field is not only impinging on the air-film interface, but also on the air-quartz interface. The coherence length of the OPO laser system is only 1 mm (as determined in Section 2.1.1), therefore there is no interference between the electric field impinging on the air-film and the air-substrate interface because the cavity length is approximately 40 cm. The resulting electric field intensity profile in the thin film is determined by adding up the intensity distribution arising from the electric field impinging from the air-film interface and the intensity distribution arising from the electric field impinging from the air-substrate interface.

![Figure 4.8: Schematic representation of interference in a thin layer when an electric field with intensity $I_\alpha/2$ is impinging from both the air-film and air-substrate interface.](image)

For calculating the resulting electric field intensity profile in the thin film it is assumed that the incident electric field intensity impinging from the air-film interface is equal compared to the electric field intensity impinging from the air-substrate interface. In Section 3.2.2 is shown that this assumption is justified.

The electric field distribution in the thin film can than be expressed via an extention of Eq. (4.14) to the case where the electric field is impinging from both sides:

$$I(x, \lambda) = \frac{1}{2} \left[ I_0 \frac{n_2^{2} r_{12}^{2}}{n_1} \frac{1 + r_{23}^{2} + 2 r_{23} \cos[2k(d - x)]}{1 + r_{21}^{2} r_{23}^{2} - 2 r_{21} r_{23} \cos(kd)} + I_0 \frac{n_2^{2} r_{43}^{2} r_{32}^{2}}{n_1} \frac{1 + r_{21}^{2} + 2 r_{21} \cos(2kx)}{1 + r_{23}^{2} r_{21}^{2} - 2 r_{23} r_{21} \cos(2kd)} \right], \quad (4.15)$$

where 1-4 refer to medium 1-4, respectively, as indicated in Fig. 4.8.
Figure 4.9: Electric field intensity in a 300 nm a-Si:H film on a synthetic quartz substrate, as a function of the position in the film (left) for a photon energy of 1.24 eV and as a function of the photon energy at position $x=d$ in the film (right) when the electric field is impinging from both the air-film and air-substrate interface.

In Fig. 4.9 it can clearly be seen that the electric field intensity observes modulation as a function of the position in the film (left of Fig. 4.9) and as a function of the photon energy (right of Fig. 4.9) due to interference. In the right of Fig. 4.9 also the change in refractive index can be observed by the change in amplitude of modulation. In Fig. 4.4 it is clear that the refractive index of a-Si:H increases from 3.5 to 4.1 in the 0.7-1.7 eV range, thereby changing the Fresnel coefficients resulting in an altering modulation of the interference fringes.
Figure 4.10 Electric field intensity profile in a 300 nm a-Si:H film on a quartz substrate as a function of the photon energy and position in the film, when the electric field with intensity $I_0/2$ is impinging from both the air-film and air-substrate interface.

In Fig. 4.10 the electric field intensity profile is shown as a function of the photon energy and position in a 300 nm a-Si:H film on a quartz substrate, when the electric field is impinging from both the air-film and air-substrate interface. In Fig. 4.10 can clearly be seen that the number of maxima and minima of the electric field intensity in the thin film is increasing for increasing photon energy.

As mentioned, the aim of this section is to relate the additional cavity loss to the absorption coefficient. Equation (4.15) describes the electric field intensity profile in the thin film as a function of the position in the film and the wavelength. To relate the additional cavity loss to a $\alpha d$ value also an estimate has to be made of the distribution of the absorbers.

In tf-CRDS the spatial resolution ($x$ direction) in the thin film is lost. Therefore an estimate has to be made for the distribution of the absorbers in the thin film to correct the additional cavity losses for interference. For the first estimate a homogeneous defect distribution, $D(x) = 1$, will be assumed. The correction function, $C(\lambda)$ can than be calculated by integrating Eq. (4.15) multiplied with the defect distribution function, $D(x)$ and normalizing for the film thickness:

$$C(\lambda) = \frac{1}{d} \int_{x=0}^{d} I(x, \lambda) D(x) dx.$$  

(4.16)
In Fig. 4.11 the correction function are shown for a 300 nm a-Si:H film (left) and 1000 nm (right) a-Si:H on a quartz substrate. Again it can clearly be seen that the amplitude of the modulation is altered by the changing refractive index of a-Si:H for higher photon energies.

Figure 4.11: Correction function for a 300 nm (left) and 1000 nm (right) a-Si:H films on a quartz substrate assuming a homogeneous defect distribution within the film.

In Fig. 4.12 the additional cavity loss and \( \alpha d \) values are shown for a 1031 nm a-Si:H layer. The \( \alpha d \) values are obtained after correcting the additional cavity losses for interference by Eq. (4.16). From Fig. 4.12 it is clear that it is possible to correct for interference by using the correction model developed in this section.

The four mirror regions (as discussed in Section 2.1.2) are fitted separately, because the thickness of the a-Si:H varied up to 10% over the total sample, as found by transmission spectroscopy. Therefore the probed a-Si:H thickness can vary within 10% for each mirror energy range.
Figure 4.12 Additional cavity loss and \( \alpha d \) value of a 1031 nm a-Si:H film. The additional cavity loss is corrected for interference by Eq. (4.15) by assuming a homogeneous defect distribution.

The Mod values in Fig. 4.12 indicate an additional fitting parameter needed to correct for the interference in the additional cavity loss measurements. The Mod factor is used to adjust the observed amplitude of the modulation to the theoretical amplitude of the modulation. The additional fitting parameter is necessary because the modulation of the interference fringes can be altered by thickness variation of the thin film and by the distribution of the absorbers as will be discussed below.

It is well known from TR measurements that the interference fringes are suppressed by variation of the a-Si:H thickness along different positions of the sample [38]. In the model developed in this section no thickness fluctuation of the thin a-Si:H film is assumed. As already discussed the thickness of the a-Si:H film varied 10% over the sample. Therefore one can expect that the thickness will also vary over the probed area in the tf-CRDS measurements and therefore the interference fringes can be suppressed.

Asano and Stutzman [39] have shown that the distribution of the absorbers can influence the amplitude of the interference fringes as well. A different \( D(x) \) will result in a different correction function \( C(\lambda) \) via Eq. (4.16), and a resulting change in modulation. The defect distribution will be discussed thoroughly in Section 6.2.3.

In the next section the results obtained on the 8 a-Si:H films will be presented.
4.3 Absorption measurements on thin a-Si:H films

In Chapter 3 the validity of tf-CRDS is shown, and the additional cavity loss is shown to be directly related to absorption losses in sample inserted in the optical cavity. In Section 3.3 the absorption spectrum of the used substrate material is determined, and is shown to be dominated by OH related absorption peaks. The substrates show a variation in OH content, prominent in the additional cavity losses of the thin a-Si:H films. Correction for the OH inhomogeneity is shown to be straightforward and the additional cavity loss of the a-Si:H films on a quartz substrate can straightforwardly be corrected for the substrate inhomogeneity. In Section 4.1 the thickness and refractive index of the 8 a-Si:H films is determined by means of transmission spectroscopy. In Section 4.2 an ab initio model is derived describing the electric field intensity in a thin film placed in an optical cavity. By taking the convolution of this model with an assumed defect distribution the additional cavity losses can be corrected for interference.

With the tools presented above it is possible to extract the $\alpha d$ values from the additional cavity loss determined by tf-CRDS. The $\alpha d$ values as a function of the photon energy of the 8 a-Si:H films are presented in Fig. 4.13 and 4.14. The resulting $\alpha$ as a function of the photon energy is presented in Fig. 4.15 and 4.16. The optical absorption spectrum of a-Si:H will be discussed thoroughly in Chapter 5 and 6.
Figure 4.13 $\alpha d$ values of thin a-Si:H films deposited in deposition series 1, obtained after correcting the additional cavity loss for interference by Eq. (4.14) assuming a constant defect distribution.

Figure 4.14 $\alpha d$ values of thin a-Si:H films deposited in deposition series 2, obtained after correcting the additional cavity loss for interference by Eq. (4.14) assuming a constant defect distribution.
Figure 4.15 $\alpha$ (cm$^{-1}$) values as a function of photon energy for the a-Si:H films deposited in the first deposition series.

Figure 4.16 $\alpha$ (cm$^{-1}$) values as a function of the photon energy for the a-Si:H films deposited in the second deposition series.
4.4 Conclusions

In conclusion, transmission spectroscopy is used for determining the refractive index and thickness of the 8 a-Si:H films on synthetic quartz substrate.

From ab initio the electric field intensity profile for a thin film on a quartz substrate placed in an optical cavity is derived. It is shown that by using the electric field intensity profile combined with an assumed defect distribution it is possible to correct the additional cavity losses determined by tf-CRDS for interference. Finally the optical absorption spectra of the 8 a-Si:H films are shown.
5. Comparison of tf-CRDS with commonly used techniques: the a-Si:H absorption spectrum

In this chapter the optical absorption spectra obtained by tf-CRDS will be compared with the spectra obtained by commonly used absorption techniques to check the validity of tf-CRDS.

First the optical absorption coefficient determined by transmission spectroscopy will be compared to the optical absorption coefficient obtained by tf-CRDS. Thereafter PDS will be introduced and discussed in detail. Finally the optical absorption spectrum obtained by PDS will be compared with the optical absorption spectrum obtained by tf-CRDS.

5.1 Comparison between optical absorption coefficients obtained by transmission spectroscopy and tf-CRDS

In this section the optical absorption coefficient determined by transmission spectroscopy will be compared to the optical absorption coefficient determined by tf-CRDS. The transmission spectroscopy measurements are performed on a variable angle spectroscopic ellipsometer (Woollam Co. M-2000) in transmission mode. As already discussed in Section 4.1, transmission spectroscopy is a direct absorption technique that can yield the absorption coefficient of thin films. Absorptions as small as $1 \times 10^{-2}$ per pass can be determined by using the spectroscopic ellipsometer in transmission mode, as depicted schematically in Fig. 5.1. The data is analyzed using the WVASE32 program [40] solving Eq. (4.12) to yield the refractive index and absorption coefficient as a function of the photon energy as well as the thickness of thin a-Si:H film on a quartz substrate.

Figure 5.1 Schematic representation of a transmission measurement.

In Fig. 5.2 the optical absorption coefficient is shown for the 289 nm (left) and 1031 nm (right) a-Si:H film on a quartz substrate. It can clearly be seen that there is excellent agreement between the absolute values obtained by transmission spectroscopy and tf-CRDS in the Urbach region around 1.7 eV. Also the spectral dependence of the
absorption coefficient obtained by tf-CRDS and transmission spectroscopy in the Urbach region agrees pretty well for the 289 nm and 1031 nm a-Si:H film.

![Graph](image1)

Figure 5.2 Optical absorption coefficient determined by tf-CRDS and transmission spectroscopy for a 289 nm (left) and 1031 nm (right) a-Si:H film.

In Fig. 5.3, the optical absorption spectra for a 3.5 nm (left) and a 9.1 nm (right) a-Si:H film obtained by transmission spectroscopy and tf-CRDS are shown. Unfortunately due to lack of sensitivity the absorption coefficient cannot be determined for photon energies around 1.7 eV by transmission spectroscopy for the 3.5 and 9.1 nm a-Si:H films, and therefore the absolute values of the absorption coefficient cannot be compared. The spectral dependence of the absorption coefficient shows reasonable agreement for the optical absorption coefficient determined by transmission spectroscopy and tf-CRDS.

![Graph](image2)

Figure 5.3 Optical absorption coefficient determined by tf-CRDS and transmission spectroscopy for a 3.5 nm (left) and 9.1 nm (right) a-Si:H film.

By comparing tf-CRDS and transmission spectroscopy it can be concluded that tf-CRDS is capable of determining directly the absolute absorption coefficient in the Urbach region. For comparison in the defect related part of the optical absorption spectrum, tf-CRDS will be compared with PDS.
5.2 Photothermal deflection spectroscopy

PDS is a commonly used indirect sub-gap absorption technique. Therefore PDS is an excellent candidate for comparing the defect related region of the optical absorption spectrum of a-Si:H with the optical absorption spectrum obtained by tf-CRDS.

First the principle and experimental setup of PDS will be discussed briefly. Thereafter two calibration methods of PDS will be discussed that are commonly used to obtain absolute $\alpha$ values from the PDS measurements. Finally PDS results on a-Si:H will be compared to the results obtained by tf-CRDS.

5.2.1 Principle of photothermal deflection spectroscopy (PDS)

As schematically depicted in Fig. 5.4, a periodically modulated (typically 10 Hertz) monochromatic pump beam is focussed on a sample. Part of the optical energy of the pump beam is absorbed by the sample and is converted into heat via non-radiative recombination of the photo generated electron-hole pairs. The periodic heating generates heat waves, diffusing from the absorbing area to the surrounding area of the sample as well as to the surrounding medium. Because the index of refraction of the surrounding liquid medium (Fluorinert) is temperature dependent, the temperature gradients are accompanied by gradients in refractive index. This change in refractive index can be determined by measuring the deflection of a probe laser beam. This deflection of the probe laser beam is changed and can be related to the optical absorption coefficient. The operation range of PDS is about 3-4 orders of magnitude from the saturation value (as discussed in the next section) [41,42].
5.2.2 Experimental setup for PDS measurements

![Diagram of experimental setup](image)

Figure 5.5 Schematic representation of the PDS setup used at the Limburgs Universitair Centrum [41].

A schematic representation of the PDS setup used at Limburgs Universitair Centrum (LUC) is shown in Fig. 5.5. A broadband light source (quartz tungsten halogen lamp Oriel Instruments) in combination with a monochromator (Acton Research Corporation SpectraPro 275) is used to generate monochromatic light to act as the pump beam. The used deflection medium is fluorinert, which is transparent from 0.6-5.9 eV. The pump beam intensity is monitored by a pyrodetector (ORPHIR laser power monitor 150 A series type 2176), and the ratio of the PDS signal to the pyrodetector signal is used to compensate for the intensity profile of the broadband light source. A high pointing stability (<1 μrad) He-Ne laser is used as probe beam laser. The laser beam is directed parallel to the sample surface and is focussed in front of the sample by means of a lens with a focal length of 7 cm. The deflected laser beam is monitored by a position sensitive Si-photodiode (Hamamatsu Large area PSD series Pin-Cushion type S2044) with a spatial resolution of 1 μm [41].

5.2.3 Determining the absolute optical absorption coefficient $\alpha$ from PDS measurements

The measured quantity in a PDS measurement is the deflection $\theta$ of the probe laser beam. The deflection is proportional to the heat generated in the sample. Assuming all photo generated electron-hole pairs will recombine non-radiatively, the generated heat is
proportional to the intensity loss, $I_{loss}(E)$, of the pump beam in the thin film. Using Lambert-Beer law (Eq. (1.1)) the deflection of the probe beam can be written down as:

$$\theta(E) \sim I_{loss}(E) = I_0(E)[1 - e^{-\alpha(E)d}], \quad (5.1)$$

with $I_0(E)$ the pump beam intensity and $d$ the film thickness. By taking into account the energy dependence of the pump beam intensity $I_0(E)$ (as monitored by the pyrodetector), the PDS signal, $S(E)$, can be defined as follows:

$$S(E) = \frac{\theta(E)}{I_0(E)} = S_{sat}[1 - e^{-\alpha(E)d}], \quad (5.2)$$

with $S_{sat}$ the scaling parameter, containing all the experimental parameters. From Eq. (5.2) it can be seen that the PDS signal will equal $S(E)=S_{sat}$ when $\alpha(E)d>>1$. For $\alpha(E)d>>1$ all the incident power is completely absorbed in the sample, and therefore the PDS signal will be maximal. As shown in Fig. 5.6, the parameter $S_{sat}$ can be determined from the PDS measurement at higher photon energies. This calibration method is the so-called “auto-calibration” method. When $d$ is known, $\alpha(E)$ can be determined straightforwardly from Eq. (5.2):

$$\alpha(E) = \frac{1}{d} \ln(1 - S(E)/S_{sat}). \quad (5.3)$$

In the left of Fig. 5.6 is shown that the PDS signal is saturating for higher photon energies (>1.9 eV) for a 312 nm a-Si:H film on a 0.5 mm Corning 7059 substrate. By using the saturation value $S_{sat}$ in the left of Fig. 5.5 and Eq. (5.3), the optical absorption spectrum of the 312 nm a-Si:H film can be calculated, as shown in the right of Fig. 5.6.

![Graphs showing the determination of $S_{sat}$ and absorption coefficient $\alpha$](image)

**Figure 5.6** Determination of $S_{sat}$ from the PDS measurement ($\alpha d>>1$) for a 312 nm a-Si:H film on a 0.5 mm Corning 7059 substrate (left). Resulting absorption coefficient $\alpha$ as a function of the photon energy (right), by using Eq. (5.3).
In the left of Fig. 5.6 it can also clearly be seen that the PDS signal observes modulation due to interference, interference fringes in PDS measurement are generally averaged out.

For some samples $S_{\text{sat}}$ cannot be determined in the PDS measurement, because saturation is not reached in energy range measured by PDS (e.g. for thin a-Si:H films). $S_{\text{sat}}$ can then be determined by linking the PDS measurements to transmission-reflection spectroscopy (TR) measurements.

In the high absorption region ($\alpha d > 0.01$), in addition to PDS, also the TR spectra are measured. The spectral dependence of the optical absorption coefficient $\alpha$ is calculated by using Eq. (5.3) with an arbitrary value of $S_{\text{sat}}$. The calculated PDS absorption spectrum is then fitted to the high absorption region of the TR absorption spectrum. By scaling PDS measurement to TR measurement, $S_{\text{sat}}$ in Eq. (5.3) is determined.

For the PDS measurements presented in the Section 5.2.4 the absolute value of the optical absorption coefficient will be obtained by linking the PDS measurements at $\alpha d = 0.1$ to optical absorption coefficient obtained by transmission spectroscopy, as shown in Fig. 5.7 for a 312 nm a-Si:H film on a 0.5 mm C7059 substrate.

The deviation between the $S_{\text{sat}}$ determined from the PDS measurement and by linking to transmission spectroscopy is only 2% for the 312 nm a-Si:H film on a quartz substrate. Determining $S_{\text{sat}}$ by linking to TR is most commonly used in literature to obtain an absolute value of the optical absorption coefficient by PDS [43,44].

![Figure 5.7](image.png)

Figure 5.7 Linking the optical absorption coefficient obtained by PDS to the optical absorption coefficient obtained by transmission spectroscopy for a 289 nm a-Si:H film on a 0.5 mm corning substrate.
5.2.4 Absorption coefficient obtained by PDS compared to tf-CRDS

For comparison of the tf-CRDS technique with the commonly used PDS technique, also thin a-Si:H films were deposited on C7059 corning glass in the same batch as the a-Si:H films deposited on synthetic quartz. The PDS measurements were performed at LUC in Diepenbeek in the group of Milos Nesládek.

\[ \begin{align*}
\text{Figure 5.8 Optical absorption coefficient as a function of the photon energy obtained by PDS (0.5 mm C7059 substrate) and tf-CRDS (1.59 mm quartz substrate) of a 1031 nm (left) and 312 nm (right) a-Si:H films. The absolute } \alpha \text{ value of the PDS measurements was obtained by linking to } \alpha \text{ values obtained by transmission spectroscopy.}
\end{align*} \]

In Fig. 5.8 it can be seen that the optical absorption coefficient of a 1031 nm (left) and 312 nm (right) a-Si:H film show reasonable agreement in the sub-gap absorption region. Both the determined spectral behaviour and absolute value of the optical absorption coefficient show excellent agreement. It must be noted that the absorption coefficient determined by transmission (quartz substrate) and PDS (C7059 substrate) show different spectral behaviour in the Urbach region for the 1031 nm sample. This can be caused by flaking of the 1031 a-Si:H film deposited on the C7059 sample due to stress in the rf-deposited a-Si:H film.

The spectral dependence in the Urbach region also shows reasonable agreement between the optical absorption spectrum obtained by PDS and tf-CRDS for the 1031 nm and 312 nm a-Si:H films. The deviation of the absolute value of \( \alpha \) in the Urbach region is within a factor of 2 for the \( \alpha \) values obtained by PDS and tf-CRDS, and therefore shows reasonable agreement.
PDS was also performed on the 98 nm and 289 nm a-Si:H film on a 0.5 mm C7059 substrate. The optical absorption spectrum for the 98 nm (left) and 289 nm (right) a-Si:H films obtained by tf-CRDS and PDS are shown in Fig. 5.9. For the 289 nm a-Si:H film the spectral dependence of the optical absorption coefficient shows excellent agreement in the Urbach region. For photon energies \( E < 1.6 \text{ eV} \) the optical absorption coefficient obtained by PDS is significantly higher than obtained by tf-CRDS and also the spectral dependence deviates. In the sub-gap absorption region there is no agreement between the \( \alpha \) values obtained by PDS and tf-CRDS. For the 98 nm sample the optical absorption spectrum obtained by PDS and tf-CRDS show no agreement in the 0.7-1.7 eV energy region. The deviation between PDS and tf-CRDS for the 98 nm and 289 nm a-Si:H film can be explained by the influence of substrate absorption as addressed next.

In the left of Fig. 5.10 the PDS signals, \( S(E) \), are shown for a 98 nm and 289 nm a-Si:H film on a C7059 substrate. It can clearly be seen that the PDS signals are roughly the equal for photon energies lower than \( E < 1.6 \text{ eV} \), possibly caused by substrate absorption. For a-Si:H films of 98 nm and 289 nm deposited in the same deposition series it is not expected that the absorption is equal in the Urbach region. The absorption in the Urbach region is determined by transitions from the valence band to the conduction band and therefore the absorption of the 98 nm a-Si:H film is expected to deviate approximately a factor of 3 from the absorption of a 289 nm a-Si:H. This is not observed in the PDS measurement as shown in the left of Fig. 5.10.

During PDS measurement also the phase difference between the pump beam modulation (induced by chopping the pump beam) and the probe beam deflection is monitored. The phase signal can give insight into the question whether the deflection of the probe laser beam is caused by heat generated in the thin film or in the substrate. Heat generated in the thin film diffuses through the thin film to the deflection medium and therefore there will a time difference (phase difference) between the pump beam modulation and the deflection modulation of the probe beam caused by heat generated in the thin film. Heat generated in the substrate has to diffuse through the substrate and the thin film to the deflection medium. Therefore there will phase difference between the modulation of the deflection of the probe beam if the heat is generated in the substrate.

Figure 5.9 Optical absorption coefficient obtained by PDS (0.5 mm C7059 substrate) and tf-CRDS (1.59 mm quartz substrate) of a 98 nm (left) and 289 nm (right) a-Si:H film. The absolute \( \alpha \) value of the PDS measurements was obtained by linking to \( \alpha \) values obtained by transmission spectroscopy.
instead of the film. If the phase signal is roughly constant during a PDS measurement, the deflection of the probe arises from heat generated in the film. In the right of Fig. 5.10 it is clear that the phase of the PDS signal is not constant over the 0.5-2.5 eV energy range. Therefore, the deflection of the probe beam is probably not constantly arising from heat generated in the thin film, but for photon energies <1.6 eV the deflection is probably mainly caused by heat generated in the substrate.

![Figure 5.10 PDS signal (left) and PDS phase signal (right) for a 289 nm and 98 nm a-Si:H film on a 0.5 C7059 substrate (left) as a function of the photon energy.](image)

It can be concluded that for photon energies <1.6 eV the absorption coefficient of the 98 nm and 312 nm a-Si:H films on a 0.5 mm C7059 substrate cannot be determined by performing PDS, because the absorption, $\alpha d$, of the substrate material is apparently exceeding the absorption of the a-Si:H film. In Section 3.3 the absorption of a 0.5 mm C7059 substrate is determined by tf-CRDS to be around $1 \times 10^{-3}$ per pass in the 1.1-1.3 photon energy range. Consequently an absorption below $1 \times 10^{-3}$ cannot be determined by PDS, for a-Si:H films on a 0.5 mm C7059 substrate. For the 312 nm and 1031 nm a-Si:H films $\alpha d$ is similar to the substrate, therefore the PDS signal is still caused by the a-Si:H film.
5.3 Conclusions

In conclusion it is shown that tf-CRDS is capable of directly determining the absorption coefficient in the Urbach and sub-gap region.

By comparing the optical absorption spectrum obtained by transmission spectroscopy and by tf-CRDS is shown that tf-CRDS is well capable of directly determining the absorption coefficient in the Urbach region, and measures the same spectral dependence as a function of the photon energy in the Urbach region.

By comparing the absorption coefficient in the sub-gap determined by PDS and tf-CRDS is shown that tf-CRDS is capable of directly measuring the absorption coefficient in the sub-gap energy region.

The sensitivity of PDS is shown to be strongly limited by the substrate absorption. Therefore preferentially a low absorbing substrate material (e.g. synthetic quartz) should be used for PDS measurements.
6. Analysis of the optical absorption spectrum obtained by tf-CRDS

In this chapter material properties of the a-Si:H films will be derived from the optical absorption spectra obtained by tf-CRDS. First the Urbach energy and defect density will be determined from the optical absorption spectrum of a-Si:H. A relatively simple model will be used to extract the surface and bulk defect densities to give insight in the defect distribution in the thin film. Finally the spectral information of the tf-CRDS measurements will be used to extract a spectral signature of the surface and bulk defects, which can give insight into the dominant type of defect present in the bulk and surface.

6.1 Determining the Urbach energy from the optical absorption spectra obtained by tf-CRDS

As already discussed in Section 1.2, the exponentially decaying part of the optical absorption spectrum of a-Si:H can be characterized by the so-called Urbach energy, defined in Eq. (1.2). Experimental data show a distinct relation between the Urbach energy and the defect density, therefore the Urbach energy can give a rough indication of the a-Si:H material quality, as shown in Fig. 1.3.

The Urbach energy is determined by a linear fit from 1.5-1.7 eV [46] in the logarithmic plot of the absorption coefficient as shown in Fig. 6.1.

![Linear fit](image)

Figure 6.1 Absorption coefficient $\alpha$ as a function of the photon energy for a 289 nm a-Si:H film. A linear fit of $\alpha$ from 1.5-1.7 results in a Urbach energy of 55 meV.

The determined Urbach energies of the 8 a-Si:H films are summarized in Table 6.1. For the thin a-Si:H films (3.5 nm and 9.1 nm) it is impossible to determine the Urbach energy from the tf-CRDS measurements. For the optical absorption spectrum of the 3.5 and 9.1 nm a-Si:H the Urbach region is not yet reached in the measured energy range (0.7-1.7), therefore the Urbach energy could not be determined. Also for the slightly thicker a-Si:H films (30-200 nm) the Urbach energy can only be determined in a small energy range and therefore the determined Urbach energies are only a first estimate.
Clearly there is a deviation between the determined Urbach energies of the a-Si:H films deposited in deposition series 1 and 2. The determined Urbach energies of the a-Si:H films deposited in deposition series 2 are significantly higher, indicating lower a-Si:H quality.

The determined Urbach energies (55-115 meV) are also commonly reported in literature [23]. Also is known in literature that the Urbach energy increases for thin a-Si:H films [43] as can clearly be observed for deposition series 1. In the next section the defect densities will be determined from the tf-CRDS measurement.

<table>
<thead>
<tr>
<th>Sample Thickness (nm)</th>
<th>Deposition serie</th>
<th>Urbach Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>289</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>98</td>
<td>1</td>
<td>74</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>115</td>
</tr>
<tr>
<td>9.1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>1031</td>
<td>2</td>
<td>93</td>
</tr>
<tr>
<td>312</td>
<td>2</td>
<td>102</td>
</tr>
<tr>
<td>177</td>
<td>2</td>
<td>71</td>
</tr>
<tr>
<td>3.5</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

### 6.2 Determining defect densities and defect distributions from tf-CRDS measurements

#### 6.2.1 Determining the defect density from tf-CRDS

Another material property that can be extracted from the optical absorption spectrum is the integrated defect density. The sub-gap absorption is assigned to transitions from the extended valence band to the defect states and from defects states to extended conduction band, as discussed in Section 1.2. Therefore one would expect a direct correlation between the magnitude of sub-gap absorption and the number of defects.

The excess absorption due to defects can be defined as the determined absorption, corrected for absorption due to the transitions between the exponentially decaying conduction and valence band (i.e., transitions associated with the Urbach edge). The excess absorption due to defects, as depicted in Fig. 6.2, can be calculated by [47]:

\[
\alpha_{ex} = \alpha - \alpha_{Urbach} = \alpha - \alpha_0 e^{(E_i/E_u)},
\]

where \(\alpha_0\) is a scaling parameter of the optical absorption coefficient in the Urbach region.
The number of defects can according to Jackson et al. [43] be calculated via the excess absorption by:

\[ N_d = 7.9 \times 10^{15} \int_{0.8eV}^{1.7eV} \alpha_{ex} dE. \]  

(6.2)

The total defect densities for the 8 a-Si:H films is determined by Eq. 6.2 and is summarized in Table 6.2, for clarity also the determined Urbach energies are summarized in Table 6.2. For the 3.5 nm and 9.1 nm a-Si:H the Urbach edge could not be determined, therefore the total absorption in the sub-gap is defined as excess absorption due to defects.

<table>
<thead>
<tr>
<th>Sample Thickness (nm)</th>
<th>Deposition series</th>
<th>Urbach Energy (meV)</th>
<th>Averaged defect density (10^{16} \text{cm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>289</td>
<td>1</td>
<td>55</td>
<td>8</td>
</tr>
<tr>
<td>98</td>
<td>1</td>
<td>74</td>
<td>19</td>
</tr>
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<td>30</td>
<td>1</td>
<td>115</td>
<td>54</td>
</tr>
<tr>
<td>9.1</td>
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<td>-</td>
<td>96</td>
</tr>
<tr>
<td>1031</td>
<td>2</td>
<td>93</td>
<td>2.8</td>
</tr>
<tr>
<td>312</td>
<td>2</td>
<td>102</td>
<td>10</td>
</tr>
<tr>
<td>177</td>
<td>2</td>
<td>71</td>
<td>10</td>
</tr>
<tr>
<td>3.5</td>
<td>2</td>
<td>-</td>
<td>335</td>
</tr>
</tbody>
</table>

For the Urbach energies and defect densities summarized in Table 6.2 only the defect density as a function of the Urbach energy for the 289 nm, 177 nm and 98 nm a-Si:H films fall within the shaded region of Fig. 1.4, which indicates that the Urbach energy only can be used for a rough characterization of the defect density of a-Si:H films.

In Fig. 6.3 the defect density is plotted as a function of the film thickness. It can be seen that the defect density is not constant as a function of the film thickness. The defect density rapidly increases when the film thickness is decreasing, indicating the presence of the high defective surface/interface layer, as will be discussed in the next section.

Figure 6.2 Schematic representation of determination of excess absorption due to defects.
Figure 6.3 Defect density determined by integrating excess absorption for a-Si:H films of different thickness.

6.2.2 Defect distribution models

It is well known from literature [47-50] that the defect density of the surface and the bulk region can deviate. To account for the difference between the bulk and surface defect density two defect distributions are commonly assumed.

Jackson et al. [47] proposed a defect distribution, as depicted in the left of Fig. 6.3, with all the surface defects present in a defective layer with thickness $d_0$. If the defective layer thickness, $d_0 \rightarrow 0$, the defect density distribution can be expressed as follows:

$$n_d(z) = N_s \delta(z) + N_b,$$

(6.2)

with $N_s$ (cm$^2$) and $N_b$ (cm$^{-3}$) the surface and bulk defect density, respectively and $z$ the position in the layer. The averaged defect density, $N_d$ (cm$^{-3}$), as a function of the film thickness $d$ can than be determined by integrating Eq. (6.2) over $\{0,d\}$ and dividing by $d$:

$$N_d(d) = \frac{1}{d} \int_{z=0}^{d} n_d(z)dz = \frac{N_s}{d} + N_b.$$  

(6.3)
A more sophisticated model, taking into account a finite thickness $d_0$ of the defective surface layer, is proposed by Favre et al. [49]. As schematically depicted in the right of Fig. 6.3, the defect density is proposed to decrease exponentially from the high defective surface to a constant bulk defect density:

$$n_d(z) = N_0 e^{-z/d_0} + N_b. \quad (6.4)$$

with $N_0$ (cm$^{-3}$) the surface defect density, and $N_b$ (cm$^{-3}$) the bulk defect density. The averaged defect density over the film thickness $d$ can be determined by integrating Eq. (6.4) over the film thickness $d$:

$$N_d(d) = \frac{1}{d} \int_{z=0}^{d} n_d(z) dz = \frac{N_0 d_0}{d} (1 - e^{-d/d_0}) + N_b. \quad (6.5)$$

In the model of Favre, the surface defect density (cm$^{-2}$) is defined as $N_0 d_0$.

In Fig. 6.4 the defect density as a function of the film thickness is fitted by Eq. (6.5). In Section 6.1 is shown that deposition series 1 and 2 deviated in a-Si:H quality, and are
therefore fitted separately. The averaged defect densities obtained for deposition series 1 can be fitted reasonably by Eq. (6.5), in contrary to the averaged defect densities for deposition series 2. The resulting surface defect density of the a-Si-H films are $1.8 \times 10^{12}$ cm$^{-2}$ for deposition series 1 and $1.9 \times 10^{12}$ cm$^{-2}$ for deposition series 2. In Table 6.3 it can be seen that these surface defect densities are commonly reported for rf-deposited a-Si:H films. The bulk defect densities determined to be $1.5 \times 10^{16}$ cm$^{-3}$ for deposition series 1 and $1 \times 10^{16}$ cm$^{-3}$ are also in agreement with bulk defects densities reported in literature, as summarised in Table 6.3, for rf-deposited a-Si:H films. The obtained values for the defective surface layer $d_0$ of 14 nm for deposition series 1 shows reasonable agreement with the 20 nm defective layer thickness obtained by Favre et al. [49]. The obtained defective layer thickness of 3.6 nm for deposition series 2 is significantly smaller than obtained by Favre et al.

If an atomic density of $5.0 \times 10^{22}$ cm$^{-3}$ is assumed for a-Si:H [51], it can be concluded that roughly $1 \times 10^{-4}$ of the surface atoms Si constitutes a defect and $1 \times 10^{-6}$ of the bulk atoms.

Table 6.3: Surface and bulk defect densities for rf-deposited intrinsic a-Si:H reported in literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Surface defect density (10$^{12}$ cm$^{-2}$)</th>
<th>Bulk defect density (10$^{16}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Favre et al. [49]</td>
<td>1</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>Jackson et al. [50]</td>
<td>1-3</td>
<td>0.4-200</td>
</tr>
<tr>
<td>Smith et al. [47]</td>
<td>3-8</td>
<td>0.5-3</td>
</tr>
<tr>
<td>Leblanc et al. [44]</td>
<td>-</td>
<td>1.8</td>
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For deposition series 1 the defect density $n_d(z)$ can also be determined by solely use the definition of the defect density. The defect density is defined as the derivative to the thickness $d$ of the averaged defect density multiplied by the thickness $d$. Because $N_d(d)$ is determined for only a finite number of thicknesses, the defect density only can be defined at a finite number of points:

$$\frac{\partial (dN_d(d))}{\partial d} \sim \frac{d_2 N_d(d_2) - d_1 N_d(d_1)}{d_1 - d_2} \sim n_d \left(\frac{d_1 + d_2}{2}\right).$$  \hspace{1cm} (6.6)

The defect distribution obtained for deposition series 1 by using Eq. (6.6) is shown in Fig. 6.5. Also Fig. 6.5 suggest that there is a high defective surface layer and the defect density saturates to a constant bulk value.
In conclusion the determined defect densities of the 8 a-Si:H films clearly indicate the presence of a highly defective surface/interface layer. And the obtained values of the bulk and surface defect density agree well with literature.

The Urbach edge and defect density are both averaged quantities that do not benefit from the additional spectral information determined by tf-CRDS. In the next section the spectral dependence of thin (<30 nm) and thick (>300 nm) a-Si:H films will be compared to obtain the spectral signature of bulk and surface defects.
6.3 Spectral signature of bulk and surface defects

A striking difference in the optical absorption spectrum of a-Si:H is the spectral dependence of the absorption coefficient for a relative thick (1031 nm) and thin (3.5 nm) a-Si:H films in the sub-gap region (0.7-1.4 eV) as shown in Fig. 6.6.

![Image](image)

Figure 6.6 Absorption coefficient as a function of the photon energy of a 3.5 nm and 1031 nm a-Si:H film. Note the difference in slope in the low energy region.

As determined in Section 6.2.3 the surface layer has roughly 100 times more defects per cm\(^3\) compared to the bulk. The highly defective surface layer was determined to be around 14 nm therefore it can be stated that a-Si:H films \(<300\) nm are dominated by surface defects and a-Si:H film \(\geq 300\) nm are dominated by bulk defects. The absorption coefficient in the sub-gap region is ascribed to defect related transitions. Apparently the spectral dependence of surface defects deviates from the spectral dependency of bulk defects. The optical absorption coefficient can directly be related to the DOS as discussed in Section 1.2, therefore the DOS of the surface of a-Si:H must deviate from the DOS of the bulk of a-Si:H. In particular the positioning of the defect in the band-gap will deviate for the surface and bulk.

In Fig. 6.7 a schematic representation is shown for a DOS of the bulk (left) and surface (right) that can account for the different optical absorption spectrum for the surface and bulk dominated a-Si:H films. The position of defects and the number of defects in the DOS of the bulk and the surface deviates in the schematic model presented in Fig. 6.7. The number of defects in the bulk is significantly lower compared to the surface as determined in Section 6.2.3. The defects are proposed to be positioned mid-gap for the bulk and close to the valence band for the surface defects.
The difference in DOS of the bulk and surface can possibly be explained by the dominant type of defect. A defect on a silicon atom can be presented in the a-Si:H matrix as an 3-fold coordinated atom, a dangling bond, or a 5-fold coordinated Si atom, a floating bond. These two types of defect will show at different distribution in the band-gap. Also a heavily strained 4-fold coordinated Si atom will contribute states in the band-gap, these heavily strained Si atoms could easily be present at the surface. In Fig. 6.8 the DOS of states is depicted of a 3-fold coordinated surface (left) and a surface that is dominated by strained 4 fold coordinated Si atoms and fivefold coordinated Si atoms (right) calculated by Monte-Carlo simulations within the empirical potential approach [52]. The spectral dependence of the absorption coefficient of the surface dominated a-Si:H films could be explained by domination of the surface by strained Si atoms and 5-fold coordinated defects. The slope of the DOS of the 5-fold defect determines the relative steep slope of the optical absorption coefficient in the sub-gap absorption region. The dominant defect in the bulk of a-Si:H could be the dangling-bond, resulting in a slow dropping absorption coefficient for lower photon energies due to the density of defect states in the mid-gap.

Fig 6.8: Electronic density of states of a surface (left) that is dominated by threefold coordinated Si atoms, the threefold atoms are apparent by the peak distribution in the band gap. In the right the electronic density of states is shown for a surface that is dominated by 5-fold and distorted 4-fold atoms. The states in the band-gap mainly arise from the strained 4-fold coordinated atoms. [52]
6.4 Conclusions

In this chapter clearly the potential of the tf-CRDS technique is shown. The Urbach energies of 8 a-Si:H films with varying thickness is determined to be 55-115 meV in agreement with values found by other authors for rf-plasma deposited a-Si:H films. Also is shown that the Urbach energy only can be used for a very rough indication of the a-Si:H material quality.

The defect densities of 8 a-Si:H films are determined and show the presence of a highly defective surface/interface layer. The bulk defect density is determined to be 1-1.5×10^{16} cm^{-3} and the surface defect density is determined to be 1.8-1.9×10^{12} cm^{-2} by using the model proposed by Favre et al.

The spectral signature of the bulk and surface defect is shown to deviate. Possibly explained by the different dominant type of defect in the bulk and surface.
7. Conclusions and recommendations

7.1 Conclusions

The purpose of this research was to further develop an ultra-sensitive direct absorption technique based on CRDS for studying defect related absorption in thin films. The previous experiments performed by Van Helden and Smets [31,52] involved the application of single wavelength (1064 nm, 1.17 eV) cavity ringdown on thin (10-3000 nm) a-Si:H films on 7059 Corning glass substrates. Also the build-up of the electric field inside the optical cavity was investigated by van Helden and Smets and it was shown that an the changes in cavity output signal does not significantly changes if the reflectivity of the sample is lower than the reflectivity of the mirrors.

The research described in this report has been performed in a broad spectral range (0.7-1.7 eV) by the use of an optical parametric oscillator (OPO) laser system. The applicability of tf-CRDS is further affirmed by rigorous studies of the following issues: the stability and mode formation of an optical cavity has been studied by means of a 2D finite element method. The change in roundtrip time due to insertion of the additional sample is shown to be insignificant. The losses caused by the surface roughness of the sample have been estimated by scalar theory employing surface morphology data from atomic force microscopy. It is shown that surface scattering eventually will limit the absorption sensitivity of tf-CRDS. The sensitivity and reproducibility of tf-CRDS is improved by using high quality synthetic quartz as the substrate material. The absorption of the synthetic quartz substrates is determined to be below $1\times10^{-4}$ for most of the 0.7-1.7 eV energy range. Unfortunately inhomogeneity in the OH content of the synthetic quartz substrates has been determined, but correction is shown to be straightforward. The sensitivity of tf-CRDS is determined at $<1\times10^{-7}$ per pass if 400 averages are used.

Furthermore interference effects in tf-CRDS have been observed, interference was never reported in literature before for CRDS on thin films. Interference effects in the a-Si:H were modeled in a straightforward but complete manner using Fresnel reflection- and transmission coefficients to determine the intensity distribution in the a-Si:H film as a function of the wavelength. The data measured for films of different thickness could easily be corrected for interference effects using this model and the spatial distribution of the defects in the thin film can be determined.

As a proof-of-principle tf-CRDS has been performed on several thin a-Si:H films and the optical absorption spectra show good agreement with results obtained by transmission spectroscopy and photothermal deflection spectroscopy. Furthermore material properties such as the bulk (1-1.5$\times10^{16}$ cm$^{-3}$) and surface defect density (1.8-1.9 $\times10^{12}$ cm$^{-2}$) and the Urbach energy (55-115 meV) can be determined from the optical absorption spectrum and show good agreement with literature. The spectral signature of a surface dominated (3.5 nm) and bulk dominated (1031 nm) a-Si:H film is shown to deviate, possibly caused by a different dominant type of defect.
7.2 Recommendations

The *ex situ* tf-CRDS technique can be improved by using a substrate material with a lower absorption and that is not dominated by spectral features in the desired energy range. For example c-Si can be used as substrate material for photon energies < 1.1 eV.

The electric field intensity model can be improved by including the extinction coefficient (directly related to absorption), this will improve the correction of the additional cavity losses especially in the 1.4-1.7 eV energy region.

Tf-CRDS can also be used during light soaking experiments to study the Staebler-Wronski effect [1]. Tf-CRDS can relatively easy be applied *in situ* during real-time film growth to study the growth mechanism of a-Si:H, intermediate species and weakly adsorbed radicals. Furthermore tf-CRDS can also be employed for studying the cross-section or density of impurities (e.g. rare earth metals) in thin films.

All the above indicate that tf-CRDS has an enormous potential for a broad range of thin film research fields.
References

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Dank jullie wel!

Bram Hoex

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