Optical Properties of Thin Semiconductor Films

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1 Introduction

Optical experiments provide a good way of examining the properties of semiconductors. Particulary measuring the absorption coefficient for various energies gives information about the band gaps of the material. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and is therefore of great practical interest.

This document describes experiments of this kind. Using the techniques of transmission and reflection spectroscopy and the more advanced method of photothermal deflection spectroscopy (PDS) to measure absorption coefficients we studied the properties of three thin semiconductor films.

2 Experimental setup

2.1 Transmission/Reflection Spectroscopy

For transmission and reflection spectroscopy we used a commercial spectrophotometer that was capable of recording spectra in the visible range as well as in the near infrared and UV. To compensate for the complicated intensity distribution of the light source the spectrometer did not measure absolute values but compared the signal from the sample to a reference beam. Additionally, a baseline was recorded prior to the actual measurements to calibrate the instrument.

However the transmission and reflection measurements are limited to wavelengths at which the sample has an average absorption coefficient. For high absorption there is virtually no transmission. As both reflection and transmission spectra are required to calculate the absorption coefficient α this method is no more applicable then. If α is too low however thin film intereference effects will appear because light waves that are reflected on the two sides of the sample film will overlay. Therefore, spectrophotometry has to be used in combination with other techniques in order to obtain a complete absorption spectrum for a sample.

2.2 Photothermal Deflection spectroscopy (PDS)

One method for measuring low values of α with high accuracy is photothermal deflection spectroscopy which measures the heating of the environment which occurs when a sample absorbs light. Therefore a pumping beam of monochromatic light with an adjustable wavelength is directed onto the sample which is contained in a cuvette of perfluorhexane (C_6H_{14}). Perpendicular to the pumping beam a laser beam passes through the cuvette directly in front of the sample. When the sample absorbs part of the pumping beam it slightly heats the surrounding C_6H_{14}. As this liquid has a low heat conductivity, this causes relatively steep temperature gradients and, as C_6H_{14} also has a refraction index n that very is sensitive to temperature fluctuations, steep gradients of n. The laser beam passing through the liquid is therfore slightly deflected. This deflection which is proportional to the absorption is finally measured by an optical detector.

To obtain a better signal to noise ratio a lock in amplifier is used. Before explaining the role of this device in our experiment, we will briefly describe how it works. A lock in amplifier is used to filter one specific frequency from an input signal, so it is acutually a very accurate band pass filter. It does this by overlaying the signal with a sinusoidal reference signal at the desired frequency and then integrating over several periods. While all

unwanted frequency components cancel out in the integration the component at the frequency of the reference signal is amplified. The output of the lock in is a voltage that is proportional to the the amplitude of this frequency component. Mathematically this corresponds to the calculation of a Fourier coefficient of the signal according to the formula

$$U_{out} \propto \int U_{in} \cdot \cos(\omega t + \varphi) dt \tag{1}$$

What is also important is the phase relation between the input and reference signals: For example, if the two signals are identical but for a phase difference of exactly 90 °, formula (1) becomes

$$U_{out} \propto \int \sin(\omega t) \cdot \cos(\omega t) dt = 0 \tag{2}$$

A similar calculation shows that for a phase difference of 180 ° the output signal would be negated.

In our PDS setup the pumping beam was chopped up so that the detector signal oscillated at the frequency of the chopper wheel. This was used as reference signal for the lock in amplifier which filtered out all other frequency components, i.e. all sorts of unwanted background noise.

Although PDS is very accurate for low absorption, it becomes useless if α gets too high. If too much light is absorbed in the sample, temperature gradients would become so steep that heat conduction can no more be neglected. This results in saturation effectes on the output signal.

3 Results of Transmission/Reflection measurements

In this section we will present the results of our transmission and reflection measurements and derive several properties of our semiconductor samples from them.

3.1 Transmission

Figure 1 shows the transmission of three different semiconductor samples in dependance of the photon energy. The samples consisted of a thin semiconductor film (amorphous hydrogenated silicon a-Si:H, crytalline silicon c-Si or gallium nitride GaN respectively) that was imposed on a quartz substrate that did not absord light itself in the visible, near IR and UV ranges. The thickness of the film was 690 nm for a-Si:H, 20 μm for c-Si and 1 μm for GaN.

The diagram shows that for high energies there is no transmission because all the light is absorbed. For low energies however there are no appropriate electronic transitions possible so transmission is very high in this range. It is not 100% however, because of reflection. There is a relatively sharp delimitation between the areas of high and low absorption.

The energy at which absorption starts seems to be characteristic for each material: For GaN it corresponds to the direct band gap at 3.4 eV. As crytalline silicon is an indirect semiconductor which cannot absorb a photon without simultaneously creating a phonon, absorption does not start at the band gap (1.1 eV) but at an energy that is high enough for exciting an electron and creating a phonon with the appropriate impulse. For our sample of amorphous silicon there exist many possible transitions around 2 eV. However this cannot be generalized because the properties of a-Si:H depend on many parameters and will therefore be different for different samples.

For low energies we observe thin film interference effects that result from the overlaying of light that is reflected on both sides of the thin film. If this interference is constructive or destructive depends on the wavelength. For c-Si, this effect is not visible because the thickness of this sample (20 μm) was too great to allow coherent overlaying of the two reflected beams.

3.2 Reflection

The interpretation of the reflection spectra in figure 2 is not so straightforward as that for the transmission. For high energies, where absorption is high according to the transmission diagram, reflection increases as well. This can only be explained by a theoretical treatment of the interaction between light and matter.

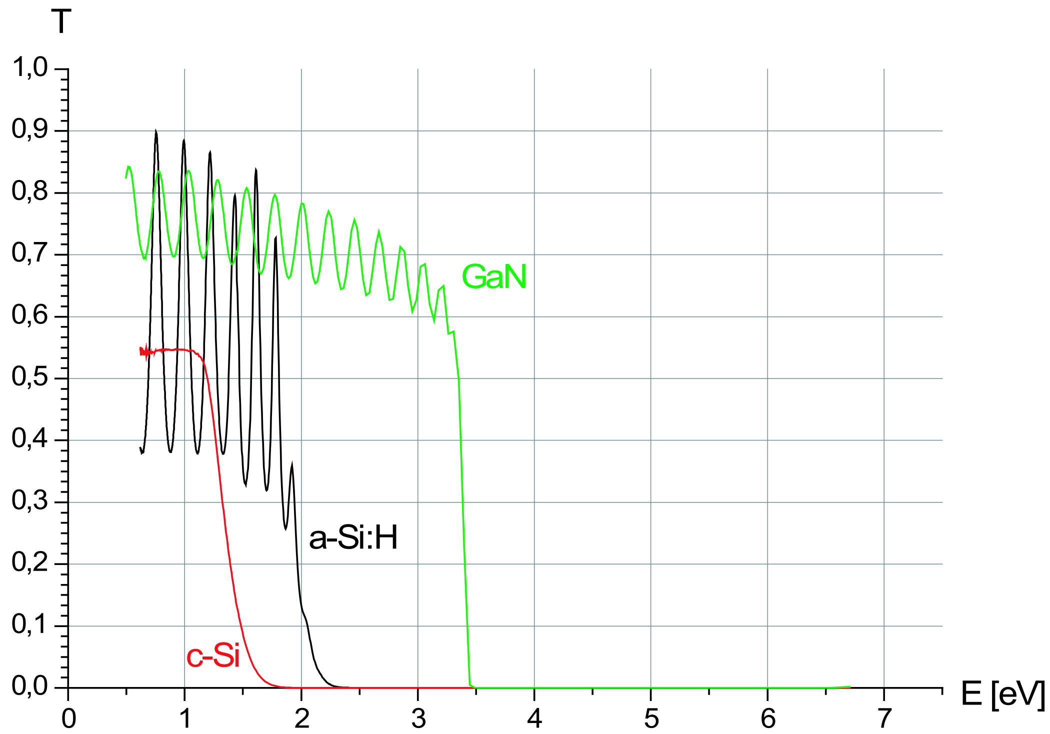

Figure 1: Transmission spectra for samples of amorphous hydrogenated silicon (a-Si:H), crystalline silicon (c-Si) and gallium nitride (GaN)

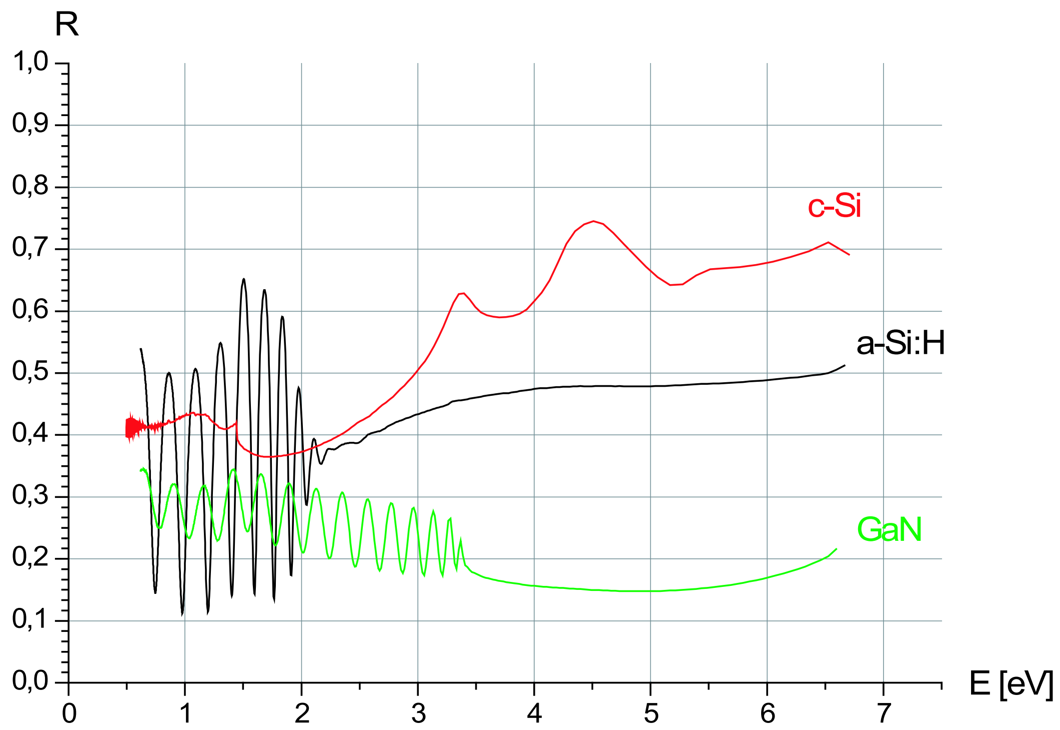

Figure 2: Reflection spectra for samples of amorphous hydrogenated silicon (a-Si:H), crystalline silicon (c-Si) and gallium nitride (GaN)

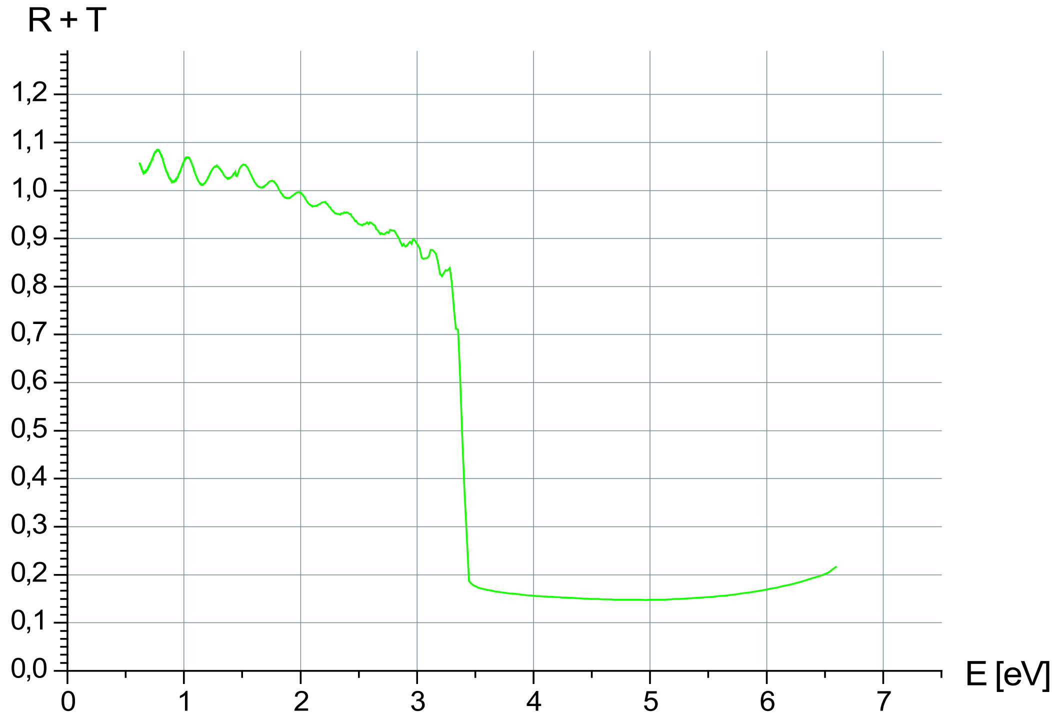

Figure 3: Sum of reflection and transmission for GaN

An interesting observation are the various maxima that appear in the reflection spectrum of c-Si in figure 2 at energies of 1.1 eV, 3.3 eV, 4.4 eV and 6.5 eV. These energies correspond exactly to the indirect band gap (1.1 eV), the direct band gap (about 3.2 eV), the sum of the two band gaps and twice the direct band gap. Explainig the reason for the appearance of these Maxima would again require some theoretical effort.

In the near infrared and visible ranges, there is again the problem of thin film interferences for a-Si:H and GaN. One would expect the interferences in the transmission and reflection spectra to cancel out because if transmission T is very high there can be only few reflection R as — neglecting absorption — $R + T$ must equal 100%. Indeed, there are only very weak interferences left in the graphical plot of $R + T$ for GaN in figure 3. However they do not cancel out completely. What is also quite remarkable is the fact that R exceeds 100% for low energies which is physically impossible.

The explanation for both observations is probably an imperfect calibration of the spectrometer in the reflection measurements. When recording the baseline by which the device calibrated the point of 100% of reflection, a mirror was inserted in the place of the sample. Although it was made of a special material that shows almost total reflection in the desired wavelength range, it is not perfect and absorbs or transmits a small portion of the light. This results in the 100% point to be adjusted a little too low, so that all reflection data that is corrected with this baseline would be slightly too high.

For energies above the absorption edge figure 3 shows that $R+T$ gets very low because in the spectral range most photons are absorbed by the sample. As all light that is neither reflected nor transmitted must be absorbed the difference $1 - R - T$ is equal to the absorption A. In a rough approximation we could now calculate the absorption coefficient α according to the equation

$$R + T = e^{-\alpha d} \tag{3}$$

where d is the thickness of the sample. However this calculation does not consider the fact that some of the light is reflected at the back of the sample. Most of these photons will not appear in the detector because they are absorbed on their way back through the semiconductor. In a later section we will apply a more accurate formula for calculating α.

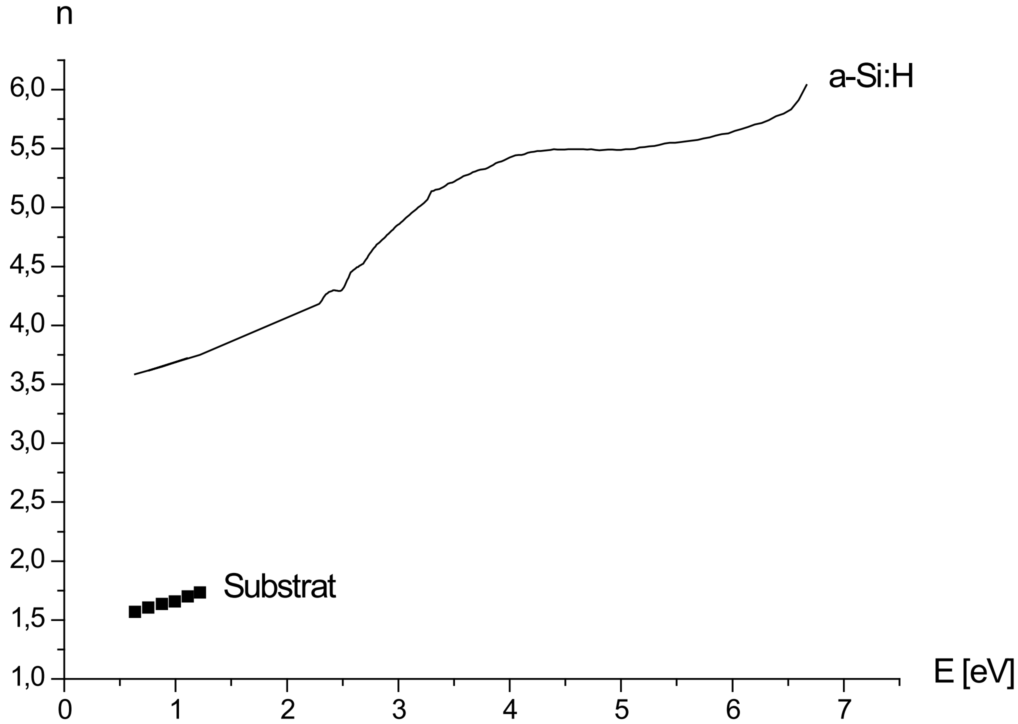

Figure 4: Refraction indices n_f of the sample and n_S of the substrate for a-Si:H

3.3 Calculation of refraction indices

Besided providing information about the absorption of the sample, transmission and reflection spectra can give us important information about the refraction indices of the sample and the underlying quartz substrate. In this section we will perform the corresponding calculations for a-Si:H.

If absorption is high and interferences can be neglected the sample refraction index n_f can be calculated according to

$$R = \left(\frac{n_f - 1}{n_f + 1}\right)^2$$

$$\Leftrightarrow n_f = \frac{1 + R + \sqrt{R}}{1 - R} \quad (4)$$

This is how the high energy part of the curve in figure 4 was derived for a-Si:H.

If interference effects have to be taken into consideration things become more complicated. From the maxima in the transmission spectrum one can derive the refraction index of the substrate by the following equation:

$$T_{max} = \frac{2n_S}{n_S^2 + 1}$$

$$\Leftrightarrow n_S = \frac{1 + \sqrt{1 - T_{max}^2}}{T_{max}} \quad (5)$$

As this formula is limited to cases were absorption can be completely neglected we performed it only for the three leftmost transmission maxima (cp. figure 1). The resulting values for n_S showed an approximately linear behaviour so we fitted a straight line to them to obtain intermediate values of n_S which were required in the following calculations. As you can see in figure 4, n_S is slightly above 1.5 an increases with E. This behaviour is expected for most materials.

The refraction index of the sample n_f for low energies can be obtained from the transmission minima by applying the given formula

$$n_f = \sqrt{M + \sqrt{M^2 - n_S^2}} \qquad \text{where } M = \frac{2n_S^2}{T_{min}} - \frac{n_S^2 + 1}{2} \tag{6}$$

This is how the leftmost part of the curve in figure 4 was obtained.

There is an energy range from around 1.2 eV up to 2.3 eV where neither of the two above methods can be applied because interference effects render the first one useless and beginning absorption the second. In this range, we simply interpolated n_f linearily, which results in a smooth curve as you can see in the diagram.

3.4 Thickness of the semiconductor films

Now that we know the refraction index of our semiconductor film we can derive its thickness d from the condition for constructive and destructive interference:

$$2n_f d = k\frac{\lambda}{2} \tag{7}$$

where the order k is even for constructive interference and uneven for destructive.

The only problem is that we do not know the order of the maxima we observed. However it can be easliy derived by dividing equation (7) for two successive extrema:

$$\begin{aligned} \frac{n_f(\lambda_k)}{n_f(\lambda_{k+1})} &= \frac{k}{k+1}\frac{\lambda_k}{\lambda_{k+1}} \\ \Leftrightarrow k &= -\frac{1}{\frac{n_f(\lambda_k)}{n_f(\lambda_{k+1})} - \frac{\lambda_k}{\lambda_{k+1}}} \end{aligned} \tag{8}$$

In our case the first minimum had $k = 5$, the first maximum $k = 6$, and so on.

Now we had all the information required to calculate d from equation (7). We performed this calculation for the first three maxima and minima and then calculated the average value which turned out to be $d = 678.6 \pm 0.017$ nm. The error given here is purely statistical. When considering systematic limitations and errors introduced by the approximations we made in the process of our calculations, this value would certainly increase to several nm. However, our abosulte value for d deviates by only 1.7% from the given value of 690 nm. As there was no information available for the accuracy of this value we will trust our own measurements and use $d = 678.6$ nm for further calculations.

3.5 Absorption coefficients

In this section we will finally derive the absorption coefficients α from the transmission and reflection measurements. We will use the approximation formula

$$\begin{aligned} T &\approx (1-R)^2 e^{-\alpha d} \\ \Leftrightarrow \alpha &= -\frac{1}{d}\ln\left(\frac{T}{(1-R)^2}\right). \end{aligned} \tag{9}$$

The resulting curves are plotted with a semilogarithmic scale in figure 5. As you can see there were no meaningfull results for low energies. α started to oscillate and even became negative which makes no physical sense. This is because equation (9) is only valid for high α. For high absorption, the transmission T became so close to 0 that the results are doubtfull in this range as well. For c-Si and GaN, the spectrometer actually recorded small negative values for T which are of course not applicable in the $\ln$-formula of equation (9).

For a-Si:H, T did not become negative but remained constant at slightly positive values. This behaviour is also very suspicious and results probably from an incorrect calibration of the spectrometer or some stray light from outside the spectrometer. Therefore the curve for a-Si:H above 2.4 eV should be regarded with extreme care.

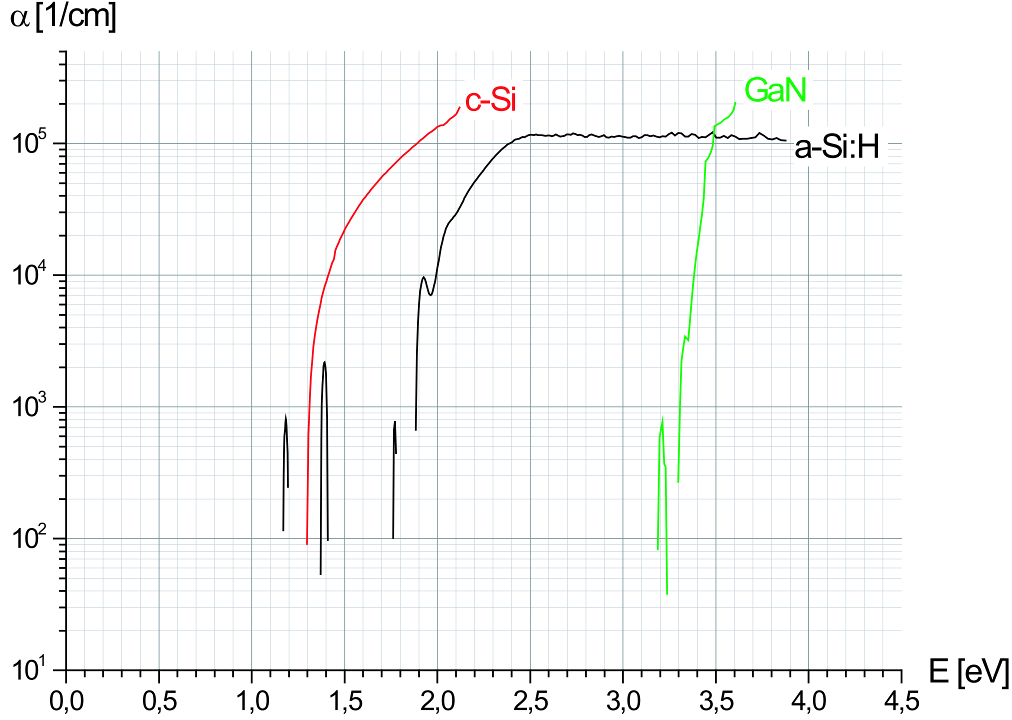

Figure 5: Absorption coefficients derived from transmission/reflection spectroscopy

3.6 Determination of Band Gaps

From the plots in figure 5 we can now derive the band gaps of our three samples.

Theoretical calculations show that for GaN, which is a direct semiconductor, α obeys the equation

$$\alpha(\hbar\omega) \propto \frac{\sqrt{\hbar\omega - E_{gap}}}{\hbar\omega} \tag{10}$$

around the band gap. Therefore an obvious thing to do is plotting the photon energy $\hbar\omega$ over $(\alpha \cdot \hbar\omega)^2$ and fitting a straight line to this plot. The constant term of its equation is equal to E_{gap}. This is shown in figure 6a. The resulting value is $E_{gap} = 3.42 \pm 0.005$ eV which is already very close to the given value of 3.4 eV. The above error value is merely statistical and does not consider systematic uncertainties.

For the indirect semiconductor c-Si the theoretical expression for α is

$$\alpha(\hbar\omega) \propto \frac{(\hbar\omega - E_{gap})^2}{\hbar\omega}. \tag{11}$$

Therefore we must now plot $\hbar\omega$ over $\sqrt{\alpha \cdot \hbar\omega}$ as it is shown in figure 6b. Here the result is $E_{gap} = 1.23 \pm 0.002$ eV which deviates from the correct value of 1.1 eV by 11%.

For amorphous silicon the band gap is blurred very much because there exist many quantum mechanical energy level outside the actual conduction and valence bands. One usually defines the band gap E_{04} as the energy at which the absorption coefficient reaches 10^4 1/cm. In our case $E_{04} \approx 1.9 – 2.0$ eV.

4 Results of Photothermal Deflection Spectroscopy

4.1 Scaling the experimental data

As we saw in the previous sections, transmission and reflection spectroscopy is useless for low energies. In this section we will present the results of our PDS measurements and combine them with the transmission/reflection

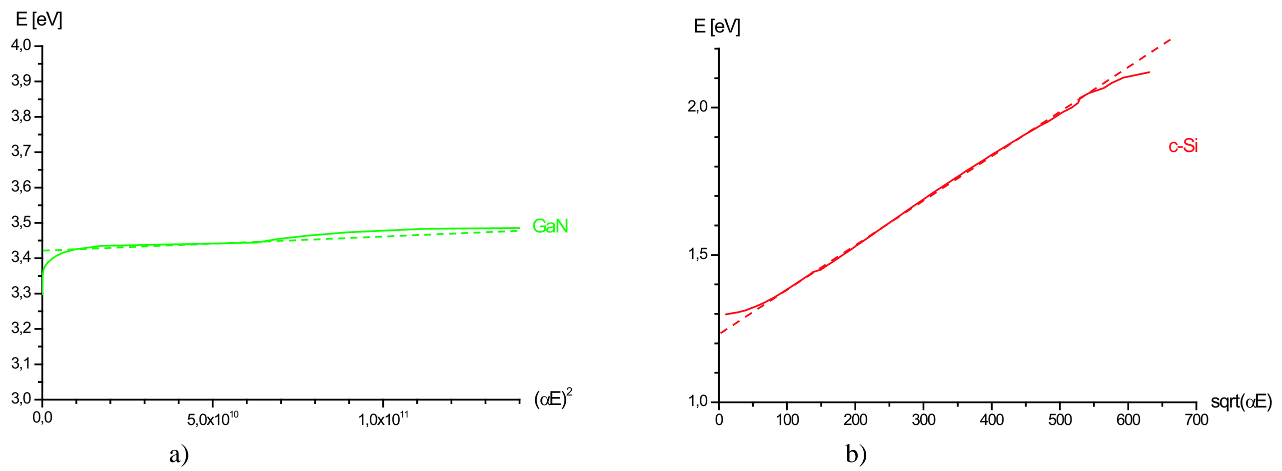

Figure 6: Determination of band gaps for GaN (a) and c-Si (b) from reflection/transmission data

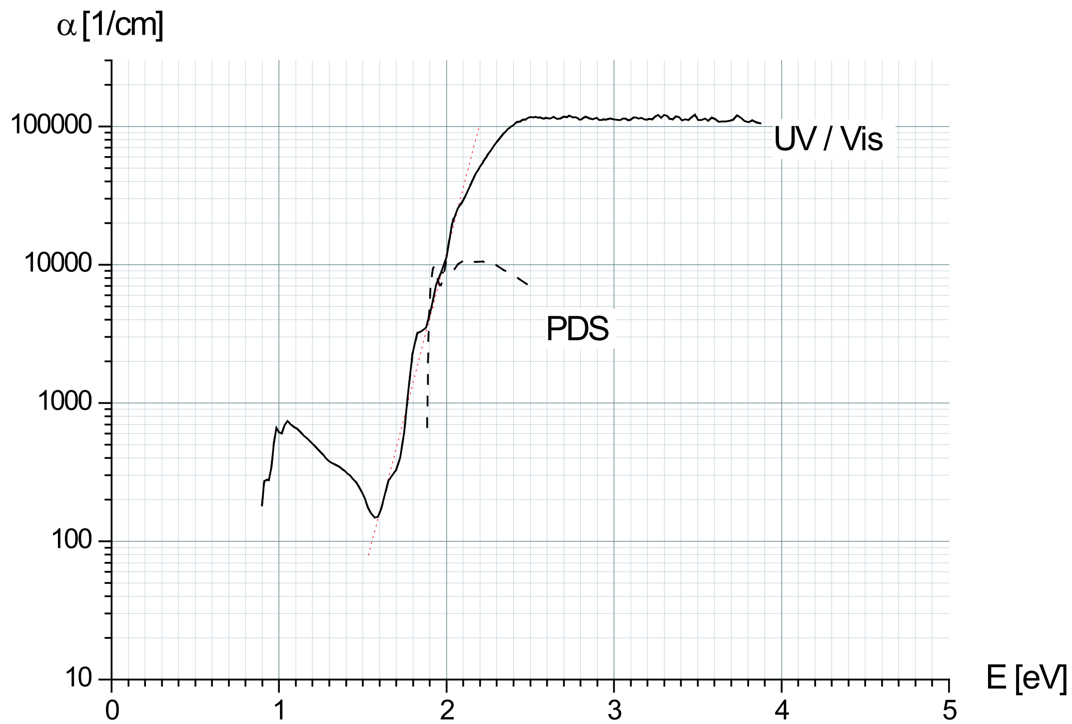

Figure 7: Absorption coefficient derived from PDS for a-Si:H. The straight line drawn in red will be used to calculate the Urbach energy later.

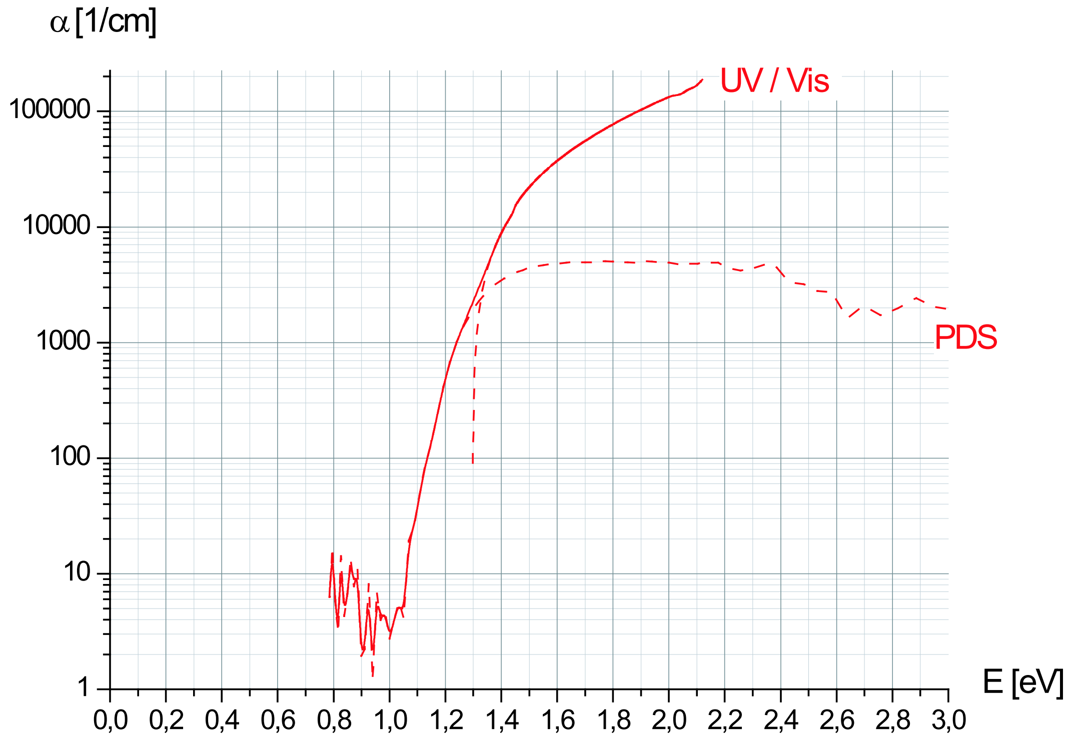

Figure 8: Absorption coefficient derived from PDS for c-Si

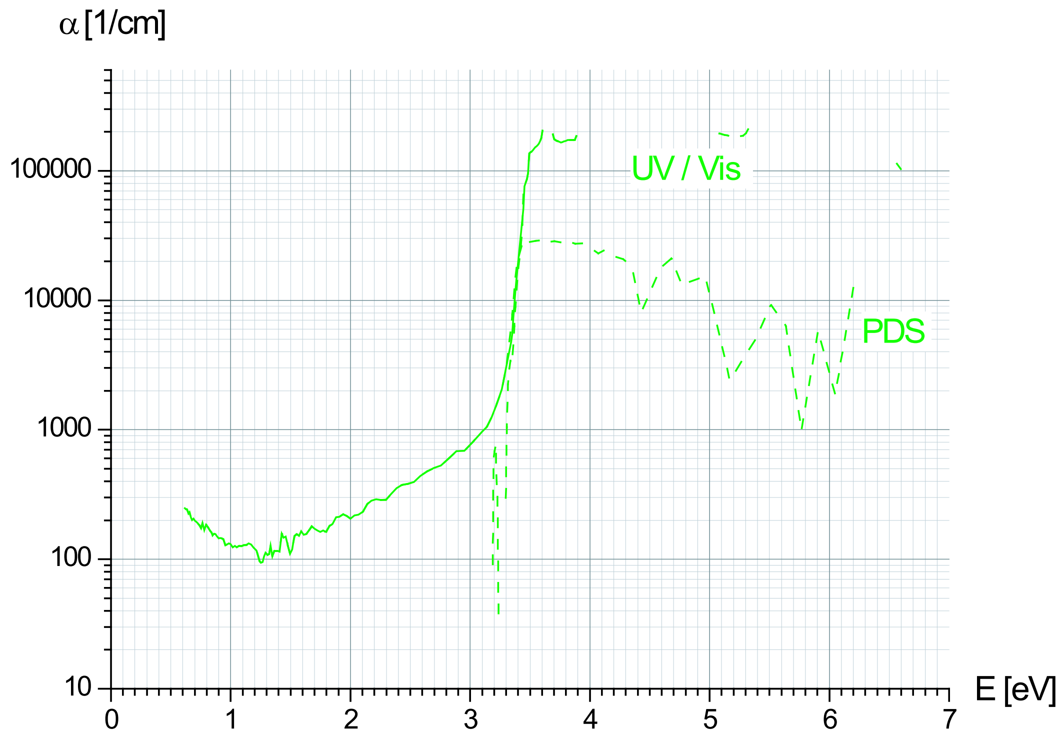

Figure 9: Absorption coefficient derived from PDS for GaN

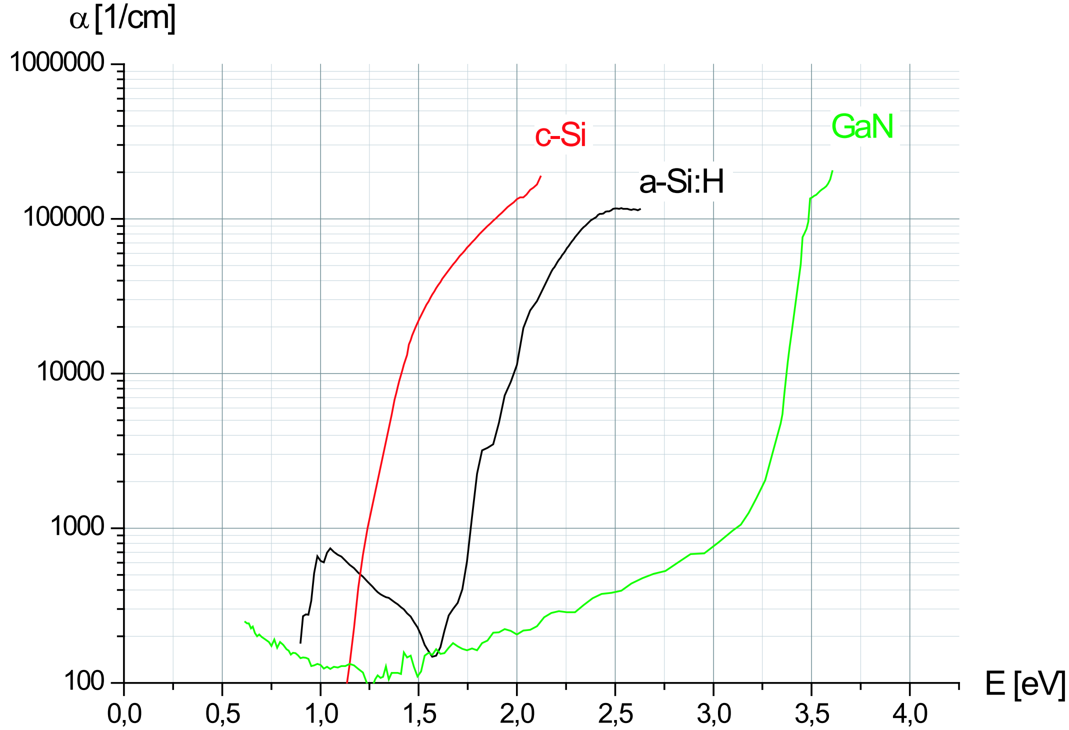

Figure 10: Final result: Absorption coefficient for a-Si:H, c-Si and GaN, combined from transmission/reflection spectroscopy and PS

data to obtain accurate absorption curves that cover a wide range of photon energies.

To obtain α from the PDS measurements approximately we applied the empirical formula

$$\alpha \approx -\frac{1}{d} \cdot \ln(1 - 0.96 \cdot \text{PDS signal}) \tag{12}$$

However, as the results from the PDS are relative values it is necessary to adjust them by some factor. It can be determined by plotting both the PDS and the transmission/reflection data into one diagram and then adjusting the scaling factor until both curves overlap for those energies were both methods provide accurate results.

This is shown in figures 7, 8 and 9 for our samples. The broken curves indicate the reflection/transmission data and the properly scaled PDS data. The solid curve is a combination of both curves. For low energies the PDS values were used, for high energies the reflection/transmission data. In the area of the overlap, the final curve was calculated by averaging and interpolation to obtain a smooth curve.

For c-Si the overlap was very poor because in the corresponding energy range there were already interference effects in the transmission/reflection data and saturation in the PDS data. Therefore, the results for c-Si have probably a greater error than those for a-Si:H and GaN.

As you can see from the plots, saturation occurs for high values of α because of heat conduction effects as explained in section 2.2.

4.2 Discussion of final results

Figure 10 shows the final α-curves for all three samples in one diagram, taking into account only those data points that are not distorted by experimental effects.

For c-Si the absorption coefficient rises slowly, beginning shortly above the band gap at 1.1 eV. Unfortunately our experiments did not provide useable data for energies higher than 2.1 eV, so it was impossible to detect the effects of the direct band gap at above 3 eV.

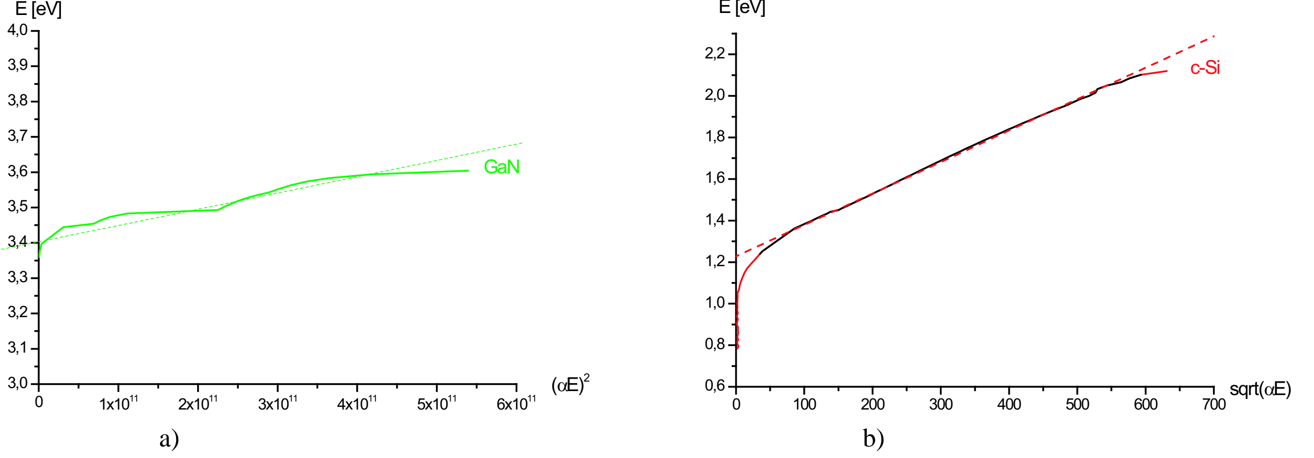

Figure 11: Determination of band gaps for GaN (a) and c-Si (b) from combined reflection/transmission and PDS data

The absorption of amorphous silicon starts at higher energies. However there is some absorption between 1.8 eV and 1.5 eV. This is caused by dangling bond defects in the material. However the shape of the curve looks very unusual in this range. Therefore further measurements should be made to examine whether this absorption is perhaps caused by some experimental distortion such as dust or fingerprints on one of the optical components or some mechanical defect of the sample.

GaN shows low absorption below its band gap at 3.4 eV. At this point however, α steeply increases.

In section 3.6 we derived accurate values for the band gaps from only the reflection and transmission data. We will now repeat this calculation for the final data from figure 10.

The necessary plots are shown in figure 11a for GaN and in figure 11b for c-Si. The results are $E_{gap} = 1.23 \pm 0.003$ eV for c-Si and $E_{gap} = 3.40 \pm 0.008$ eV for GaN. The value for GaN is in perfect agreement with the accepted value of 3.4 eV, while that for c-Si is slightly above the expected 1.1 eV. This is probably caused by an inaccurate scaling of the PDS measurements, as discussed in section 4.1 .

The band gap E_{04} for amorphous silicon (i.e. the energy where α exceeds 10^4 1/cm) is at 2.0 eV.

Another characteristic quantity for a sample of amorphous silicon is the Urbach energy E_0 which describes the "blurring" of the valence and conduction bands. It is defined by the formula

$$\alpha \propto \exp(E/E_0) \tag{13}$$

which describes the quasi-exponential slope of alpha around the band gap. In our semilogarithmic plots this slope becomes linear as shown by the red line in figure 7. The recipcrocal value of the gradient of this line is just E_0. For our sample, we obtained $E_0 = 0.213$ eV. Very good samples of amorphous silicon have an Urbach energy around 0.05 eV so our sample was of average quality with respect to the blurring of the energy bands.

Finally we will calculate the dangling bond density for a-Si:H which is defined as

$$N_{DB} = 2 \cdot 10^{16}\text{cm}^{-2} \cdot \alpha(1.3\text{eV}) \tag{14}$$

In our case we obtained a value of $N_{DB} = 3.5 \cdot 10^{16}\text{cm}^{-3}$. Compared to very good amorphous silicon which has a dangling bond density of about 10^{15}cm^{-3} our sample is of average quality with respect to dangling bonds as well.