CdS Reflection Coefficient Determination via Photocurrent Spectroscopy

Yang Wang

A Thesis
Submitted to the Graduate College of Bowling Green State University in partial fulfillment of
the requirements for the degree of
MASTER OF SCIENCE
December 2008

Committee:
Dr. Bruno Ullrich, Advisor
Dr. Lewis P. Fulcher
Dr. Mikhail Zamkov
ABSTRACT

Reflectance is a very essential property of every semiconductor and the topic of this thesis was to determine the reflection coefficient of CdS by unusual means, i.e., by using photocurrent spectroscopy. Reflectance and photocurrent of the CdS sample and a silicon photodiode were measured using the lock-in amplifier. The photocurrent of the diode was required in order to correct the CdS photocurrent spectra, which are influenced by the experimental setup. By means of photocurrent, the absorption coefficient was determined using the density of states (DOS), Urbach rule, and the appropriate expression for the photocurrent. Measurement and the theory matched very well, and finally, using the absorption coefficient the dispersion of the CdS reflection was plotted.
# Table of Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Semiconductor and Reflection</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Semiconductors</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Reflection</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Objective</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>II-VI Semiconductors and Photocurrent</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>II-VI Semiconductor</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Cadmium Sulfide (CdS)</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Photocurrent</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Sample and Equipments</td>
<td>10</td>
</tr>
<tr>
<td>3.1</td>
<td>CdS Sample</td>
<td>10</td>
</tr>
<tr>
<td>3.2</td>
<td>Equipments used</td>
<td>11</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Light source</td>
<td>11</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Monochromator</td>
<td>12</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Chopper</td>
<td>12</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Lens</td>
<td>13</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Silicon photodiode</td>
<td>14</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Filter</td>
<td>14</td>
</tr>
<tr>
<td>3.2.7</td>
<td>Lock-in amplifier</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Measurements</td>
<td>16</td>
</tr>
<tr>
<td>4.1</td>
<td>Measurement of CdS photocurrent</td>
<td>16</td>
</tr>
</tbody>
</table>
4.2 Measurement of the reflectance ................................. 18
4.3 Measurement of the silicon photodiode photocurrent ....... 20

Chapter 5. Results and Analysis ................................. 21

5.1 Results .......................................................... 21
   5.1.1 Responsivity .............................................. 21
   5.1.2 Reflectance ............................................... 23

5.2 Analysis ..................................................... 24
   5.2.1 Absorption coefficient $\alpha$ ............................ 24
   5.2.2 Reflection coefficient ................................. 26

5.3 Conclusion .................................................. 27

References ......................................................... 28
Chapter 1

Semiconductor and Reflection

1.1 Semiconductors

Generally, solids can be divided into three classes: insulators, conductors, and semiconductors based on their electrical resistivity and conductivity. Typically, the resistivity of insulators is higher than $10^{12}$ Ohm-cm, the resistivity of conductors is between $10^{-5}$ and $10^{-6}$ Ohm-cm, and the resistivity of semiconductors is between $10^{11}$ and $10^{-5}$ Ohm-cm, as shown in Table 1.1. The important feature is here that the resistivity of a semiconductor, in contrast to insulators and conductors, can be drastically changed with illumination or doping.

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity (Ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insulator</td>
<td>$&gt;10^{12}$</td>
</tr>
<tr>
<td>Conductor</td>
<td>between $10^{-5}$ and $10^{-6}$</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>between $10^{11}$ and $10^{-5}$</td>
</tr>
</tbody>
</table>

Furthermore, the electrical resistivity of semiconductors is strongly dependent on temperature. With these properties, semiconductors have many applications such as, transistors, switches, diodes, temperature sensors, and detectors. Figure 1.1 shows the structure of silicon, which is the best known semiconductor.
In semiconductors, there are two energy bands, i.e., conduction band and valence band. The band gap is the energy difference between the lowest point of the conduction band and the highest point of the valence band [2]. The band diagram is shown in fig. 1.2.

Figure 1.1: The structure of silicon in different viewing directions.

Figure 1.2: Most simple band diagram of a semiconductor.
When an electron in the valence band gets enough energy (e.g. through impinging light), it will be excited to the conduction band and leaves a hole in the valence band behind. The electrons in the conduction band and the holes in the valence band contribute to the increase in the electrical conductivity.

1.2 Reflection

When light passes thin-film material, three basic effects take place: reflection, transmission, and absorption. To describe this process we need to consider the internal reflections between the surface and backface. Fig. 1.3 shows the process - $I_0$ is the incident light intensity, $R$ is the reflection coefficient of the surface and backface, $\alpha$ is the absorption coefficient, and $x$ is the thickness of the film.

Figure 1.3: Light beam through a thin-film [4]: The figure schematically illustrates the multiple internal reflections.
We can see that the intensities of the first order, second order, and third order reflection are \( R I_0, R(1-R)^2 I_0 e^{-2\alpha x}, R^3 (1-R)^2 I_0 e^{-4\alpha x} \). The entire intensity of reflection is the sum of all reflected intensities and is given by [4]:

\[
I = R I_0 [1 + \frac{(1-R)^2 e^{-2\alpha x}}{1-R^2 e^{-2\alpha x}}] \quad (1.1)
\]

The reflectance \((Re)\) is the ratio between \( I \) and \( I_0 \):

\[
Re = R[1 + \frac{(1-R)^2 e^{-2\alpha x}}{1-R^2 e^{-2\alpha x}}] \quad (1.2)
\]

Usually, the intensities of the third order reflection and above are very weak, and we only consider the first two orders. In this way, the formula can be simplified to [5]:

\[
Re = R[1 + (1-R)^2 e^{-2\alpha x}] \quad (1.3)
\]

Using the same method, we can get the transmittance \((Tr)\):

\[
Tr = \frac{(1-R)^2 e^{-\alpha x}}{1-R^2 e^{-2\alpha x}} \quad (1.4)
\]

Consider the first two orders, the formula becomes:

\[
Tr = (1-R)^2 e^{-\alpha x} \quad (1.5)
\]

Due to energy conservation, the sum of reflectance, transmittance, and absorption \((A)\) is one:

\[
Re + Tr + A = 1 \quad (1.6)
\]

1.3 Objective

The purpose of this thesis was to determine the reflection coefficient of thin-film CdS. To achieve this, first of all, we need to measure the reflectance of the thin-film. As we mentioned before, we have the formula for reflectance:
\[ Re = R[1 + (1 - R)^2 e^{-2\alpha} ] \]

Hence, to determine the reflection coefficient \( R \), we need to know \( \alpha \), which is the absorption coefficient. To determine \( \alpha \), we will measure the photocurrent of the thin-film and make use of the relation between the photocurrent and absorption coefficient. We will introduce the relation in a later chapter. Before that, let’s take a look at the II-VI semiconductor, especially CdS.
Chapter 2

II-VI Semiconductors and Photocurrent

2.1 II-VI Semiconductor

The compound II-VI semiconductors are composed of elements out of group II and VI in the periodic table of chemical elements. Their chemistry and physics is in general more complex than that of single element semiconductor, such as Si and Ge. Typical examples for II-VI semiconductors are zinc oxide (ZnO), zinc sulfide (ZnS), and cadmium sulfide (CdS). Fig. 2.1 shows the structure of these compounds.

![Structure of II-VI semiconductors: (a) ZnO, (b) ZnS, (c) CdS](image)

Figure 2.1: Structure of II-VI semiconductors: (a) ZnO, (b) ZnS, (c) CdS
II-VI semiconductors have appealing technological features such as extreme light sensitivity and band gaps in the visible range. Furthermore, in many cases, straightforward technologies (e.g. vacuum evaporation, spray and pulsed-laser deposition) result in useful thin-film devices on various substrates. Hence, thin-film II-VI compounds are widely used for fundamental research.

2.2 Cadmium Sulfide (CdS)

CdS has the molecular weight of 144.47, average atomic weight of 72.24, average atomic number of 32. Table 2.1 shows some properties of CdS [1].

<table>
<thead>
<tr>
<th>Property</th>
<th>CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameter at 300K</td>
<td>0.582nm</td>
</tr>
<tr>
<td>Density at 300K</td>
<td>4.87g·cm⁻³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1750 °C</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.506</td>
</tr>
<tr>
<td>Energy Gap (E₉) at 300K</td>
<td>2.50eV</td>
</tr>
</tbody>
</table>

2.3 Photocurrent [4]

When light impinges a semiconductor, photons having $\geq E_g$ will excite electrons in the valence band to the conduction band, leaving holes in the valence band, as shown in Fig. 2.2. In this way, the electron-hole pairs are generated contributing to the electrical conductivity. If an external electric field is applied the electrons and holes move in opposite directions, which produce photocurrent, as shown in Fig. 2.3.
Fig. 2.2 Excitation of electrons

(a)
Figure 2.3: Photocurrent: (a) The most simple circuit (b) Photocurrent in a semiconductor thin-film.
Chapter 3
Sample and Equipments

3.1 CdS Sample

The sample used in this research is thin-film CdS on glass realized with pulsed-laser deposition. The parameters and the actual sample are shown in table 3.1 and Fig. 3.1, respectively.

Table 3.1: Parameters of Sample G180 [7]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness $d$</td>
<td>200nm</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.7</td>
</tr>
<tr>
<td>Energy Gap $E_g$</td>
<td>2.44eV</td>
</tr>
<tr>
<td>$\tau_{SR} / \tau_{ph}$</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 3.1: Image of the sample used.
3.2 Equipments used

This section summarizes the most important equipment, which was light source, monochromator, chopper, lens, silicon photodiode, and lock-in amplifier. The purpose and the function of the items are discussed below.

3.2.1 Light source

The light source used in this research is the LSH-T250 light source. Its 200 W halogen lamp generates white light driven with the power supply AL 924A. Light source and power supply are shown in figure 3.2.

Figure 3.2: LSH-T250 light source (front) and AL 924A power supply (back).
3.2.2 Monochromator

The monochromator is the key equipment for spectroscopy requiring monochromatic light. The employed monochromator was a Czerny-Turner type (SPEX 500M). The monochromator in conjunction with the light source, which was directly attached to the monochromator, provided the photonic excitation for the reflection and photocurrent measurements. The monochromator used is shown in Fig. 3.3.

Figure 3.3: SPEX 500M monochromator. On the right, the tube of attached light source can be seen, while an optical chopper is placed at the exit slit of the monochromator.

3.2.3 Chopper

The optical chopper used is shown in figure 3.4. A wheel with 10 slots was employed. The chopper was controlled by a power supply allowing precise adjustments of the chopper frequency. The periodic interruptions of the light was required in order to provide the reference signal for the lock-in amplifier, which operates on the base of a phase-locked loop (PLL) device.
3.2.4 Lens

A 10 cm convex lens was used behind the chopper to focus the monochromatic light onto the sample. The lens is shown in Fig. 3.5.

Figure 3.4: The chopper used located at the exit of the SPEX 500M.

Figure 3.5: Lens used to focus the signal onto the thin-film.
3.2.5 Silicon photodiode

A calibrated silicon photodiode was used to correct the photocurrent of the CdS sample. After the corrections the results are expressed in terms of responsivity (A/W). Figure 3.6 shows the silicon photodiode. The diode was used for the reflectance measurements as well.

![Calibrated silicon photodiode used in order.](image)

3.2.6 Filter

Usually, the sensitivity of silicon photodiode is too high driving the lock-in amplifier into the state of overload. In order to avoid this difficulty a neutral density filter (OD=1.0, i.e., reduces the light intensity by one order of magnitude) was used to reduce the output current of the photodiode.
3.2.7 Lock-in amplifier [3]

The lock-in amplifier was used to measure the photoresponse of the thin-film CdS sample and the photodiode as well. As previously mentioned the heart of the device is a PLL circuit. During the last 30-40 years, lock-in technique has established itself as a precise low-noise measuring method. The only drawback is that this technique measures extrinsic sample features rather than the intrinsic ones. The lock-in amplifier used was the SR530 lock-in amplifier and is shown below in Fig. 3.7.

![Figure: 3.7 Two channels SR530 Lock-in amplifier.](image)

Basically, the lock-in amplifier measures the complex sample response, i.e., channel 1 corresponds to the $x$-axis (real part) and channel 2 correspond to the $y$-axis (imaginary part) of the measured signal. Most of the time the radius, which is given by $(x^2+y^2)^{1/2}$, is the parameter of interest.
Chapter 4

Measurements

4.1 Measurement of CdS photocurrent

The schematic of the setup for the CdS photocurrent measurements is shown in Fig. 4.1. The white light coming from the source was converted to monochromatic illumination by passing through the monochromator. After that, the already monochromatic light passed the chopper and, finally, was focused with a convex lens onto the CdS sample. The impinging monochromatic light incident caused photocurrent, which was recorded with the connected lock-in amplifier. The electrical contacts have been realized with Al electrodes on the sample surface. The connection between sample and lock-in amplifier is shown in Fig. 4.2. The circuit consisted of a power supply, a resistor, the sample, and the lock-in amplifier. The resistor is connected to the A-B input of the lock-in amplifier.

![Figure 4.1: Schematic of the photocurrent experiment.](image_url)
During the measurement, the wavelength range was set to be 400 - 650 nm, and the chopper frequency was 17 Hz. The shunt was a resistor of 1.5 MΩ, and the power supply was set to 10 V. The experiments have been computer controlled and Fig. 4.3 shows a typical result of the photocurrent measurements and Fig. 4.4 shows the entire setup used.

![Figure 4.3: Typical CdS photocurrent result.](image)

Figure 4.2: Actual measuring circuit.
Figure 4.4: The actual setup used for the CdS photocurrent measurements. The sample is mounted on the breadboard in front of the picture. The cardboard next to the light source helped to reduce stray light.

4.2 Measurement of the reflectance

The schematic of the reflectance measurements is shown below in Fig. 4.5.

![Setup for the reflectance measurements.](image)

Instead of connecting the sample to the lock-in amplifier, the silicon photodiode was connected to the lock-in amplifier. In this case, the photodiode was directly connected to
the current input of the lock-in amplifier. The reflectance was measured under the same experimental conditions as the photocurrent and a typical result is revealed below in Fig. 4.6.

Figure 4.6: Typical reflectance spectrum of the CdS sample.

Figure 4.7: Actual setup for the reflectance measurements.
4.3 Measurement of the silicon photodiode photocurrent

The setup for the photocurrent measurements using the Si photodiode is shown in the following sketch (Fig. 4.8).

![Fig. 4.8 Experimental arrangement using the Si photodiode.](image)

Instead of the CdS sample the Si photodiode was excited and connected to the current input of the lock-in amplifier. To prevent overload of lock-in amplifier, the OD=1 neutral density filter was placed in front of the Si photodiode. As for the other experiments, the wavelength range scanned was 400 – 650 nm and the chopper frequency was kept at 17 Hz. The result of the measurement is shown in the graph below (Fig. 4.9).

![Photocurrent of Si Photodiode](image)

Figure 4.9: Photocurrent of the Si photodiode.
Chapter 5

Results and Analysis

5.1 Results

5.1.1 Responsivity

The lock-in measured a voltage drop across a 1.5 MΩ shunt resistor. In order to convert the measurements into current the Ohm’s law was used:

\[ PC_{\text{CdS}} = \frac{ME_{\text{CdS}}}{1.5 \times 10^6} \]  \hspace{1cm} (5.1)

\( PC_{\text{CdS}} \) and \( ME_{\text{CdS}} \) stand for the photocurrent in A and the voltage of the CdS measurement (see Fig. 4.2), respectively. To get the photocurrent of the Si photodiode, measurement of the Si photodiode is divided by a factor 10^6 A/V, which corresponds to the conversion factor of the current input of the lock-in amplifier:

\[ PC_{\text{Si}} = \frac{ME_{\text{Si}}}{10^6} \]  \hspace{1cm} (5.2)

\( PC_{\text{Si}} \) and \( ME_{\text{Si}} \) stand for the photocurrent in A and the recorded signal of the Si photodiode, respectively.

Responsivity (A/W) is a very important parameter in photocurrent spectroscopy. It represents the achieved output photocurrent per radiant power input. The relation between the responsivity of CdS (\( Re_{\text{CdS}} \)) and the responsivity of Si photodiode (\( Re_{\text{Si}} \)) is:

\[ Re_{\text{CdS}} = \frac{PC_{\text{CdS}}}{PC_{\text{Si}}} \times Re_{\text{Si}} \]  \hspace{1cm} (5.3)
The responsivity of Si photodiode is provided by the seller and is shown below:

![Figure 5.1: Responsivity of Si photodiode.](image1)

Using the formula 5.1, 5.2, and 5.3, the responsivity of CdS is calculated and the result is shown in Fig. 5.2.

![Figure 5.2: Responsivity of thin-film CdS on glass.](image2)
5.1.2 Reflectance

According to the definition, the reflectance is the ratio between the sample reflection and the signal measured with the Si photodiode (=incoming light). If $ME_{Re}$ stands for the measured reflection, then the reflectance of the CdS film is:

$$ Re = \frac{ME_{Re}}{ME_{Si}} \quad (5.4) $$

The result of the calculation is shown below:

![Graph](image_url)

Figure 5.3: Reflectance of CdS.
5.2 Analysis

5.2.1 Absorption coefficient $\alpha$

To calculate the reflection coefficient, two parameters are needed: $Re$ (see chapter 1.2) and $\alpha$, while the latter is determined by two formulas [6]:

$$E_{cr} = E_g + \frac{kT}{2\sigma} \quad (5.5)$$

When $E \geq E_{cr}$, $\alpha$ described by the density of states (DOS):

$$\alpha(E) = A\sqrt{E - E_g} \quad (5.6)$$

When $E \leq E_{cr}$, $\alpha$ described by the Urbach rule:

$$\alpha(E) = A\sqrt{\frac{kT}{2\sigma}} \exp\left[\frac{\sigma(E - E_g)}{kT} - \frac{1}{2}\right] \quad (5.7)$$

In these equations above, $E_g$ is the band gap energy, $\sigma$ is a dimensionless phenomenological parameter, which describes the crystallinity of the material, $k$ is the Boltzmann constant, $T$ is the temperature, and $A$ is a constant representing $\alpha(E)$ for $E$ much larger than $E_g$. For the sample investigated, the values of the parameters are listed in table 5.1. Using (5.6) and (5.7), $\alpha$ was calculated and is presented in Fig. 5.4.

Table 5.1 Parameters of the sample used [7]

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>2.44eV</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.7</td>
</tr>
<tr>
<td>$A$</td>
<td>$10^5 , cm^{-1} , (eV)^{-1/2}$</td>
</tr>
<tr>
<td>$kT$</td>
<td>25.8meV</td>
</tr>
</tbody>
</table>
Fig. 5.4 Spectrum of $\alpha$ for the parameter shown in Table 5.1.

The formula to calculate photocurrent spectra - which correctly speaking corresponds to the responsivity of the film - is expressed by [6]:

$$I_{ph}(E) \propto \{1 - \exp[-\alpha(E)d]\} - \frac{\alpha(E)L_d(1 - \exp[-d(\alpha(E) + 1/L_d)])}{(1 + \tau_{tr}/\tau_{ph})(1 + \alpha(E)L_d)}$$  \hspace{1cm} (5.8)

For sample used, $d = L_d = 200nm$. By substituting $\alpha$ into (5.8), $I_{ph}$ is determined as the curve below:

Fig 5.5 Photocurrent from the theory
Normalizing the responsivity and the theoretical photocurrent a fairly close agreement was achieved between theory and measurements as can be seen in Fig. 5.6.

![Figure 5.6: Comparison of theoretical and measured photocurrent.](image)

5.2.2 Reflection coefficient

Now $Re$ and $\alpha$ can be used to determine the reflection coefficient $R$ of the CdS film. The relation between $Re$, $\alpha$ and $R$ is:

$$Re = R[1 + (1 - R)^2 e^{-2\alpha d}] \quad (5.9)$$

$d$ is the thickness of the sample (200nm). Equation (5.9) is a cubic equation, and a C++ program was used to solve it. Substituting the values of the $Re$ and $\alpha$ into Eq. (5.9), the reflection coefficient is determined and the result of the calculations is shown in Fig. 5.7. It shows that the reflection coefficient is between 0.1 and 0.3, which is very reasonable.
Fig. 5.7 Reflection coefficient dispersion of CdS.

5.3 Conclusion

In this thesis it was demonstrated how the reflection coefficient of thin-film CdS (or a different material) can be found by reflection and photocurrent spectroscopy. The key idea is to get the energy dependence of the absorption coefficient out of the responsivity of the sample, while the reflection of the film can be directly measured. The last hurdle is the solution of the cubic Eq. (5.9). The method demonstrated here was apparently not used before in the literature to find the surface reflection coefficient of a thin-film.
References


