# PHOTOCURRENT SPECTROSCOPY OF CdS/PLASTIC, CdS/GLASS, AND ZnTe/GaAs HETERO-PAIRS FORMED WITH PULSED-LASER DEPOSITION

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# Thin-film CdS script on plastic produced by pulsed-laser deposition

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### ABSTRACT

### Bruno, Ullrich, Advisor

This dissertation presents photocurrent (PC) spectroscopy of thin-film cadmium sulfide (CdS) on plastic, CdS on glass, and zinc telluride (ZnTe) on gallium arsenide (GaAs) heteropairs. All samples have been prepared with pulsed-laser deposition (PLD) and the thesis is organized into three principal sections. The first section presents the PLD essentials and characterization of CdS thin films on transparent plastic substrates. The second part focuses on the exploitation of CdS films on glass to quench or modulate alternating photocurrent (APC) by additional constant blue light illumination. Finally, PC spectra modification of *n*-GaAs due to ZnTe PLD will be investigated.

First, the merger of a transparent plastic substrate with thin-film CdS for photonic application was realized using low-temperature PLD, where low-temperature PLD means the substrates were not externally heated. Although plastic is not considered to be a favored substrate material for semiconductor thin-film formation, the deposited CdS film possessed good adhesion to the plastic substrates and showed a blue-shifted photosensitivity with peak at 2.54 eV. The CdS deposition rate was monitored at different laser fluences and the maximum rate was found at 2.68 J/cm<sup>2</sup>. The visualization of the surface using an atomic force microscope (AFM) revealed its mosaic structure and electron probe microanalysis showed that target composition was maintained in the film. The study of thickness distribution revealed that the film deposition area is significantly increased with increase in laser fluence. The achieved results demonstrate the capability of PLD to form novel heterostructures with appealing and useful technological properties such as plasticity and low weight. In the second part, APC control via blue light illumination employing thin-film PLD CdS on a glass is introduced. In fact, the APC driven through the CdS film in conjunction with bias was quenched when the sample was additionally illuminated with a blue light emitting diode (LED). It occurred that the quenching magnitude depends on the blue light intensity, chopped light intensity and its energy, and applied electric field. The quenching phenomenon is attributed to the shortening of available APC carriers because of the generation of direct current channels in the film and is described using a straightforward band diagram model.

Finally, the PC spectra modification of a *n*-GaAs substrate due to the PLD of thin-film ZnTe is presented. The intrinsic and extrinsic room temperature PC spectra of the *n*-GaAs and ZnTe/*n*-GaAs samples were investigated with lock-in technique by employing various optical chopping frequencies and biases. The PC magnitude of the bulk *n*-GaAs was increased with increasing chopper frequency, while PC of the ZnTe/*n*-GaAs sample showed an increase and decrease with frequency in the lower and higher energy range, respectively. Noteworthy, a frequency independent isosbestic point was observed at the crossover between these two behaviors at 1.88 eV. Additionally, a defect related PC peak at 1.37 eV was observed only for ZnTe/*n*-GaAs sample. The magnitude of the peak-and even its appearance-was found to be sensitively dependent on the sign of bias. This phenomenon caused by PLD created defect states on *n*-GaAs surface referred to "photonic-doping".

This dissertation is dedicated to my family members, especially, to my wife Shobha, daughter Eliza, and son Kushal for their company, love, and support that always inspired me to succeed.

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### ABBREVIATION AND ACRONYMS

- AES: Auger electron spectroscopy
- AFM: Atomic force microscopy
- APC: Alternating photocurrent
- As: Arsenic
- CB: Conduction band
- CdS: Cadmium sulfide
- CW: Continuous wave
- eV: Electron volt
- DPC: Direct photocurrent
- ETRI: Electronics and telecommunications research institute
- Ga: Gallium
- GaAs: Gallium arsenide
- GaSb: Gallium antimonide
- GPIB: General purpose interface bus
- He-Ne: Helium neon
- HOMO: Highest occupied molecular orbital
- HRTEM: High resolution transmission electron micrograph
- HWE: Hot wall epitaxy
- *I-V*: Current versus voltage
- IR: Infrared
- LED: Light emitting diode
- LUMO: Lowest unoccupied molecular orbital

MBE: Molecular beam epitaxy

meV: Millielectron volt, 10<sup>-3</sup> electron volt

min.: Minute

MOCVD: Metal-organic chemical vapor deposition

ms: Millisecond, 10<sup>-3</sup> second

mW: Milliwatt, 10<sup>-3</sup> W

Nd:YAG: Neodymium doped yttrium aluminum garnet

nm: Nanometer, 10<sup>-9</sup> meter

ns: Nanosecond, 10<sup>-9</sup> second

PC: Photocurrent

PL: Photoluminescence

PLD: Pulsed-laser deposition

PR: Photoreflectance

PET: Polyethylene terephthalate

RHEED: Reflection high energy electron diffraction.

S: Sulfur

SEM: Scanning electron microscopy

Si: Silicon

SIMS: Secondary ion mass spectroscopy

SQUID: Superconducting quantum interference device

Subs.: Substrate

TGVPD: Temperature gradient vapor phase deposition

TGVTD: Temperature gradient vapor transport deposition

Te: Tellurium

TEM: Transmission electron microscopy.

Temp.: Temperature

VB: Valance band

XRD: X-ray diffraction

YBCO: Yttrium barium copper oxide

ZnTe: Zinc telluride

# **1 BACKGROUND AND MOTIVATION**

# 1.1 Outline

The investigations presented in this dissertation are divided into three sections. In the first section, PLD of CdS thin films on plastic substrates followed by their characterization is presented. The second part mainly comprises the application of CdS thin films on glass to control APC by employing blue light. Finally, the detailed PC spectra modification of GaAs due to the deposition of ZnTe on it using PLD is discussed. These subjects will be elaborated in the subsequent chapters organized in the following way:

- Chapter 1 contains the general background and objectives of this dissertation.
- Chapter 2 provides an introduction to semiconductors, photoconductivity, and photocurrent spectroscopy followed by an introduction and applications of PLD.
- Chapters 3 and 4 include PLD and characterizations of CdS films on plastic substrates.
- Chapter 5 presents the APC control in the thin-film CdS on glass by continuous illumination of blue light.
- Chapter 6 describes the modification of GaAs PC spectra by the deposition of thin-film ZnTe using PLD.
- Chapter 7 provides the summary followed by the appendix, which contains a publications list, materials and equipment, properties of materials used, and a bibliography.

### **1.2 General background**

The general background of the above mentioned three sections are presented in the following paragraphs.

First, the mastery of technologically useful combinations of semiconductors with different materials is one of the challenges of modern semiconductor device engineering. In particular, the fields of optoelectronics, photovoltaics, and photonics require the merger of various materials in order to provide top performance and versatility at the same time.<sup>1, 2</sup> A promising set of materials is CdS, ZnTe, GaAs, plastic, and glass. CdS, ZnTe, and GaAs all are direct band gap semiconductors with particular attractive features. The band gaps of CdS and ZnTe lie in the green spectral region, which coincides with the top sensitivity of the human eye and GaAs is currently one of the main players in the field of optoelectronics.<sup>3, 4, 5</sup> The combination of these semiconductors with plastic, glass, and other semiconductors is an important first step to realize many photonic as well as optoelectronic devices. Specifically, the combination of semiconductors with a plastic is of great significance because plastic is transparent, lightweight, sturdy, and flexible. Only a few attempts have made so far to make thin films of different materials on plastic using PLD, which are summarized in table 3.2. Consequently, PLD of CdS films on plastic followed by their characterization is presented in detail.

Second, nowadays in almost all technological fields, it is necessary to control and manipulate electronic and optical signals employing thin-film semiconductors in order to make faster devices. A simple and well-known way to control or switch PC signals of a semiconductor is to illuminate the sample with a primary light and an additional secondary infrared (IR) light, *i.e.*, optical quenching of PC due to IR illumination.<sup>6</sup> The other way is to modulate the

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transmission and reflection of light using light, which is known as all-optical switch. In this context, our research group previously studied transmission and reflection of green laser light of thin-film CdS and GaAs by additional impingement of red laser irradiation at the same spot in order to realize examples of all-optical modulation.<sup>7, 8</sup> In this dissertation, the control of the APC signal of thin-film CdS on glass using blue photons is introduced and discussed for the first time. The terms APC control, quenching, and modulation are used interchangeably in this dissertation.

Finally, the merger of ZnTe and GaAs is definitely of technological interest because the operational range of this hetero-pairing covers the visible to near-infrared spectral regions. The *p-n* junction in heterostructures is one of the core elements of modern electronic device architectures like light emitting diodes (LED), transistors, lasers, and solar cells. However, the lattice mismatch between ZnTe and GaAs is more than 7%, which is not a promising condition for high-quality hetero-pairing of ZnTe and GaAs. In spite of these unfavorable conditions, ZnTe/GaAs mergers have been made with various thin films preparation techniques as described in section 6.1.3. These studies were focused on structural, optical, electronic, and strain related properties of the deposited ZnTe films, while in this dissertation, PC properties of ZnTe/n-GaAs are presented in detail.

### **1.3** Objectives of the research

High-tech thin-film preparation techniques, such as molecular beam epitaxy (MBE), are very costly and have flux control problems for each component for multi-component materials deposition.<sup>9</sup> To address these problems, PLD has emerged as a promising technique for film preparation for varieties of complex materials.<sup>10</sup>

Due to the fact that PLD is an effective thin-film preparation technique, this research was inspired by the substitution of a plastic for conventional fragile substrates, such as glass, silicon,

and quartz. In fact, this research is focused on the low-temperature PLD of CdS thin films on plastic followed by their surface, structural, and optoelectronic characterizations. Subsequently, a novel technique of optical control of APC employing thin-film CdS has been introduced, and finally photocurrent spectra modification of *n*-GaAs due to the formation of ZnTe/*n*-GaAs heterostructures by PLD was investigated and is presented in detail.

The research was driven by the following questions.

- 1. Is it possible to prepare technologically useful thin-film CdS on flexible plastic substrates?
  - a. What are the surface and crystallographic properties of the film?
  - b. What are the composition and thickness distribution of the films?
  - c. What are the optoelectronic properties of the film?
- 2. Can thin-film PLD CdS be used to quench APC signals using additional blue light excitation?
  - a. How does the quenching vary with applied biases and quenching blue light intensity?
  - b. What is the possible APC quenching mechanism?
- 3. Can we heteropair ZnTe with GaAs employing low-temperature PLD?
  - a. How does the photocurrent property of GaAs change after the deposition of thinfilm ZnTe?
  - b. What could be the possible explanation for the PC spectra modification of GaAs due to PLD thin-film ZnTe?
  - c. Is it possible to dope GaAs with Zn and Te using PLD; *i.e.*, establish "photonic doping"?

In summary, this dissertation comprises three different topics: CdS/plastic formation by PLD, CdS photocurrent quenching by blue light, and the GaAs photocurrent spectra modification by PLD ZnTe.

# **2** INTRODUCTION AND FUNDAMENTALS

### 2.1 Semiconductors

Semiconductors are materials whose electrical conductivity value lies between conductors and insulators. The conductivity of a semiconductor can be changed significantly by light illumination, changing the impurity concentration, or changing the temperature. Semiconductors are one of the major components of all modern electronics, optoelectronics, and photovoltaics appliances. Semiconductors are either elements (such as Si and Ge) or are compounds of different elements (such as CdS and GaAs). Regarding the electronic transition mode, semiconductors are direct or indirect, *i.e.*, absorption and emission processes take place without participation of phonons or with their involvement, respectively.

### 2.1.1 Energy bands in semiconductors

To understand photoconductivity, electrical conductivity, and related phenomena, it is required to understand energy bands and the doping of semiconductors. The law of quantum mechanics says that electrons in isolated atoms can have only certain discrete energy values. When isolated atoms are brought together to form a crystal, the electrons are not restricted to a single energy level, but rather to ranges of allowed quasi-continuous energies called bands. The bands correspond to the solution of the Schrödinger wave equation for periodic potentials created by the atoms defining the lattice of the solid. Each band consists of a huge number of discrete energy levels, which can be understood as quasi-continuum.<sup>11</sup> The simplified energy band diagrams of insulators, semiconductors, and metals are shown in figure 2.1.





Figure 2.1: Energy band diagrams of (a) insulator, (b) semiconductor, and (c) metal

The highest filled energy level is called a valence band, which is similar to the highest occupied molecular orbital (HOMO) because it contains the valence electrons of the atoms. The unoccupied energy level just above this is called a conduction band, which is similar to the lowest unoccupied molecular orbital (LUMO). The gap between conduction band and valence band or LUMO and HOMO is called the forbidden gap or band gap energy. The transport of electrons is possible in the conduction band, while the holes, which are the counterparts of electrons, move along the valence band.

The band gap energy of semiconductors is situated between 0.1 to 3 eV. At absolute zero, all electrons are confined in the valence band and the material is supposed to be a perfect insulator. Above absolute zero, some electrons have sufficient thermal energy to make a transition to the conduction band where, they are free to move and conduct current through the crystal under bias. The amount of energy required for an electron to transfer from the valence

band to the conduction band depends on temperature, the kind of material, its purity, and doping profile.

### 2.1.2 Doping in semiconductors

The magnitude of conductivity as well as *p*-and *n*-type conductivity in many semiconductors can be changed substantially by the incorporation of other elements. Foreign elements in a semiconductor are called impurities and the deliberate addition of a foreign element is called doping. If the dopant has an excess of electrons it is called a donor and if the dopant has a deficiency of valence electrons it is called an acceptor. For example, if an element from group<sup>\*</sup> V replaces silicon (Si) atoms in the bulk Si, it forms an *n*-type material and if an element from group III replaces Si it forms a *p*-type materials. Similarly, for GaAs, if group VI element replaces As it forms *n*-type and if group II element replaces Ga it forms *p*-type semiconductor, respectively. For example, Zn is an acceptor<sup>†</sup>, whereas Te is a donor. The donor atoms ionize to positive atoms giving electrons to the conduction band, while acceptor atoms may capture electrons becoming negative ions. If the ionization energy is low the defect is called shallow, but it is called deep otherwise.

If an atom either foreign or native is accommodated in a crystal outside a host lattice, it is called interstitial but a foreign atom in a lattice is called substitutional. Such native-atoms and impurities create new energy states in the forbidden gap. There are two main common kinds of native defects in semiconductors, namely vacancies and anti-sites. The vacancy is created by empty lattice sites, whereas the anti-site is created by the substitution of native host atoms by

<sup>\*</sup> Here group means group in the periodic table of the elements.

<sup>&</sup>lt;sup>†</sup> If a substitution of an element by another element causes deficiency in electrons, the substituted element is called acceptor but donor otherwise.

partner atoms. For example, an anti-site defect in GaAs is created by the substitution of Ga sites by As atoms or vice versa.<sup>12</sup> Doping is usually done by mixing calculated amount of dopant material in the semiconductor during the crystal growth.

In general, II-VI semiconductors exhibit intrinsically a particular conductivity type preference because of unbalanced stoichiometry. For example, CdS and ZnS are *n*-type because of S (donor) vacancy where as ZnTe is *p*-type because of Zn (acceptor) vacancy. Only ZnSe and CdTe can be prepared in both *n*-type and *p*-type material.<sup>13</sup>

# 2.2 Photoconductivity

Photoconductivity is a phenomenon in which a material increases conductivity due to free charge carriers generated by the absorption of light. Photoconductivity is quite common for semiconductors and this phenomenon was first observed by W. Smith in Selenium in 1873,<sup>14</sup> and Godden and Pohl discovered the photosensitivity of CdS in 1920. Photoconductivity, PC, and responsivity are directly related to each other; therefore, these terms are used interchangeably in this dissertation.

There are two types of PC, namely primary and secondary. The primary PC is linearly proportional to the light intensity and applied low electric field. In this case, the maximum quantum efficiency (QE)<sup>‡</sup> of 1 is possible. The QE is less than 1 if charge carriers freed by light are trapped at some site in the material before they reach the electrode. Secondary PC is more complex in its origin and PC spectral response depends on the polarity of the biases and the PC varies nonlinearly at high electric field and high light intensity.

<sup>&</sup>lt;sup>‡</sup> The ratio of number of charges passing between the electrodes to the number of photons absorbed in a given time interval is called quantum efficiency or gain.



Figure 2.2: Schematic comparison of the spectral shapes of the photoconductivity and absorption.

The optical absorption coefficient ( $\alpha$ ) of a material describes its capability to absorb impinging photons with a particular energy. There is a correlation between  $\alpha$  and photoconductivity as shown in figure 2.2.<sup>15</sup> For a qualitative explanation, this figure is divided into three regions. Region I, covering high excitation energies, is the highly absorptive region. In this energy range, photo carriers are produced on the surface; consequently, the photoconductivity is dominated by surface recombination. Since the number of the recombination centers near the surface is typically larger than in the bulk, the photoconductivity decreases with photon energy after reaching a maximum. Region II shows a peak of the photoconductivity, which is controlled by the bulk lifetime. In the low absorption region III the photoconductivity is proportional to the absorption coefficient. A peak in this region is due to impurity absorption. The presence of impurities extends the region of photosensitivity to the longer wavelength within the band gap of the material.

### 2.2.1 Photocurrent spectroscopy

Photocurrent spectroscopy is one of the important tools for the optical characterization of materials. A photocurrent spectrum is obtained by plotting the measured photocurrent against the energy of the light used for the excitation. When the excitation light used is a continuous wave (CW), the photocurrent is called direct photocurrent (DPC), and can be measured by an ammeter. On the other hand, if the excitation light is chopped, the photocurrent is called APC. The latter is measured by a lock-in amplifier, which reduces considerable noise as well as dark current, and provides an idea about the response time of sample with respect to chopping frequency. DPC measurements, on the other hand, inform us about the intrinsic transport features of the sample, but the spectra require a correction of the dark current. The detail of the measurement schemes will be presented in the subsequent chapters.

### 2.2.2 Photocurrent spectrum equation

The photocurrent equation is given by <sup>16</sup>

$$I_{ph} \propto \frac{I_0}{\hbar \omega} \left[ \{1 - \exp(-\alpha d)\} - \frac{\alpha L \{1 - \exp\{-d(\alpha + 1/L)\}\}}{(1 + \tau_{sr}/\tau_b) \{1 + \alpha L\}} \right]$$
(2.1)

Where,  $I_{ph}$  is the photocurrent at a particular energy,  $\alpha$  is the absorption coefficient at that energy,  $I_o$  is the impinging light intensity on the surface,  $I_o/\hbar\omega$  is the photon flux, L is the light penetration depth, d is the film thickness, and  $\tau_{sr}/\tau_b$  is the ratio of surface to the bulk recombination time. Equation 2.1 describes the proportionality between  $I_{ph}$  and the absorbance (first part of the right hand side) minus loss due to surface recombination (second part of the right hand side).

In equation (2.1), the  $\alpha$  dispersion can be calculated from density of states and Urbach rule,<sup>17</sup> and the following parameters were used to calculate the PC spectrum of CdS film: band gap energy of CdS = 2.44 eV, d = 5  $\mu$ m, and L=1 $\mu$ m, depending on  $\tau_{sr}/\tau_b$  ratios ( $\infty$ , 1, 0) three different shapes of photocurrent spectrum were obtained as shown in figure 2.3.<sup>18</sup>



Figure 2.3: Photocurrent spectra of CdS for different  $\tau_{sr}/\tau_{ph}$  ratios. Curve 1 refers to the state of no surface recombination ( $\tau_{sr} \gg \tau_b$  i.e,  $\tau_{sr}/\tau_b \rightarrow \infty$ ), curve 2 represents the case when the surface lifetime becomes equal to the bulk lifetime ( $\tau_{sr} = \tau_b$ ), and curve 3 represents infinitely small surface lifetime i.e. higher bulk lifetime ( $\tau_{sr} << \tau_b, \tau_{sr}/\tau_b \rightarrow 0$ ).

### 2.3 Pulsed-laser deposition of thin films

PLD is a physically driven deposition technique in which material is removed from the target with high-energy laser pulses followed by the deposition on a substrate. Each laser pulse creates highly energetic forwardly-directed particles forming the plume. The schematic diagram of PLD is shown in figure 2.4, which contains a laser source, focusing optics, a vacuum system, a target, and a substrate; the detailed process will be described in chapter 3.

Since their invention, lasers have been used in varieties of scientific research, one of which is the evaporation of materials. After it has been proven that PLD maintains close stoichiometry of the multicomponent high temperature superconductor (HTS) target, such as yttrium barium copper oxide (YBCO),<sup>19</sup> PLD has emerged as a cutting-edge tool for multi-component thin film deposition.



Figure 2.4: Schematic diagram of pulsed-laser deposition.

### 2.3.1 Mechanism of pulsed-laser deposition

The PLD process depends on laser wavelength, pulse width, repetition rate, fluence, background gas pressure, substrate temperature, target-to-substrate distance, as well as target and substrate materials types. For example, high-energy photons are absorbed at the surface of the target while low energy photons penetrate deep into the target resulting in a different ablation mechanism. Similarly, an elevated substrate temperature improves the crystallinity of the film by increasing the sticking coefficient and annealing effects.

To ablate a target atom, the energy delivered to the atom must exceed its binding energy. A typical ablation threshold fluence is  $0.1-1 \text{ J/cm}^2$ . Hence, a 100 fs laser pulse requires intensity above  $10^{13} \text{ W/cm}^2$ , while a 10 ns pulse can ablate around  $10^8 \text{ W/cm}^2$ . There are two prominent mechanisms of ablation, *i.e.*, thermal and non-thermal ablation depending on the laser pulse width.<sup>20</sup>

• **Thermal ablation:** When laser radiation strikes on the target it induces oscillation of the electrons, which is converted into electronic excitation. These excited electrons transfer energy to the lattice by electron-phonon collisions over thermal diffusion time. When the pulse duration is longer than thermal diffusion time, which is longer than about a picosecond, the electrons and the lattice are in thermal equilibrium, resulting in thermally driven ablation.

• Non-thermal ablation: On the other hand, when the laser pulse duration is shorter than the relaxation time, which is shorter than one ps, the target material ionizes early in the laser pulse creating a high density plasma. The electrons in the plasma absorb laser energy by inverse Bremsstrahlung absorption<sup>§</sup>. The lattice remains cold because there is not enough time to transfer energy from electrons to ions. The electrons interact with ions by electrostatic interaction

<sup>&</sup>lt;sup>§</sup> The absorption of radiation by free electrons during collisions.

due to the charge separation. If the energy absorbed by the electrons is high enough, the electrons escape from the target and pull ions from the solid, which is called electrostatic ablation.<sup>21</sup> Therefore, ultra-fast pulsed-laser deposition results in wavelength independent non-thermal ablation.

### 2.3.2 Applications of pulsed-laser deposition: an overview

PLD is a straightforward, versatile, and clean tool to make thin films of varieties of materials. Using PLD, one can engineer materials by varying ablation parameters. Materials can be stoichiometrically transferred from the target to the substrate in a vacuum or deposition can be carried out in a reactive gas producing different materials. For example, a tungsten nitride film can be deposited in nitrogen<sup>22</sup> and sulfur can be doped in zinc selenide in a hydrogen sulfide ambient.<sup>23</sup> PLD has been used for ablation of inorganic and organic materials including metals, semiconductors, insulators, polymers, and biological materials. Although it is not possible to present all PLD research, the following section gives an essence of how PLD has been used for many applications.

• **High-temperature superconductor film growth:** PLD is known to be an effective method for stoichiometric thin-film preparation of HTS oxides like YBCO. PLD-grown YBCO was used to make a superconducting quantum interference device (SQUID) microscope to detect and map small magnetic field changes.<sup>24</sup>

• Semiconductor film growth: PLD is a very effective tool to prepare thin films of wide band gap materials. Several semiconductors have been grown by PLD for photovoltaics, photonics and optoelectronic applications. For example, PLD is used for growing semiconductor layers of CdTe and CdS on ITO/glass for photovoltaic application.<sup>25</sup> Furthermore, light emitting diodes consisting of transparent *p*-Sr<sub>2</sub>CuO<sub>2</sub>/*n*-ZnO heterojunctions have been formed with PLD.<sup>26</sup> The

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compositional spread of  $Mg_xZn_{1-x}O$  has been prepared by combinatorial PLD of ZnO and MgO for fabrication of tunable ultraviolet photodetectors.<sup>27</sup>

• Super lattice formation: A superlattice is a material with periodically alternating layers of several substances. PLD has been applied to grow atomic-scale perovskite (KNO<sub>3</sub>/KTaO<sub>3</sub>) superlattices with atomically flat interfaces.<sup>28</sup>

• **Tribological coatings:** Tribology deals with the mechanism of friction, lubrication, and wear of interacting surfaces, which are in relative motion. For example, PLD has been used to prepare lubricant coatings such as molybdenum disulfide, the conductive lubricant niobium diselenide, and the high temperature solid lubricant lead manganate.<sup>29</sup> Carbides and nitrides of boron and titanium as well as diamond-like carbon for hard coating to protect surfaces from abrasion and erosion have been prepared by PLD.<sup>30, 31</sup>

• Chemical sensors: Pulsed-laser deposited oxide semiconductors have been used for varieties of gas and chemical detectors. These devices are based on the conductance change due to variation of the gas concentration. A sensor for oxides of nitrogen was fabricated using pulsed-laser deposition of tungsten oxide.<sup>32</sup> PLD has also been employed to fabricate thin-film chalcogenide glasses<sup>\*\*</sup> for heavy metals,<sup>33</sup> and aluminum oxide films for hydrogen ion<sup>34</sup> light addressable potentiometric sensors.

• **Medical applications:** Biocompatible coatings and controlled drug delivery system coating have been prepared by PLD. Calcium orthophosphate and hydroxyl apatite<sup>35</sup> formed with PLD can find applications in biocompatible coating materials because their properties are similar to the human bone. When thin-films of these materials are coated on a metallic orthopedic

<sup>\*\*</sup> A glass containing a chalcogenide element (sulfur, selenium or tellurium) as a substantial constituent.

prosthesis,<sup>††</sup> the inflammation reaction resulting from a foreign body is minimized. In a controlled drug delivery, the drug particles are coated with a polymer layer using PLD, consequently, the coated drug particles showed an increase in the drug release time.<sup>36</sup>

•Soft materials deposition: Thin films of polymer and bio-materials are important for fabrication of thin-film transistors, organic light emitting devices, electronic device coating, biomedicine, chemical, and biological sensors. PLD of soft materials have been carried out by ordinary PLD, matrix assisted pulsed-laser evaporation (MAPLE), photosensitized PLD, and resonant infrared pulsed-laser deposition (RIR-PLD). PLD of polytetrafluoroethylene (teflon) revealed that laser-induced pyrolitic decomposition with subsequent repolymerization occurs in the process.<sup>37</sup> In MAPLE, organic material is dissolved in a solvent (matrix) followed by ablation in frozen state to avoid photo-modification of the target.<sup>38</sup> The concentration of the solute is low enough; therefore, most of the laser energy is absorbed by the matrix during ablation. The photochemical decomposition of the polymers caused by high-energy UV light can be avoided by mixing the target with photosensitizer. In the photosensitized ablation, for example, polystyrene (transparent at 351 nm) is mixed with strongly absorbing photo sensitizer anthracene.<sup>39</sup> In RIR-PLD,<sup>40</sup> the ablating laser energy equivalent to a certain vibrational mode of the polymer breaks the corresponding bond, such as in polystyrene.

### 2.3.3 Restrictions of PLD

Despite all the advantages and versatile applications, PLD has several restrictions as well. The primary shortcomings of PLD are formation of particulates, inhomogeneous thickness distribution, and incongruent ablation. In a nanosecond pulse, a large volume of material is evaporated by each pulse resulting in supersaturated vapor; condensation starts during early stage

<sup>&</sup>lt;sup>††</sup> Artificial substitute for a missing part of the body.

of ablation with the formation of droplets. This problem can be eliminated if ultra-fast laser pulses are used. The resulting atomized material flux during the deposition process results in good quality film without droplets. The formation of particulates can also be avoided by velocity filter that blocks low velocity particulates but allows high velocity atomic and molecular species.<sup>41</sup> The other limitation is the transfer of non-stoichiometric materials due to thermal heating of the target at low fluences and long pulse duration. In fact it is known that the plume consists of high-intensity stoichiometric parts and low intensity non-stoichiometric evaporative parts, which dominates at large deposition angle with respect to plasma axis.<sup>42</sup> Inhomogeneous thickness is a result of the plume angular distribution, which is a strongly confined in the forward direction.

# **3** PULSED-LASER DEPOSITION OF CdS FILMS ON PLASTIC

### 3.1 General introduction

The physical and chemical properties of semiconducting thin films are primarily determined during the early stages of growth by the particular deposition technique chosen. Equally important is the choice of the substrate, which critically co-designs the film quality and properties. In the field of II-VI compound semiconductor deposition, pyrex<sup>®</sup>, soda-lime glass, guartz, and silicon<sup>43, 44</sup> are popular substrate materials because of their availability, costeffectiveness, and inert character, *i.e.*, they are stable in the required temperature range for common photonic applications. Hence, they do not chemically react with the deposited semiconductor and the hard plane surface makes the formation of optically smooth thin films fairly easy. Despite the promising results and ongoing progress in technology, the inherent weight, rigidity, and fragility of glass substrates excludes glass based devices from important areas such as aviation and space programs. Therefore, the possibility of replacing glass substrates with low-weight transparent, non-brittle, and flexible carriers is explored in this dissertation. In fact, by employing PLD, this dissertation demonstrates the formation of polycrystalline/amorphous, light-responsive thin-film CdS on a polymer-based overhead transparency, so-called-plastic commercially available at office supply stores.

This chapter describes the material properties of CdS and plastic used to prepare heteropairing, followed by the literature surveys on PLD of CdS on different substrates and PLD of different materials on flexible substrates. Additionally, the CdS deposition rate and the plume formed by different impinging laser fluences will be discussed in detail.

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## **3.2** Cadmium sulfide fundamentals

CdS is a II-VI compound semiconductor consisting of cadmium from group II and sulfur from group VI of the periodic table of elements. The properties of CdS are summarized in table 1 of the appendix. CdS is insoluble in water, but soluble in dilute mineral acids. Due to the cadmium surplus it exhibits intrinsic *n*-type of conductivity caused by sulfur vacancies and the depth of the acceptor level.<sup>45</sup> CdS has a band gap energy of 2.42 eV at room temperature and it is widely used in optoelectronics, photonics, and photovoltaics. In optoelectronics, it is utilized for making photocells, light emitting diode (LED), and lasers.<sup>46</sup> In photonics, CdS is employed to make nanocrystals,<sup>47</sup> optical filters, and all optical switches<sup>7</sup>. In photovoltaics, it has been exploited to fabricate cadmium telluride (CdTe), as well as copper indium diselenide solar cells to act as a window layer that separates charge carriers produced due to photon absorption.<sup>48</sup> Photoconductive CdS cells can work with both alternating current and direct current supplies, can withstand high voltage, and have large output current per unit area; therefore, they have been applied in analogue and digital, as well as large area devices.<sup>49</sup> CdS is also used as a pigment in paints and in engineered plastic for good thermal stability.

CdS occurs in nature either in hexagonal greenockite (wurtize) or cubic hawleyte (zincblende) crystal structures. The hexagonal and cubic forms can be prepared by passing hydrogen sulfide in cadmium halide and cadmium perchlorate, respectively. In the wurtize form the stacking sequence of the atoms is ABABAB... and so on, which is called hexagonal close packing. While, in the zincblende structure, the stacking sequence of the atoms is ABCABCA..., and so on, this is called cubic close packing. In both cases each atom is tetrahedrally coordinated with four other atoms in such a way that each atom has four nearest neighbors of the opposite kind.<sup>50</sup> Due to differences in the electronegativity of the elements, each compound with these

structures possesses ionic character in its bonding. The unit cell of the zincblende structure is shown in figure 3.1.



Figure 3.1: Zincblende crystal structure for CdS, ZnTe, and GaAs

# 3.3 Plastic (polyethylene terephthalate) fundamental

The plastic substrate used in this dissertation was polyethylene terephthalate (PET), the standard transparency used in the overhead projection. PET is a very important thermoplastic of the polyester family used for beverage bottles, plastic containers, and synthetic fibers. The structure of a PET monomer is shown in figure 3.2. Its monomer can be synthesized by the esterification reaction between terephthalic acid with ethylene glycol, and the polymerization is done immediately after esterification through a polycondensation reaction of the monomers.<sup>51</sup> PET exists both as an amorphous and as a polycrystalline thermoplastic material.



Figure 3.2: Structure of polyethylene terephthalate monomer

# 3.4 Literature review

In this section, progress on the PLD of CdS on different substrates and thin film preparations on various polymers using PLD will be discussed.

#### 3.4.1 Pulsed-laser deposition of CdS

The first review of compound semiconductor films growth by PLD is presented by Douglas H. Lowndes.<sup>52</sup> PLD of specifically CdS attracted notable research activities during the last decade. The films were formed with a CW laser<sup>53</sup> or pulsed-laser in the nano- and femtosecond regimes.<sup>54, 55</sup> Surface morphology, crystal structure, and optoelectronic properties of thin-film CdS prepared by PLD onto glass, quartz, Si, and sapphire have been extensively studied as presented in table 3.1. Emphasizing additional technological applications in optics and optoelectronics, thin-film PLD CdS deposited on glass was used for the realization of green lasers<sup>56, 57</sup> and the formation of oriented dichroic films.<sup>58, 59</sup> In addition, a hybrid photovoltaic device based on the merger of PLD CdS on glass with a di-isoquinoline perylene derivative was fabricated.<sup>60</sup> A summary of the literature survey of PLD of CdS is presented in the table 3.1.

### 3.4.2 Pulsed-laser deposition of different materials on the polymer substrate

A literature survey on PLD of various materials on the flexible polymer substrates is given in table 3.2. The low publication numbers indicate that only a little work has been done on PLD of thin films on flexible plastic substrates. These works were mainly focused on the deposition of ITO and ZnO on plastic and there is almost no work done to deposit semiconductors on a plastic substrate. This might be because a polymer cannot withstand high temperatures, which are required to improve crystallinity, and also because there will be a deformation of the plastic due the heat of the plume. It was demonstrated that a nanocrystalline barium titanate film on a flexible plastic substrate can be prepared using pulsed-laser annealing.<sup>61</sup> In this dissertation, it is demonstrated that PLD is capable of the formation of thin-film CdS on plastic. This hetero-pairing may find applications in photonics and flexible electronics.

Subs.*	Laser type,	Repetition	Laser	Subs.,	Experiments	Results, remarks	Reference
Substarget	wavelength	rate, pulse	fluence	temp. <sup>†</sup> , amb.			
distance		duration		pressure			
Quartz	Nd:YAG	10 Hz	$10 \text{ J/cm}^2$	400 °C	XRD, Raman,	Blue band gap shift of	Perna et
3 cm	532 nm	10 ns		7.5x10 <sup>-7</sup> Torr	Reflectivity,	indium doped CdS films,	al. <sup>62</sup>
					absorption, PL	(002) oriented film	
Glass	Xe-ion	1Hz	1 J/cm <sup>2</sup>	25-250 °C	XRD, Raman,	Transparency above	Dai et
4 cm	495 nm			3×10 <sup>-7</sup> Torr	transmission	85%, (002) oriented film	al. <sup>63</sup>
Quartz	Ti:Sapphire	1 kHz	1.2	100-600 °C	XRD, AFM,	Crystal quality improved	Tong et
4 cm	800 nm	50 fs	mJ/pulse	10 <sup>-6</sup> Torr	transmission,PL	at 450°C	al. <sup>64</sup>
Glass	Nd:YAG	10 Hz	4 J/cm <sup>2</sup>	Room temp.	RBS, XRD,	Cd/S varied from 1 at	Mahdavi
10 cm	1064 nm	10-12 ns			transmission,	room temp. to 2.4 when	et al. <sup>65</sup>
						target annealed at 500°C	
						due to S oxidation	

# Table 3.1: Publication list of pulsed-laser deposition of CdS

\* Substrate † Temperature

CdS	Nd:YAG	10 Hz	2 and 4	250 °C	XRD, PL,	Direction of c-axis of the	Ullrich et
3 cm	355, 1064	5 ns, 150-	J/cm <sup>2</sup>	7.5x10 <sup>-6</sup> Torr	Transmission	CdS is changed by	al. <sup>66</sup>
	nm	180 ns				varying PLD fluence.	
Glass	Nd:YAG	10 Hz	$2-5 \text{ J/cm}^2$	100-400 °C	XRD, Stress,	c-axis of CdS depends	Sakai et
3 cm	355 nm	5 ns		5×10 <sup>-6</sup> Torr	AFM	on substrate temperature	al. <sup>67</sup>
						and laser energy density.	
Quartz	Ti:Sapphire	1 KHz	$1.2 \text{ J/cm}^2$	100-600 °C	XRD, SEM,	Structural and optical	Tong et
4 cm	800 nm	90 fs		7.5×10 <sup>-6</sup>	AFM, XPS,	properties depend on	al. <sup>68</sup>
				Torr	Raman	growth temperature.	
Si and quartz,	Ti:Sapphire	1 KHz	0.5-1.5	450 °C	XRD, AFM,	Structural and optical	Tong et
3-6 cm	800 nm	90 fs	mJ/pulse	7.5x10 <sup>-6</sup> Torr	PL,	properties are the best at	al. <sup>69</sup>
					Transmission	1.2 mJ/pulse	
<i>n</i> -Si	Ti:Sapphire	1 KHz	1.2	100-600 °C	XRD, XPS,	S evaporates at high	Tong et
3-6 cm	800 nm	90 fs	mJ/pulse	7.5x10 <sup>-6</sup> Torr	Reflectivity, PL	substrate temp. Good	al. <sup>70</sup>
						quality film at 350°	

Bing Dynea et
al. <sup>25</sup>
Perna et
ic al. <sup>71</sup>
.]

Target,	Laser type,	Repetition	Laser	Substrate	Experiments	Results, remarks	Reference
Substrate,	wavelength	rate, Pulse	fluence	temp., ambient			
Distance <sup>‡</sup>		duration		pressure			
ITO	Nd:YAG	10 Hz	2.5	25 °C, 22-34	Resistivity,	Film is good quality	Yong et
Polycarbonate	532 nm	4.7 ns	J/cm <sup>2</sup>	mTorr (oxygen)	AFM, UV-	at 355 nm than 532	al. <sup>72</sup>
3-8 cm	355 nm				Vis, IR	nm	
ITO	KrF excimer	10 Hz	2 J/cm <sup>2</sup>	25-130 °C	Resistivity,	Good quality film at	Kim et
Polyethersulfone	248 nm			10-100 mTorr	Transmission,	room temp., OLED is	al. <sup>73</sup>
6.5 cm					I-V, AFM	made using the film	
InGaZnO <sub>4</sub>	KrF excimer			Room temp,	XRD,	Transparent thin film	Nomura et
PET, glass				in oxygen	Transmission,	transistor was	al. <sup>74</sup>
					Hall mobility,	fabricated	
Si	XeCl	10 Hz	3-5		SEM,	Plume has luminous	Cultrera et
Plastic	308 nm	30 ns	J/cm <sup>2</sup>	7.5x10 <sup>-8</sup> Torr	Thickness	monomers and non-	al. <sup>75</sup>

# Table 3.2: Publication list of PLD of different materials on polymer substrates

<sup>&</sup>lt;sup>‡</sup> Substrate to target distance

4 cm					distribution	luminous droplets	
ITO	KrF excimer	10 H	1.2	25, 100 °C	Resistivity,	ITO film is used for	Kim et
РЕТ	248 nm	30 ns	J/cm <sup>2</sup>	1-70 mTorr	AFM,	fabrication of OLED	al. <sup>76</sup>
5.8 cm					I-V		
ITO, Al <sub>2</sub> O <sub>3</sub>	KrF	20 Hz	3 J/cm <sup>2</sup>	Room temp.	Resistivity,	Introduction of Al <sub>2</sub> O <sub>3</sub>	Izumi et
Polycarbonate	248 nm			9.7x10 <sup>-3</sup> and	XRD, AFM	between PLD ITO	al. <sup>77</sup>
				9.7x10 <sup>-4</sup> Torr		and polycarbonate	
				oxygen		reduce ITO resistivity	
ZnO	KrF	10 Hz	3-6.2	Room-300 °C	XRD, PL	Emission life time of	Matsumu-
Polyimide	248 nm		J/cm <sup>2</sup>	0.38 Torr		free exciton and	ra et al. <sup>78</sup>
				oxygen		bound exciton were	
						212 ps and 660 ps	
ZnO ; PET,	KrF	20 Hz	200 mJ	Room temp.	XRD, SEM,	Film grow along c-	Kim et
Polyethersul-	248	23 ns		4 x10 <sup>-4</sup> Torr	AFM, XPS,	axis, $\approx 35$ nm grain	al. <sup>79</sup>
fonate, 10 cm				oxygen	resistivity,	size, 90% transparent,	
					transmittance		

## **3.5** Experimental setup

#### 3.5.1 Laser system

PLD of thin films was carried out using a Neodymium doped Yttrium Aluminum Garnet (Nd:YAG) laser. This is a Q-switched solid state laser, which emits its fundamental line at 1064 nm. This line can be up converted with non-linear crystals in order to emit at the harmonics of 532 nm, 355 nm, and 266 nm. The device used was the Spectron SL456G laser with pulse duration of 6 nanoseconds and a repetition rate of 10 Hz. The maximum pulse energy of the fundamental line is 1100 mJ, while the other emission lines are less intense because of the energy loss in the up-conversion process.

#### 3.5.2 Optical system

The pulsed-laser beam passes through the 8 mm aperture and a convex lens with 250 mm focal length before hitting the target. The lens was placed 56 mm out of focus to avoid laser induced damage on the target and to reduce the relative fluence error. It was shown that 1 mm error in position causes 20% relative error in fluence when the lens is 10 mm out of focus, while this error is reduced to 3% in case the lens is placed 5.6 cm out of focus.<sup>80</sup> When frequency upconverted line was used for ablation, the fundamental emission of the laser was suppressed by using suitable optical interference filters. In fact, for 532 nm, filter BG38 was used to block the fundamental 1064 nm line. The inlet window of the vacuum chamber is calcium fluoride, which has a very low absorption for IR, visible, and UV-region. The PLD system in the Department of Physics and Astronomy at Bowling Green State University is shown in figure 3.3.



Figure 3.3: Pulsed-laser deposition setup at Bowling Green State University

#### 3.5.3 Vacuum system

To avoid reaction of plasma plume with atmospheric gases, PLD was carried out at high vacuum, generally around  $10^{-7}$  Torr. This vacuum was attained using three different vacuum pumps *viz*. Edward mechanical, Varian turbomolecular, and Perkin Elmer ion. The mechanical pump lowers the pressure to  $10^{-2}$  Torr in about 10 minutes, the turbomolecular pump reduces the pressure to  $10^{-4}$ - $10^{-5}$  Torr in around 5 hours, and finally the ion pump lowers pressure to  $10^{-7}$  Torr. Switching from the turbo to the ion pump should be done after attaining  $5 \times 10^{-5}$  Torr. It should be noticed that these two pumps should never be run at the same time. At  $10^{-7}$  Torr, the mean free path of gas is around 700 m; therefore, the probability of reaction between the ablated particles and atmospheric gases is almost zero.<sup>81</sup>

#### 3.5.4 PLD of CdS and deposition rate

CdS was ablated by employing the 532 nm emission from a Nd:YAG laser with a pulse width of 6 ns and repetition rate of 10 Hz. During the PLD, the target was rotated 16 revolutions per minute in order to ablate the material as homogeneously as possible without local burns and the ablation was carried out in a vacuum better than  $10^{-7}$  Torr.

Thickness of the film was measured via the deposition rate using a quartz crystal in conjunction with the Sloan Digital Thickness Monitor 200. The quartz crystal was kept exactly at the substrate position holder at 6 cm from the target. The deposition rate was determined at various translational lens positions in order to locate the point corresponding to the focal length of the lens. To determine the position of the lens at the translational stage at the focal point for the laser spot on the target, deposition rate was determined at various translational lens positions and the result is depicted in figure 3.4. The solid line is the second order polynomial fit of the data. This figure shows that the minimum deposition rate occurs when the lens was put at 24.7 cm at translational stage. At this position the length between the lens and the target will be the focal length, because at this point there was a maximum interaction of the impinging laser beam with the plume, resulting in the lowest deposition rate. Therefore, for all the sample preparations, the ablation was done at 5.6 cm out of focus by keeping the lens at 19.1 cm on the translational stage to minimize the fluence error.



Figure 3.4: Deposition rate of CdS at various translational positions of the lens. This figure shows that the distance between the lens and the target is the focal length when the lens is kept at 24.7 cm on the translational stage

For the CdS deposition rate determination at various laser fluences, the lens position was kept at 5.6 cm out of focus and the ablation was carried out at various fluences by varying pockel's cell delay. The deposition rate versus fluence is plotted in figure 3.5. The result shows that the deposition rate increases with an increase in fluence and after reaching the value at 2.68 J/cm<sup>2</sup> the deposition rate drops because the plume shields the incoming laser beam. The thickness of the thin-film CdS samples was determined using the established deposition rate.



Figure 3.5: Deposition rate of CdS at 532 nm versus fluences. Plasma is seen beyond  $0.64 \text{ J/cm}^2$ , which indicates the ablation threshold fluence. The line is a guide for the eyes.

## 3.6 Plasma plume investigation

By doing the PLD of thin films, it is important that the target material is stoichiometrically transferred onto the substrate. Stoichiometric transfer of materials occurs when the fluence is higher than needed for thermal evaporation.<sup>42</sup> A rule of thumb is that the stoichiometric transfer of a material occurs at a fluence higher than that of plasma plume formation stage *i.e.*, after this point ablation starts. As in section 3.5.4, the lens was kept at 5.6 cm out of focus and the fluence was varied by changing the pockel's cell delay, and the laser ablation of CdS was carried out at various fluences and the respective optical images of the plume are shown in figure 3.6. These

images show that the ablation starts above 0.64 J/cm<sup>2</sup> because the plume formation starts at this fluence. Therefore, the rest of the samples were prepared above this fluence in order to maintain the composition of the target in the films. The visible plume size is increased with increase in the fluence due to more intense interaction of laser beam with the target.



Figure 3.6: Optical images of plasma plume at various fluences. The pictures were taken with FinePix F450 camera.

# 3.7 CdS/plastic sample preparation

CdS PLD was carried out as described in section 3.6. The substrate was either mounted at a distance of 6 cm parallel to the target or kept close to the top of the ablation chamber at 12 cm parallel to the laser beam as shown in figure 2.4. The elliptical laser beam on the target had a 2 mm horizontal length and 1 mm vertical length resulting in a footprint area of 0.0157 cm<sup>2</sup>. A low-temperature PLD was performed, *i.e.*, the substrate was not heated during the CdS films

deposition. 1 mm separated aluminum (Al) contacts on the film surface were evaporated using a vacuum evaporator to measure electrical and optoelectronic properties. A picture of CdS/Plastic device is shown in figure 3.7.



Figure 3.7: A picture of CdS/Plastic device with Al contacts.

The following CdS/plastic and CdS/glass samples were used in this section of the dissertation, which were prepared using following parameters as shown in table 3.3.

S.	Sample ID	Substrat	Dist.*	Fluence	$\lambda_{PLD}$ ,	Experiments	≈Thick-
#		e		(J/cm <sup>2</sup> )	time <sup>†</sup>		ness, nm
1	C110906	Plastic	12 cm	3.74±0.20	532 nm	AFM, PC, X-ray,	300±30
					30 min	composition	
2.	C110607-A	Plastic	6 cm	0.86±0.12	532 nm	Thickness	300±30
					15 min	distribution	
3.	C102407-A	Plastic	6 cm	3.30±0.19	532 nm	Thickness	500±50
					15 min	distribution	
4.	C103007	Glass	6 cm	3.05±	532 nm	X-ray,	400±40
				0.33	10 min	composition	

 Table 3.3: Thin-film CdS samples preparation parameters

# 3.8 Conclusions

Although a lot of work has been done on the PLD of CdS, a literature survey revealed that no studies have been published concerning the deposition of compound semiconductors on polymer based substrates. In order to ablate CdS on plastic substrates, the position of the lens was kept at 5.6 cm out of focus to minimize the fluence error. The deposition rate revealed that an increase in laser fluence increases the deposition rate, which reaches its maximum at 2.68 J/cm<sup>2</sup>. Beyond that fluence, the deposition rate was decreased due to shielding of the target by the plume. The plume image investigations shown in figure 3.6 revealed that size of the plasma increases with fluence increase causing more interaction of the impinging laser beam with the

<sup>\*</sup> Target to substrate distance

<sup>&</sup>lt;sup>†</sup> Ablation time

target itself. The examination of the CdS film revealed that the film has good adhesion with plastic, it was stable in air over time, and it was formed without pinholes. The work presented proves that PLD is a useful tool to make quality CdS thin films on plastic surfaces in a straightforward way. Other ongoing PLD experiments at BGSU showed that ZnTe and GaAs thin films can also be deposited on plastic substrates using low-temperature PLD. The results presented confirm the capability of PLD for straightforward inorganic/organic film/substrate mergers, which may be used for non-brittle and low-weight optoelectronic, photonic, and photovoltaic technologies.

# 4 CdS/PLASTIC CHARACTERIZATION

The results obtained for the surface properties, crystallographic properties, composition, thickness distribution, and the photocurrent properties of CdS films on a plastic substrate are presented and discussed in this chapter.

# 4.1 Surface characterization



Figure 4.1: Pictures of (a) thin-film CdS on plastic and (b) original plastic substrate.

Several samples of CdS on plastic substrates were prepared to optimize the growth of CdS film by varying the substrate to target distance. When the sample is close to the target, the energetic plume causes damage on the plastic and creates pinholes. When the substrate is put far away the deposition rate would be too low. Good quality films were obtained when the substrate was kept 12 cm away from the target and when ablation is carried out at relatively high fluence (3.74 J/cm<sup>2</sup>). Due to our equipment configuration the substrate was kept parallel to the incoming laser beam to ablate on a letter size substrate. The pictures of thin-film CdS on plastic compared to the plastic substrate itself are shown in figure 4.1. The thin-film CdS has yellow color, good surface quality, pinhole free appearance, and is stable in air. In this context, it should be stressed that the plastic substrate did not suffer damage or loss of flexibility due to the plume and, most noteworthy, the films showed good adhesion to the plastic foil and did not peel off when the transparency was squeezed and deformed. It should be noted here that no further treatment was performed on the sample after the PLD and all results refer to as-deposited films.

The surface properties of CdS on plastic were investigated by an atomic force microscope (AFM). Two surface images of CdS/plastic prepared at 12 cm from the target with resolution in micrometer and nanometer scale are shown in figure 4.2 (a) and (b), respectively. The images were obtained using Molecular Imaging's PicoSPM II microscope and WSxM scanning probe microscopy program<sup>82</sup>. The AFM images reveal that the film surface exhibits a mosaic structure with an average size of approximately 150 nm.





Figure 4.2: AFM images of thin-film PLD CdS on plastic with (a) micrometer and (b) nanometer resolution.

# 4.2 Crystallographic properties

The structure of the CdS films was investigated with a standard x-ray diffraction (XRD) scan. The XRD scans were performed using  $CuK_{\alpha}$  radiation in a scanning 2 $\Theta$  mode. The XRD results of a CdS/plastic, a plastic, and the CdS target are shown in figures 4.3 (a), 4.3 (b) and 4.3 (c), respectively. The remarkable feature here is that the CdS/plastic peak at 25.9° is almost identical with the plastic peak. In order to check whether the CdS film possesses polycrystalline property, another CdS film on glass was formed with low-temperature PLD, and the XRD measurement was carried out as well. The comparisons of an X-ray scan of CdS/glass with that of glass itself are shown in figure 4.3 (d) and 4.3 (e), respectively. The predominance of the CdS (002) peak on glass at 26.2 ° shows that the c-axis orientation of the wurtzite film texture is mainly perpendicular to the substrate. The additional presence of peaks demonstrates that the film is of polycrystalline nature, containing some amorphous parts as well.<sup>83</sup> These results confirm that room temperature PLD is capable of forming polycrystalline CdS on glass. These results also demonstrate that thin-film PLD CdS does not need a crystalline host in order to arrange itself with ordered texture.<sup>84</sup> Therefore, it is very likely that low-temperature PLD of CdS on plastic results in polycrystalline CdS as well. This achievement is even more remarkable since the substrate was at room temperature.



Figure 4.3: XRD diffraction scan of (a) CdS/plastic (b) Plastic (c) CdS target

(d) CdS/plastic, and (e) Glass

The average grain size of the CdS film on glass was calculated using the Scherrer formula, which is given by<sup>85</sup>

$$t = \frac{0.9\lambda}{B \times \cos\theta_{\rm B}} \tag{4.1}$$

Where,  $\lambda$  is the x-ray wavelength used (Cu<sub>Ka</sub> =  $1.54 \times 10^{-10}$  m), B is the full width at half maximum (FWHM) in rad (0.0055 rad taking into account the instrumental broadening, which is 0.0014 rad), and  $\theta_B$  is the Bragg angle at 26.2°, the crystallite size is found to be 32 nm. Similarly the grain size at 43.28° with FWHM of 0.0194 rad is found to be 15 nm. This suggests that room temperature PLD of CdS on glass forms nanocrystallites whose grain size varies from 15 to 32 nm.

## 4.3 Composition of the film

The composition of the CdS film on the plastic was determined by electron probe microanalysis (EPMA) and energy dispersive x-ray analysis (EDAX). Both methods are based on the fact that X-rays emitted by an element excited by an electron beam have a wavelength, which is characteristic for that element, and an intensity related to the element's concentration. The EPMA measurements were carried out at the Air Force Laboratory, Dayton, while the EDAX measurement was carried out at the Center for Microscopy and Microanalysis at BGSU.

For EPMA analysis, carbon paint was used to stick a piece of the specimen to an aluminum stub and coated with carbon. An accelerating voltage of 15 keV and a probe current of 40 nA were used in the measurements.  $Cd_{L\alpha}$  and  $S_{K\alpha}$  calibration were done on a bulk CdS reference material. For computing the film composition, the polymer sheet substrate was assumed to be purely carbon. Several regions of the film were analyzed by averaging groups of 10 points along a linear path, with the points spaced such that the analysis volumes would not

overlap. The averaged data from this analysis region were fed into four different calculation routines, within the GMRFilm software, which yielded the following compositions in atomic percent as shown in table 4.1. The average values obtained from these four analysis routines are  $50.0\pm2.00$  % Cd and  $50.0\pm2.00$  % S, by atom, respectively.

Table 4.1: Composition of CdS thin films on plastic by EPMA

S.N.	Calculation	Cd, % at.	S, % at.
1.	Packwood Matrix	52.8	47.2
2.	PAP Matrix Correction	49.5	50.5
3.	Bastin 1990 Matrix	49.6	50.4
4.	Bastin 1986 Matrix	48.0	52.0

Since the XRD peak position of plastic is similar to that of CdS film on glass, and because CdS is used in the plastic engineering for thermal stability,<sup>86</sup> plastic substrate itself CdS was checked for the presence of CdS.

# Intensity



Figure 4.4: EDAX results for (a) CdS/Plastic, (b) Plastic substrate, and (c) CdS target. The spectra show that plastic does not contain Cd and S signals. For this purpose EDAX was carried out using the x-ray detector equipped with the Hitachi 2700 SEM of the Microscopy and Microanalysis Center of BGSU. Plastic and CdS/plastic samples were put on the carbon sticky tab on the Al stub and a thin film of carbon was coated on them to make samples conductive, while for the reference purpose, the CdS single crystal was put on the carbon sticky tab on an Al stub without coating. The data were recorded using the Hitachi 2700 SEM at 20 keV with EDAX genesis software. The EDAX results for CdS/plastic, plastic, and CdS crystal are shown in figures 4.4 (a), (b) and (c), respectively. These results clearly indicate that the plastic itself does not have any Cd and S signals. Using EDAX the average composition of Cd and S in the CdS plastic film is found to be  $52.2\pm1.4\%$  and  $47.8\pm1.4\%$  by atom, respectively. In this case, a CdS single crystal was used as calibration standard for the analysis.

# 4.4 Thickness distribution

#### 4.4.1 Thickness distribution measurement setup

Thickness distribution of the film on the substrate is a very important parameter because it controls the optical properties of the thin-film devices. Non-uniform thickness distribution of the thin films deposited by PLD is one of its limitations. However, this problem can be addressed by changing, i.e., rastering, the laser spot on the target as well as rotating the substrate to get larger areas with more uniformity.<sup>87</sup>

In the presented CdS film thickness distribution measurement, it is assumed that the transmission of a 632 nm helium-neon (He-Ne, 20 mW) laser is inversely proportional to the film thickness, while the thickness distribution of the sample was calculated using transmitted signal recorded with a Si photodiode. The sample was positioned on a translation stage, which is

controlled by the Newport Universal Motion Controller Driver. The schematic diagram for thickness distribution set up is shown in figure 4.5. The sample was scanned by a He-Ne laser and the connected photodiode measured the transmitted intensity. The measurements were carried out along the major and minor axis of the elliptical samples and the data were acquired with a computer.



Figure 4.5: Schematic diagram of the thickness distribution setup.

### 4.4.2 Thickness distribution of the film

This experiment was focused on the thickness distribution of CdS thin films on plastic produced with two different laser fluences: at low and at high fluence, *i.e.*, 0.68 J/cm<sup>2</sup> and 3.31 J/cm<sup>2</sup>. The details of the sample preparation parameter are shown in table 3.3. It was observed that the films were elliptical in shape and the length of the major axis is increased with an increase in the laser fluence. The footprint of the laser on the target was of elliptical shape with 2 mm and 1 mm, corresponding to the major and minor axes, respectively. The elliptical shapes of the films are attributed to the flip-over effect that is caused by the rotation of the symmetry of the deposited film with respect to the laser spot.<sup>88</sup> The corresponding thickness distribution results

are shown in figures 4.6 (a) and (b). It is clearly seen from the graph that the film thickness is more uniform at the lower fluence over the area; however, the major axis length is increased from 50 to 90 mm when the fluence is increased from 0.68 to  $3.31 \text{ J/cm}^2$ . On the other hand, the impact of the fluence is much lower on the minor axis. The area of the film was enlarged from approximately 14 cm<sup>2</sup> to 33 cm<sup>2</sup> when the fluence was increased from 0.68 J/cm<sup>2</sup> to  $3.31 \text{ J/cm}^2$ .



Figure 4.6:Thickness distribution of thin-film CdS on plastic prepared with PLD at (a)  $0.68 \text{ J/cm}^2$  (b)  $3.31 \text{ J/cm}^2$  along major and minor axis.

#### 4.5 Photocurrent measurement

#### 4.5.1 Direct photocurrent measurement setup

The sample was excited by non-chopped monochromatic light, and consequently, the photocurrent in this case is called direct photocurrent (DPC). The schematic diagram of the DPC measurements is shown in figure 4.7. The sample was excited with a 200 W halogen lamp via a <sup>1</sup>/<sub>2</sub> m monochromator (Spex 500 M). Before exciting the sample, the monochromatic light was passed through a long-pass filter and a focusing lens. The DPC was measured along the film by connecting two surface Al contacts with a Keithley 6485 picoammeter and the bias voltage was supplied with a Keithley 230 programmable voltage source. All measurements were carried out at room temperature.

All DPC spectra have been corrected using a calibrated Si photodiode in order to express the results in responsivity (A/W), which is the electrical output from the sample in Amperes per unit optical input in Watts, and was calculated using the following equation.

$$R_{\rm D} = \frac{(I_{\rm DPC, sample} - I_{\rm DC, sample})}{(I_{\rm DPC, reference} - I_{\rm DC, reference})} \times R_{\rm reference}$$
(4.1)

Where,  $R_D$  is the direct responsivity;  $I_{DPC,sample}$  and  $I_{DC, sample}$  are DPC and dark current from the sample and  $I_{DPC, reference}$  and  $I_{DC, reference}$  are the DPC and dark current measured with the Si reference photodiode, and  $R_{Reference}$  is the responsivity of the diode itself in A/W. The responsivity spectra and the PC spectra of the reference Si photodiode used for the spectra correction are shown in figure 4.8. The responsivity of the sample is plotted versus excited photon energy in order to get the responsivity spectra. Since photocurrent and responsivity are directly related, these terms are used interchangeably in this dissertation.



Figure 4.7: Schematic diagram of DPC measurements.



Figure 4.8: The responsivity and PC spectra of Si photodiode used for the PC correction.

#### 4.5.2 Photocurrent and transmission spectra of CdS/Plastic

The main interest of this work was focused on the investigation of whether thin-film CdS plastic can be used for photonic applications such as photodetectors. The DPC spectrum was measured in the electric field of 100 V/cm as described in the preceding section. The PC spectra of CdS/Plastic compared with that of CdS single crystal are shown in figure 4.9(a).

The photocurrent for both samples starts at around 2.35 eV because of transitions in the impurities levels with a peak at 2.44 eV for the perpendicularly oriented CdS single crystal as expected.<sup>89</sup> However the peak of CdS/Plastic is situated at 2.54 eV with a blue shift. The pronounced drop of the PC signal at energies higher than the peak position is caused by effective surface recombination indicating a high density of recombination centers at surface. Due to the fair match of the film thickness and the typical light penetration depth of 0.1 µm at the CdS band gap, the whole thin film sample can be considered as a surface film without a bulk part. The transmission spectra of the CdS/plastic and the plastic substrate itself are shown in figure 4.9 (b). The comparison of the transmission spectrum and PC spectrum of CdS/plastic, which is shown in the inset of figure 4.9(b), reveals that the band gap energy of the CdS film corresponds to the steep transmission increase at 2.54 eV. On the other hand, the plastic absorption threshold starts in the region of 3.5 to 4 eV.



Figure 4.9: PC (a) PC spectrum of CdS single crystal and CdS/Plastic prepared with PLD (b) transmission spectrum of CdS/Plastic and the plastic substrate; the inset shows a comparison of the PC and transmission spectra of CdS/Plastic.

The figure 4.9 (a) shows that the PC maximum, and therefore the gap energy is located at around 2.54 eV, which is shifted towards higher energy region compared to the single CdS crystal PC measurements. It is well known that the band gap energy depends on the particle size, crystal structure, and strain in the film. The band gap increase of nano-sized structures is expressed by <sup>90</sup>

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2MR^2} \tag{4.2}$$

where,  $\hbar = h/2\pi$  and h is a Plank's constant,  $M = 1.919 \times 10^{-31}$  kg is the corresponding reduced mass for hexagonal CdS <sup>91</sup> and *R* is the radius of the crystallites. Considering  $\Delta E_g=0.10$  eV, which is the difference between PC peak position at 2.54 eV and the crystalline CdS band gap energy of 2.44 eV, the diameter of CdS crystallites is found to be 7 nm. Thus, it is possible that quantum-size effects are involved in the blue shift. However, increasing strain within the film increases the band gap energy of CdS as well.<sup>92</sup> Since the film thickness is only 300 nm, in addition to quantum-size effects, strain at the organic-inorganic interface contributes to the blue shift of the PC spectrum.

# 4.6 Conclusions

Thin-film CdS was deposited on the plastic substrate using low-temperature PLD i.e, without heating the substrate, and the preliminary results of the CdS/plastic formed with PLD have been published.<sup>93</sup> The composition analysis using EPMA and EDAX revealed that the target composition is almost perfectly maintained in the film. The 2 $\Theta$  pick position at 25.9° in the CdS/plastic XRD scan exactly coincides with that plastic substrate itself. However, the XRD scan of the CdS/glass formed at 6 cm substrate to target distance revealed that the room temperature CdS PLD forms polycrystalline films with a crystal size of 15 to 32 nm. Since polycrystalline CdS is also formed on a non-crystalline glass substrate, it is likely that CdS on plastic also forms polycrystalline texture. The sample showed photosensitivity with a blue shifted band gap at about 2.54 eV, which is attributed to the nano-size effect and/or strain in the film. In fact, the calculation of CdS size in the film produced 7 nm crystallite size. The CdS films were elliptical in shape, which is caused by the rotation of the symmetry of the deposited film with respect to the laser spot. Thickness distribution studies of the sample prepared at different fluences revealed that the area of film coverage significantly increased when the laser fluence is increased from 0.68 to 3.31 J/cm<sup>2</sup>. The films obtained show good adhesion, have mosaic structure and flat surface, and exhibited useful light sensitivity at room temperature. Therefore, CdS/plastic prepared with PLD has the potential to be used in the photonics, optoelectronics, and photovoltaics.
# 5 OPTICAL QUENCHING OF ALTERNATING PHOTOCURRENT IN CdS/GLASS

## 5.1 Introduction

The quest for knowledge coupled with the search of new functional photoelectronic devices has motivated the scientific community to explore semiconducting thin film production techniques and to exploit the films through the interaction of light. The control of electrons in semiconductors via photons is required to form hybrid devices, which may act as an interface between light and common electronic circuits. It is well known that the photoconductivity of a semiconductor decreases when illuminated with additional photons with lower energy (usually IR radiation) than used for the band gap excitation. This phenomenon is called optical quenching of photoconductivity.<sup>94</sup> It occurs when the low energy photons excite electrons from the valence band to deep levels creating free holes in the valence band, which recombine with free mobile electrons decreasing the current flow.<sup>95</sup> This phenomenon is qualitatively depicted in figure 5.1. This process can be counterproductive in the photovoltaic energy conversion; however, it is useful for the investigation of electron capture cross section, defects centers,<sup>96</sup> and optically controlled switches.<sup>97</sup>

Photocurrent



Figure 5.1: (a) Magnitude of PC due to primary illumination (I) and quenched PC due to additional IR illumination (II), (b) diagram indicating primary and secondary illumination measurement scheme, and (c) mechanism of the quenching of the PC using the band diagram, where VB and CB represents the valance band and conduction band, respectively.

Most semiconductors exhibit optical photoconductivity quenching properties and CdS is a well-studied semiconductor in which IR light has been used for quenching illumination.<sup>98</sup> Experiments on all-optical reflective and transmittive switches using laser crossing in thin-film CdS, GaAs, and ZnTe prepared by PLD have been already conducted in our laboratory and published in journal articles.<sup>8, 99</sup> However, the investigation on the control of APC signals using secondary constant blue photon illumination in thin-film semiconductors has not been reported in the literature yet. In this chapter, the variation of APC spectra at various optical chopper frequency and voltages are presented. In addition, the results obtained in the APC signal control by CW blue light excitation will be presented, and finally a model is introduced here to describe APC quenching phenomenon due to CW blue light. The work presented in this chapter has published in a conference paper as well.<sup>100</sup>

## 5.2 Experimental

Thin-film CdS on glass<sup>\*</sup> was used for all the measurements described in this chapter because it produced better APC spectra than the CdS/plastic. Although the main objective of this chapter is to investigate the APC quenching of thin film CdS/glass by blue light, it is important to know the structural and optical properties of the sample. Therefore, XRD and transmission of the sample were measured using a Rigaku x-ray diffractometer and Cary 50 UV-visible spectrophotometer, respectively. Two aluminum electrodes with 1 mm gap were formed on the film surface by vacuum evaporation and the contacts were found to be ohmic.

The APC was measured using lock-in technique with a SR 530 lock-in amplifier. This low-noise technique relies upon a reference frequency provided by an optical chopper, whereas Keithley 230 voltage source provided the biases to the sample. The sample was illuminated with a 200 W halogen lamp in conjunction with a 1/2 m monochromator (Spex 500 M). Before exciting the sample, the monochromatic light passed through a long pass filter, in order to eliminate higher order diffraction replica, and through a chopper wheel, which provided the lock-

<sup>&</sup>lt;sup>\*</sup> The sample G180 was used for all the experiments in this chapter, which was prepared in Japan. Sample preparation parameters are: Method: PLD, Wavelength: 355 nm, Laser: Nd:YAG laser, Pulse width: 5 ns, Fluence: 4.3 J/cm<sup>2</sup>, Repetition rate: 10 Hz, Pressure: 9x10<sup>-5</sup> Torr, Substrate temperature: 250°C.

in reference frequency. The light was focused between the contacts onto the sample forming an area of about 2 mm<sup>2</sup> and the typical excitation intensities were in the  $\mu$ W/cm<sup>2</sup> range. For APC quenching studies, an additional constant blue LED was employed to illuminate the film from the back through the glass substrate, as shown in figure 5.2 (a). The blue LED emission spectrum is shown in figure 5.2 (b), with its peak at around 466 nm. This spectrum was measured using an Ocean optics UV-visible charge coupled device spectrometer with a fiber optic cable. The schematic diagram of APC measurement is also depicted in detail in figure 6.2. In figure 5.3, the photos of the APC measurement setup at BGSU are shown. This setup has operational spectral range from 400 nm to 1200 nm. All the measurements were carried out at room temperature and all shown PC spectra have been corrected in order to express the results in responsivity *i.e.*, in ampere per watt (A/W) using a calibrated Si photodiode. The responsivity was calculated with the following formula.

$$R_{A} = \frac{I_{APC,sample}}{(10 \times I_{APC,reference})} \times R_{reference}$$
(5.1)

where,  $R_A$  is the alternating responsivity in A/W,  $I_{APC, sample}$  is the sample's alternating photocurrent,  $I_{APC, reference}$  is the Si diode alternating photocurrent, and  $R_{reference}$  is the responsivity of Si reference photodiode itself. Intensity of the light was reduced 10 times using a neutral density filter in order to avoid the overload of the lock-in amplifier during the Si photodiode measurement. This responsivity is plotted versus excitation photon energy to get the responsivity spectra.



Figure 5.2: (a) Schematic diagram of the APC control using blue light illumination and (b) the emission spectrum of the blue LED.



Figure 5.3: APC measurement setup at BGSU. The left side in this figure shows in detail a chopper, a lens, and the sample used in the quenching experiment.

# 5.3 Results and discussion

#### 5.3.1 Structural and optical properties

The XRD result of the CdS film on glass is shown in figure 5.4. Similar to the CdS on glass formed at room temperature PLD in figure 4.3 (d), the CdS film formed on glass at elevated substrate temperature is polycrystalline. The reflection peaks at  $2\theta = 24.9^{\circ}$ ,  $26.6^{\circ}$ ,  $28.1^{\circ}$ ,  $43.7^{\circ}$ ,  $47.5^{\circ}$ , and  $51.4^{\circ}$  correspond to the CdS (100), (002), (101), (110), (103), and (112) planes, respectively<sup>101</sup>. The co-appearance of the (100) and (101) peaks shows that the *c*-axis of the film is parallel to the substrate surface, while the (002) reflex points to a perpendicularly oriented *c*-axis. Hence, the film consists of differently oriented polycrystalline sections and the fairly weak peaks on the rather broad background imply that the CdS polycrystallites are embedded in an amorphous matrix.



Figure 5.4: XRD scan of CdS film on glass used for the APC quenching measurements.



Figure 5.5: (a) Optical transmission spectrum of the thin-film CdS and (b) optical gap determination.

The transmission spectrum of the sample is shown in figure 5.5 (a). Using the interference fringe pattern of this spectrum, the thickness of the film is approximately calculated to be around 200 nm. The optical band gap of the thin-film CdS is determined using Tauc's formula.<sup>102</sup>

$$(\alpha h v)^2 = (h v - E_{\varphi}) \tag{5.2}$$

where,  $\alpha$  is the absorption coefficient, hv is the corresponding energy of the incident photons, and  $E_g$  is the optical band gap energy. The absorption coefficient is calculated with

$$\alpha = \frac{-\ln(T_f)}{x}$$
(5.3)

where *x* is thickness of the film (200 nm),  $T_f$  is the transmittance of the film, and the  $(\alpha hv)^2$  versus *hv* plot is shown in figure 5.5 (b). From the plot the optical band gap is determined to be 2.35 eV, *i.e.*, which is fairly close to the band gap of bulk CdS (2.42 eV).

#### 5.3.2 APC spectra at different chopper frequency and voltages

APC spectra, more precisely alternating responsivity (AR) spectra, of the sample at different optical chopper frequencies at 10 V are shown in figure 5.6 (a). The PC starts around 2.2 eV, which is attributed to the presence of impurities levels, and the distinct rise in the PC starts at about 2.40 eV near the band gap of CdS. These results show that the spectral responsivity patterns at all chopper frequencies are similar; however, the PC magnitude decreases exponentially with increase in optical chopper frequency as shown in the inset of 5.6 (a). The PC decrease with increase in optical chopper frequency takes place because the CdS film is a rather "slow" material. The excited electrons are trapped, consequently, cannot relax and re-excite during faster chopping frequencies.



Figure 5.6: (a) Alternating responsivity spectra of a thin-film CdS on the glass at different optical chopper frequencies at 100 V/cm. The inset shows responsivity versus chopper frequency plot at 2.6 eV. (b) Decay of the excited state CdS film on glass. The sample was excited with a blue argon ion laser.

The lifetime of the CdS film on glass was measured by exciting the film with a chopped (18 Hz) blue laser line (argon-ion, 9 watt) and measuring the PC versus time with a 500 MHz oscilloscope. The result obtained for the PC decay curve is shown in figure 5.6 (b). The intersection of the tangent of the decay curve with the x-axis is a measure for the lifetime of the excited carrier in the CdS film, which turned out to be approximately 2.5 ms. The lifetime of the excited CdS was also estimated using the chopper frequency dependence of the PC as shown in the inset of figure 5.6 (a). The result of 5 ms is in reasonable agreement with the decay measurement in figure 5.6 (b). Although, in practice, high chopper frequency (> 100 Hz) is used to facilitate clear separation of chopped output voltage from low-frequency noise component in lock-in technique,<sup>103</sup> 18 Hz was used as a reference frequency because the CdS/glass possessed the highest APC signal at this frequency.

The electric field dependence of the AR spectra in figure 5.7 (a) shows that the responsivity increases with increase in electric field, as commonly expected from photoconductive semiconductors and figure 5.7(b) shows a fairly linear relationship between responsivity and applied bias at the excitation energy of 2.6 eV.



Figure 5.7: (a) Alternating responsivity spectra at various biases and (b) corresponding responsivity plot versus bias at 2.6 eV.

## 5.3.3 Quenching of alternating responsivity with blue light excitation

The variation of the alternating responsivity (AR) spectra of the device due to additional blue light illumination at 10 V and 20 V are shown in figure 5.8. This figure shows two facts: there is a significant APC quenching when the blue LED is on and the relative magnitude of quenching is increased with increase in voltage. The mechanism of this phenomenon will be described in the subsequent sections.



Figure 5.8: Quenching of AR at 10 V and 20 V due to additional constant blue LED illumination.

In order to check how the APC varies with the monochromatic excitation and quenching LED intensity, intensities of both the monochromator and the LED were varied by changing their power supplies. The intensity of the monochromator is determined with the calibrated Si photodiode used for the PC measurements and the quenching LED intensity is determined using an interference filter at 488 nm in conjunction with the calibrated Si photodiode.

In both cases PC were measured at 18 Hz and 20V. The corresponding results are shown in figures 5.9 (a) and (b). Figure 5.9 (a) shows that the APC goes up linearly with increase in the intensity of the monochromator output as expected. However, on the other hand, the APC decreases as shown in figure 5.9 (b) with the increase in the blue light intensity. Although in this experiment AR was reduced to about 50 % in figure 5.9 (b), it might be possible to bleach the AR signal completely if enough quenching intensity were provided. On the contrary, experimental results showed that it is not possible to control DPC generated from blue LED using chopped light from the monochromator even at very low blue LED intensities and high monochromatic excitation intensities.

Figure 5.10 shows how the ratio of direct responsivity (DR) to alternating responsivity (AR) signal varies at different voltages. It should be noted here that in both DR and AR measurements, the monochromatic output light was kept at 516 nm and the intensities were kept same. The DPC signals for both curves in figure 5.10 were measured with a Keithley ammeter without chopping. This figure shows that beyond the threshold value of about 5 V, the DR signal is approximately ten times larger than the AR value when blue light is off; however, the DR to AR ratio increases about six times when additional blue light is on. Therefore, this phenomenon is attributed to the conversion of APC carriers into DPC carriers or due to generation of more DPC carriers by the LED. For the following explanation, it should be stressed that the basic difference between IR quenching: in the former electrons are pumped into deep centers, whereas in the latter electrons are pumped to the conduction band by the secondary (quenching) illumination.

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Figure 5.9: AR of CdS/glass at 20 V at (a) various excitation intensities from the monochromator at 488 nm when the blue LED is off, and (b) AR versus various quenching intensities from the blue LED at constant monochromatic chopped excitation at 488 nm.



Figure 5.10: DR/AR versus biases under constant monochromatic illumination at 516 nm when blue LED is on/off. Here DR and AR correspond to the DPC and APC, respectively.

## 5.3.4 Explanation of the quenching phenomenon

Based on the former experimental results a model is proposed in figure 5.11 for the explanation of AR quenching by blue light illumination. As depicted in figure 5.11, there is a conversion of available APC carriers to DPC carriers due to the pumping of electrons to direct current channel by the blue LED following the stimulated recombination of APC carriers with holes created by the non-chopped excitations. A similar model has used to explain photonic switching due to laser crossing.<sup>104</sup>



Figure 5.11: Proposed mechanism of APC quenching by blue light.

# 5.4 Conclusions

The experiments described in this chapter demonstrates that thin-film CdS can be used for APC quenching or switching purposes employing a lock-in technique in conjunction with low power blue light in a simple and straightforward way. A model is proposed for the explanation of APC quenching. The basic ideas are that the quenching has been achieved due to shortening of APC charge carriers due to the increase in DPC carriers following stimulated recombination of APC electrons with holes generated by the blue LED. The degree of quenching can be varied by changing the optical chopping frequency, chopped excitation energy, intensity of quenching light, and the applied bias. Summarizing, the work emphasizes the application of the lock-in principle for modulation or quenching techniques in optoelectronics rather than for applications in metrology only. This phenomenon might ultimately find applications in photoelectronics to modulate alternating electrical signals using photons.

# 6 PHOTOCURRENT SPECTROSCOPY OF ZnTe/n-GaAs

## 6.1 Introduction

This chapter deals with the fundamental properties and applications of ZnTe and GaAs followed by the literature survey on the ZnTe/GaAs heteropairs. The experimental section describes the APC and current-voltage (*I-V*) measurement schemes and finally in the end of the chapter, the obtained results will be presented and discussed in detail.

#### 6.1.1 Zinc Telluride

ZnTe is a II-VI compound semiconductor, which consist of zinc from group II and tellurium from group VI of the periodic table of elements. It is a direct transition semiconductor with a band gap energy of 2.26 eV at room temperature. It can be synthesized by the reaction between sodium telluride and zinc acetate. ZnTe is insoluble in water and occurs as zincblende and wurtzite forms. There is a very little energy difference between these structures; therefore, both structures occur simultaneously in nature. The physical properties of ZnTe are summarized in the table 8.1 ZnTe is used in tandem solar cells,<sup>105</sup> green light emitting diodes,<sup>106</sup> and terahertz pulse generation and detection.<sup>107, 108</sup>

## 6.1.2 Gallium Arsenide

GaAs is a III-V compound semiconductor consisting of gallium from group III and arsenic from group V of the periodic table of the elements. It is a direct transition semiconductor with a band gap energy of 1.42 eV at room temperature. III-V semiconductors are usually prepared by direct combination of constituent elements in their highest purity state, followed by controlled crystallization of the melt. To change electrical properties, a calculated amount of

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dopant is added to the melt. GaAs single crystal is manufactured by Bridgeman technique, because the Czochralski process is difficult due to mechanical properties. GaAs is also prepared at a temperature well below the melting point by reducing gallium halide with arsenic. GaAs oxidizes above 600°C in air; corrosion by acid is usually slow except in the presence of oxidizing acids. The physical properties of GaAs are summarized in table 8.1 in the appendix. The electron mobility in GaAs is relatively high; therefore, GaAs is commonly used for integrated circuits and fast central processing units. GaAs is also employed for high-efficiency solar cells,<sup>109</sup> light emitting devices, <sup>110</sup> terahertz devices,<sup>111</sup> particle detectors,<sup>112</sup> and photodetectors.<sup>113</sup>

#### 6.1.3 ZnTe/GaAs heteropairs

The merger of ZnTe with GaAs is an appealing technological hetero-pairing between II-VI and III-V compound semiconductors. Both materials are direct band gap semiconductors with particular attractions: The ZnTe bandgap energy coincides with the human eye sensitivity maximum, whereas GaAs is currently one of the main players in the field of optoelectronics. The spectral operation range of the devices based on these materials will cover the spectral range from visible to near infrared, which may be adjusted by suitable fabrication techniques and operation modes.

With respect to GaAs, ZnTe is much lesser exploited and, by far, does not match the industrial importance of GaAs and related compounds. Despite the notable applications of both materials in optoelectronics, their merger was used for passive applications such as buffer layers for epitaxy of CdTe<sup>114</sup> rather than for active device realizations. These rather low research and application profiles are caused by the large lattice mismatch (7%), which creates severe difficulties for the formation of high-quality ZnTe/GaAs hetero-pairings. Further problems arise from the diffusion of Ga and As atoms into the ZnTe film.<sup>115</sup> Regardless of these unfavorable

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conditions, ZnTe/GaAs heterostructures have been prepared by MBE, MOVPE, hot-wall epitaxy (HWE), temperature-gradient vapor transport deposition (TGVTD), and PLD. In the overall regard of the field of thin-film preparation, PLD is a lesser employed deposition technique but shows an increasing impact on semiconductor hetero-pairing. Previous publications of the ZnTe/GaAs heterostructures are listed in table 6.1. These publications focus on the structural, optical, and electronic properties including the strain on the ZnTe film as well as carrier dynamics. However, no work has been done regarding the PC properties of ZnTe/GaAs heterostructures formed by PLD. Previous investigation of ZnTe in our laboratory covered surface roughness, texture of ZnTe on Si and glass.<sup>116</sup> This chapter mainly focuses on the investigation of room temperature APC spectra of PLD ZnTe/*n*-GaAs, which will be compared with the APC spectra of *n*-GaAs substrate itself. The APC dependence on the chopping frequency of the exciting light source and on the applied bias will be studied and compared with that of the *n*-type GaAs substrates as well.

Table 6.1: Publication	list of ZnTe/GaAs	heterostructures
------------------------	-------------------	------------------

Film growth	Substrate temp.	Experiments	Results	Reference
method	Deposition condition			
PLD, KrF	320 °C , N <sub>2</sub> ambient	RBS, Hall	ZnTe film was doped with Nitrogen	Rouleau et al. <sup>117</sup>
excimer	(50-200 mTorr)	measurement		
TGVTD	250-450 °C	XRD, AES, TEM	Large lattice mismatch, no inter-diffusion	Kim et al. <sup>118</sup>
			problem at 320° C substrate temperature.	
MBE	200°C with ZnTe	RHEED, XRD, AFM	Low temperature ZnTe buffer reduces the	Lee at el. <sup>119</sup>
	buffer and 300 °C		deformation	
MOVPE	320-440 °C	XRD, growth rate	Good quality ZnTe crystal formed at 430°C	Kume at el. <sup>120</sup>
TGVTD	320 °C	AES, SIMS,	Sharp heterostructures,	Kim et al. <sup>121</sup>
		TEM	Compressive strain, and dislocation	
MOVPE	290-310 °C	Carrier dynamics,	Career lifetime 1670 ps, diffusion constant	Mizeikis et al. <sup>122</sup>
			value is 32 cm <sup>2</sup> /s	
MOVPE	410 °C	AFM, RBS,	Stranski-Krastanow growth of ZnTe	Lovergine et al. <sup>123</sup>

TGVTD	400 °C	XRD, Raman,	Lattice mismatch, splitting of valance band	Lee et al. <sup>124</sup>
		photoreflectence	maximum, resonant excitation	
MBE	330 °C	RHEED, PL,	Near band-edge PL reflecting high quality	Rajakaurunanana
			film, GaSb is the best buffer layer	yaka et al. <sup>125</sup>
MOVPE	350 °C	TEM, HRTEM, RBS,	Threading dislocation in ZnTe epilayer,	Lovergine et
			compressive strain in the heterostructures	al. <sup>126</sup>
MBE	250-320 °C	Reflectance, PL,	Tensile strain is independent on layer	Dang et al. <sup>127</sup>
		optical pumping	orientation and present up to 6 µm	
MOVPE	410 °C	AFM, RBS	The aspect ratio <sup>*</sup> of nano-island decreased	Longo et al. <sup>128</sup>
			with increase in homoepitaxial GaAs	
			wetting layer thickness	
HWE	300-440 °C	Double crystal	Optimum growth substrate temperature is	Nam et al. <sup>129</sup>
		rocking curve	390-400 °C, large thermal tensile strain.	
HWE	380 °C	HRTEM	Dislocation relieves localized misfit strain	Dan et al. <sup>130</sup>

<sup>\*</sup> Ratio between height to diameter

MBE	280 °C, 10 <sup>-8</sup> Torr	PL, XRD, AFM, PR,	Crystallinity of ZnTe increased using ZnSe	Kim et. al <sup>131</sup>
		TEM, Raman	buffer layer.	
HWE	-	XRD, TEM	Dislocation, stacking faults	Shindo et. al <sup>132</sup>

## 6.2 Experimental

#### 6.2.1 Device formation

The ZnTe/n-GaAs samples were prepared with a low-temperature, *i.e.*, without substrate heater, PLD in vacuum (5  $\times 10^{-7}$  Torr). The material was ablated from a ZnTe target (99.99%) by employing the pulsed (6 ns, 10 Hz) fundamental (1064 nm) emission of a Q-switched Nd:YAG laser. The target surface was 45° tilted with respect to the impinging laser beam and was rotating with 16 rpm in order to ablate the material as homogeneously as possible. The Si doped *n*-GaAs substrate used was a (100) oriented vertical gradient freeze grown wafer obtained from Wafer Technology Limited with carrier concentration and thickness of  $3 \times 10^{16}$  cm<sup>-3</sup> and 511-520 µm, respectively. The GaAs substrate was mounted at a distance of 6 cm parallel to the target and the PLD was carried out with a laser fluence of  $0.78\pm0.09$  J/cm<sup>2</sup>. Since strain in the ZnTe film on GaAs is expected to be reduced with increase in the ZnTe thickness, <sup>133</sup> a fairly thick ( $\approx 0.8 \mu m$ ) ZnTe film was prepared. The substrate was not heated in order to avoid interface stress and deformation during cooling. Using EPMA, the average ratio of Zn to Te atoms is found to be 0.96, demonstrating that the film is closely but not quite stoichiometric. Electrical contacts to the film surface and the rear, *i.e.*, the substrate, were realized with the evaporated aluminum (Al) and silver (Ag) paste, respectively. For reference purposes, *I-V* analysis and APC measurements were performed by solely using the *n*-GaAs substrate with an identical electric contact configuration, as employed with the heteropaired device.

#### 6.2.2 *I-V* characteristics setup

*I-V* characteristics of the samples were measured using a Keithley 2400 sourcemeter, which provides precision voltage output ( $\pm 5\mu V$  to  $\pm 200V$ ) as well as current measurement( $\pm 10pA$  to  $\pm 1A$ ). The source meter is connected to a computer through a GPIB interface and the data were collected using KottanSpec software. The experimental setup for the *I-V* characteristic study is shown in figure 6.1. According to the schematic, the *I-V* curve was measured using the top Al contact (1) and bottom Ag contact.



Figure 6.1: *I-V* measurement setup.

#### 6.2.3 Alternating photocurrent measurement setup

The APC was measured with the SRS 530 lock in amplifier as described in detail in section 5.2. In this case, the only difference from the previous measurement is that the sample was excited using the monochromator only. The schematic diagram of the APC measurements is shown in figure 6.2.



Figure 6.2: Schematic diagram of the alternating photocurrent measurements.

Like *I-V* measurements the PC spectra were also measured using front Al and rear Ag contacts. Data were collected with a computer running KottanSpex software. All measurements were carried out at room temperature and the spectra were corrected with the calibrated Si diode as described in section 5.2.

## 6.3 Results and discussion

In this section, the *I-V* characteristics and intrinsic APC spectra of ZnTe/n-GaAs as well as *n*-GaAs at different optical chopper frequencies and biases will be presented. The various features observed in the PC spectra including an isosbestic point and photonic doping of GaAs with Zn and Te are explained in detail.

#### 6.3.1 *I-V* characteristics

Figure 6.3 shows the peculiar *I-V* characteristics of the ZnTe/*n*-GaAs heterostructure compared with the *n*-GaAs substrate itself. The samples show neither ohmic nor clearly rectifying behavior. Due to the similar curve shapes for both samples, the *I-V* behavior is dominated by the Al/*n*-GaAs/Ag sequence. However, the notable difference is that for negative top polarization, the current of the heterostructure drops two orders of magnitude in comparison to the *n*-GaAs sample, indicating a more blocking ZnTe/*n*-GaAs interface. This peculiar non-rectifying *I-V* characteristic of ZnTe/*n*-GaAs may be due to the amorphous texture of the ZnTe film and interfacial defects.



Figure 6.3: Dark *I-V* characteristics of the ZnTe/*n*-GaAs and *n*-GaAs samples. Here Al (+) and Al (-) polarity means top ZnTe film is connected with the positive and negative terminals of the power supply via the Al electrode. *n*-GaAs also has the same polarity configuration.

#### 6.3.2 Intrinsic photocurrent spectra of ZnTe/n-GaAs heterostructures

Figures 6.4 (a) and 6.4 (b) show the intrinsic (without any bias) responsivity spectra of ZnTe/*n*-GaAs and *n*-GaAs at different optical chopper frequencies, respectively. Responsivity was observed at zero bias pointing to the fact that the sample possesses a built-in potential. Clearly, the fundamental absorption edge of GaAs starting at 1.41 eV defines the de facto PC threshold of the samples. In spite of that common feature, the PC spectra of the investigated structures are quite different: First, the spectral pattern of the ZnTe/*n*-GaAs device is narrower because the PC is almost fading away at higher energies with respect to the *n*-GaAs device. The PC signal decrease is caused by the effective absorption in the ZnTe layer and simultaneously by its amorphous texture, which prevents effective carrier transport across the heterojunction. As a further consequence of the non-crystallinity, there is no PC spectra feature at the intrinsic ZnTe band gap (2.26 eV). Second, in contrast to the *n*-GaAs sample, the PC of the ZnTe/*n*-GaAs hetero-pairing exhibited a frequency independent point in the proximity of 1.88 eV, where all measured PC spectra met within a small jitter of 10 meV. The obvious feature of this point is the inversion of the PC dependence on frequency, *i.e.*, at photon energies larger than 1.88 eV, slower chopping frequencies result in the larger PC response as expected for "slow" amorphous materials. Consequently, the energy of 1.88 eV represents the isosbestic point of the formed sample. Considering the pulsed-laser deposited ZnTe absorption coefficient of about 10<sup>4</sup> cm<sup>-1</sup> at 1.88 eV  $^{134}$ , the typical penetration depth is 1  $\mu$ m, which corresponds to the thickness of the deposited ZnTe layer. As a consequence, for energies below 1.88 eV, the ZnTe film becomes more and more transparent and the PC signal is dominantly carried by the "fast" GaAs substrate. Hence, the crossover between the absorption regions causes the isosbestic PC feature of the hetero-pairing.



Figure 6.4: Intrinsic APC spectra of (a) ZnTe/*n*-GaAs and (b) *n*-GaAs devices at different optical chopper frequencies.

#### 6.3.3 Photonic Zn and Te doping in GaAs by PLD

A further difference between the responsivity spectra in figures 6.4 (a) and (b) is that the ZnTe/*n*-GaAs heterostructure exhibits a tiny feature below the GaAs band gap centered at 1.37 eV after all signals dropped to zero at about 1.40 eV. It looks as if the PC below the GaAs absorption edge might have caused by absorption in the ZnTe film since the optical band gap of infrared PLD ZnTe on glass is at 1.32 eV. However, the contribution to the intrinsic PC of ZnTe below absorption edge of GaAs is not expected because of its low crystallinity. Additionally, the narrow line width of the observed feature does not compare with the previously reported broad ZnTe PC in ref. 134. Therefore, the sharp peak below 1.37 eV is attributed to the absorption transition in the GaAs substrate, which was caused by Zn and Te doping. In fact, Zn and Te atoms are known dopants for GaAs, and therefore, during PLD doping might have resulted due to the forced build in of Zn and Te atoms simultaneously in the lattice of the GaAs. Consequently, acceptor and donor levels are formed and the absorption below the GaAs band gap is caused by acceptor-to-donor transitions, whose energy is expressed by <sup>135</sup>

$$E = E_{\rm g} - E_a - E_d + \frac{e^2}{4\pi\varepsilon\varepsilon_0 r}$$
(6.1)

where  $E_g$  is the band gap energy,  $E_a$  is the acceptor ionization energy,  $E_d$  is the donor ionization energy, e is the elementary charge,  $\varepsilon$  is the permittivity of GaAs (=13.1),  $\varepsilon_0$  is the permittivity of vacuum, and r is the spatial separation between donors and acceptors. Due to the rather low doping concentration of the GaAs substrate, it is fair to use the intrinsic value for the band gap, i.e.,  $E_g$  =1.424 eV. For GaAs, with  $E_a$ =0.031 eV for Zn and  $E_d$ =0.030 eV for Te<sup>136</sup>, the value of  $E_g - E_a - E_d$ =1.363 eV, which is 0.015 eV smaller than 1.378 eV. Attributing the difference to the Coulomb term in Eq. (6.1) requires r=73 Å, which is approximately ten times the lattice constant. This result is rational since large values of r are common in GaAs due to the shallow impurity ionization energies. Based on the result of Eq. 6.1, it is concluded that Te and Zn doping of GaAs during PLD cause the narrow PC peak below 1.4 eV. This acceptor-donor transition is depicted in the figure 6.5 with a band diagram.



Figure 6.5: Band structure modification of GaAs due to doping of Zn and Te atoms.

#### 6.3.4 Bias dependence of the responsivity of ZnTe/n-GaAs

Figure 6.6 (a) depicts the bias dependence of the responsivity of the ZnTe/*n*-GaAs heterostructure at constant chopping frequency of 650 Hz. Here positive bias means that ZnTe was connected via the top Al contact with the positive terminal of the power supply; negative bias assigns reversed polarity. Figure 6.6 (b) shows the equivalent measurements on the *n*-GaAs reference sample. Above 1.4 eV, both samples show an increase in the responsivity with negative bias while a positive bias moves the signal below the intrinsic response at 0 V. That behavior implies that the sample acts like a photodiode with its anode at the Al contact. Below

1.4 eV in figure 6.6 (a), the impact of the bias is inversed, *i.e.*, a strong growth of the PC response is observed for positive bias. Furthermore, it is worthwhile to stress that zero touchdowns between lock-in recorded PC features indicate current inversion within the hetero-pairing pointing to a photonic bandstructure modification, which reverses the intrinsic device polarization. It is stressed that ZnTe/*n*-GaAs samples were also prepared employing PLD at 532 nm and 355 nm, and all the above mentioned features of the heterostructures were observed in these samples as well.



Figure 6.6: APC spectra at 650 Hz of (a) ZnTe/*n*-GaAs and (b) *n*-type GaAs at different biases. Definition of bias polarity is identical with figure 6.3.

# 6.4 Conclusions

ZnTe/*n*-GaAs heterostructures were formed with low-temperature PLD using nanosecond laser pulses at 1064 nm. By employing a lock-in technique, frequency as well as bias dependence of the PC was studied and the results have been published.<sup>137, 138</sup> Intrinsic PC was observed though the sample did not exhibit a distinct diode like characteristic such as previously formed PLD ZnTe/*n*-Si structures.<sup>139</sup> Based on this result, the influence of the ZnTe film is of passive nature because the PC spectra are determined by the absorption alteration of the GaAs substrate due to Zn and Te doping during PLD rather than by active absorption in the deposited ZnTe film itself.

These results are of more peculiar character than the studies on ZnTe/*n*-Si structure because of the observation of a peak below the GaAs band gap energy and the appearance of an isosbestic point. Specifically, since the isosbestic points have their applications in spectrometer calibration,<sup>140</sup> transient spectroscopy,<sup>141</sup> and oximetry,<sup>142</sup> it is probable that chopper frequency independent points of semiconductor PC spectra might find technological utilizations as well. The isosbestic point, whose origin is apparently caused by the absorption crossover at the amorphous-crystalline interface of ZnTe/GaAs heteropairing, justifies further research on the merging of amorphous films with crystalline materials and, eventually, will pave the way for technological applications in the field. Furthermore, the results show that PLD might find applications to dope semiconductor surfaces in a "photonic" manner, which might be ultimately exploited for the technological applications.

# 7 SUMMARY

The research presented in this dissertation comprises several novel findings that include the successful merger of CdS with plastic, APC quenching in thin-film CdS using blue light, PC spectra modifications of GaAs employing PLD. All these findings are reported for the first time and led to three publications, which are listed in the appendix. The summaries of the thesis are given below.

First, this work proved that an inorganic semiconductor such as CdS can be merged with a light-weight, flexible, and sturdy organic host in a simple and straightforward way employing low-temperature PLD. The CdS film on plastic surface was investigated by AFM that showed an elongated mosaic like structure with a smooth surface. On the other hand, PLD CdS films on glass results in nanocrystalline structures embedded in the amorphous matrix. The EPMA of the film showed that the stoichiometry of the target is fairly preserved in the film. The thickness distribution studies revealed that the film area was significantly growing when the fluence was increased. The CdS on plastic was photosensitive with a blue shifted photocurrent peak at 2.54 eV with respect to the CdS single crystal. The shift is attributed to the nano-size effect and/or strain in the film-substrate interface. The formed photosensitive CdS/plastic heteropairing might be exploited to make inorganic/organic hybrid photodetectors. In conclusion, it is proved that PLD is an effective tool to form smooth, stoichiometric, and photosensitive thin-film CdS on plastic. The results demonstrated the versatility of PLD to form technologically useful semiconductor thin films on substrates with or without specified crystal structure.

Second, in order to exploit the application potential of thin-film CdS in optoelectronics, APC quenching experiments using blue light excitation were carried out. The experiments demonstrate that thin-film CdS can be used for APC quenching and modulation purposes by

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employing a lock-in technique in conjunction with low-power blue LEDs in a simple and straightforward way. APC quenching is achieved by shortening of APC charge carriers into DPC carriers and due to stimulated recombination of APC electrons with DPC holes generated by the blue LED. The degree of quenching depends on the optical chopping frequency, intensity of quenching light, and the applied bias. The work emphasizes the application of CdS film and lock-in principle for modulation and quenching techniques in optoelectronics rather than for applications in metrology only. This phenomenon might be used in future optoelectronic devices to control APC using constant light.

Third, the final portion of this dissertation is committed to PC spectroscopy of ZnTe/*n*-GaAs heterostructures prepared by PLD. This sample did not exhibit the diode characteristics but shows intrinsic PC response. It is found that the PC spectrum of GaAs is modified by the deposition of thin-film ZnTe on top of it. The PC spectra are strongly influenced by the absorption alteration of the GaAs due to Zn and Te doping of the GaAs substrate during PLD rather than by active absorption in the deposited ZnTe film itself. The isosbestic point formed is caused by the absorption crossover at the amorphous-crystalline interface of ZnTe/GaAs heteropairing. All these findings emphasize the capability of PLD to dope materials resulting in unique optoelectronic properties that might find applications in the future optoelectronic devices.
## 8 APPENDIX

#### 8.1 Publications and patent list

#### 8.1.1 Refereed journal articles

- Acharya, K. P.; Khatri, H.; Ullrich, B. "Physical characterization of *n*-GaAs on *p*-Si formed by low-temperature pulsed-laser deposition," *J. Appl. Phys.*, 2009, 105, 103111.
- Acharya, K. P.; Erlacher, E; Ullrich, B. "Responsivity properties of ZnTe/GaAs heterostructures formed with pulsed-laser deposition," *Sol. Energy Mater. Sol. Cell* 2009, 93, 25.
- Liyanage, C.; Acharya, K. P.; Ullrich, B. "Photonic laser digitizing and pattern variation with flexible CdS and GaAs films," *J. Opt. Soc. Am. B*, 2009, 96, 254.
- Acharya, K. P.; Skuza, J. R.; Lukaszew, R. A.; Liyanage, C.; Ullrich, B. "CdS thin films formed on flexible plastic substrates by pulsed-laser deposition," *J. Phys.: Condens. Matter*, 2007, 19, 196221.
- Acharya, K. P.; Erlacher, A.; Ullrich, B. "Responsivity of ZnTe/*n*-GaAs heterostructures formed by infrared nanosecond laser deposition," *J. of Appl. Phys.*, 2007, 102, 073107.
- Acharya, K. P.; Erlacher, A.; Ullrich, B. "Optoelectronic properties of ZnTe/Si heterostructures formed by nanosecond laser deposition at different Nd:YAG laser lines," *Thin Solid Films*, 2007, 515, 4066.

#### 8.1.2 Proceedings article

Acharya, K. P.; Ullrich, B. "Responsivity modulation of thin-film CdS by means of lockin technique," *Proc. SPIE* **2008**, 6890, 68900Q

#### 8.1.3 Patent under review

Ullrich, B.; Acharya, K. P. "Method and apparatus for producing cadmium sulfide layers on flexible substrate and devices incorporating same," US patent application 12/074, 518, filed March **2008** (US patent pending).

## 8.2 Materials and equipment used in the experiment

#### 8.2.1 Materials

- **ZnTe**: Type: Hot pressed polycrystalline; Supplier: Target Material Inc.; Purity: 99.999%; Diameter: 25.5 mm; Thickness: 6.2 mm,
- CdS: Type: Hot pressed polycrystalline; Supplier: Target material Inc.; Purity: 99.99%;
   Diameter: 25.6 mm; Thickness: 6.4 mm.
- GaAs: Type: Single crystal (100); Supplier: Wafer Technology Ltd, UK; Dopant: Si; Career concentration: 3x10<sup>16</sup> cm<sup>-3</sup>; Growth method: Vertical gradient freeze; Thickness: 511-520 μm, Diameter: 5 cm
- Plastic: Polyethylene terephthalate, Supplier: Staples.

#### 8.2.2 Equipment list

- Spectron laser system Nd: YAG laser, 6 ns, 1100 mJ.
- Coherent field master GS power energy analyzer.
- Sloan digital thickness monitor 200
- Edwards rotary vane E2M18 mechanical pump
- Varian turbo-V60 pump
- Perkin Elmer Ultek ion pump

- Keithley 2400 general purpose source meter
- Keithley 6485 picoammeter
- Molecular Imaging's PicoSPM II AFM
- Ushio 250 W halogen lamp
- Spex 500 M monochromator
- SR 230 lock-in amplifier
- Scientific instruments optical chopper
- Keithley 230 power supply
- Oceanoptics UV-Visible spectrometer.
- Newport universal motion controller driver and stage
- Cary 50 Scan UV-Visible spectrophotometer
- XPERT-PRO X-ray Diffractometer.
- Hitachi 2700 Scanning electron microscope.
- JDS Uniphase 1136P HeNe laser, 633 nm
- Agilent oscilloscope, 54610B, 500 MHz
- Melles Griot, argon ion laser

Properties	Materials				
	CdS	ZnTe	GaAs		
Transition type	Direct	Direct	Direct		
Band gap energy, eV	2.50 (496 nm)	2.26 (551 nm)	1.42 (873nm)		
Crystal structure	ZB and W*	ZB and W	ZB		
Lattice constant, Å	$a_0 = 5.82$	$a_0 = 6.10$	<i>a</i> <sup>0</sup> =5.653		
$(a_0, c_0 \text{ axex })$	$(a_0=4.13, c_0=6.71)$	$(a_0=4.27, c_o=6.99)$			
Molecular weight	144.47	192.99	144.64		
Density, gm cm <sup>-3</sup>	4.82 (W),4.50 ( ZB)	5.72	5.32		
Melting point, K	1750	1568	1510		
Electron mobility( cm <sup>2</sup> /V.s)	300	340	8000		
Hole mobility( cm <sup>2</sup> /V.s)	50	100	340		
Thermal expansion coeff. K <sup>-1</sup>	3.5 x10 <sup>-6</sup>	8.6x10 <sup>-6</sup>	5.7x10 <sup>-6</sup>		
Static dielectric constant	11.6	9.7	12.8		
Specific Heat J/(kg K)	470	608	330		
$\Delta G_{f}^{o}^{*}$ (kcal/mole)	-37.4 (ZB)	-27(ZB)	-16.2		
$\Delta H^{o}{}_{f}^{\dagger}$ (kcal/mole)	-38.7 (ZB)	-28.1(ZB)	4.13		

# Table 8.1: Physical properties of CdS, ZnTe, and GaAs.<sup>143,144,145</sup>

\* ZB: Zincblende (cubic), W: wurtize (hexagonal)

<sup>\*</sup> Standard free energy of formation † Standard heat of formation

## Table 8.2: Cadmium sulfide X-ray diffraction data<sup>‡</sup>

System: Hexagonal

2Θ	Relative intensity	h	k	1
24.929	631	1	0	0
26.660	449	0	0	2
28.328	999	1	0	1
36.821	253	1	0	2
43.905	420	1	1	0
48.117	406	1	0	3
51.148	62	2	0	0
52.108	305	1	1	2
53.077	133	2	0	1
54.919	20	0	0	4
58.601	49	2	0	2
61.212	20	1	0	4
67.164	115	2	0	3
69.647	75	2	1	0
71.263	85	2	1	1
72.829	40	1	1	4
75.975	91	1	0	5
78.343	8	2	0	4

<sup>&</sup>lt;sup>‡</sup> Inorganic Crystal Structure Database, International Center for Diffraction Data, # 067776.

80.709	43	3	0	0
83.766	101	2	1	3
86.840	44	3	0	2
87.526	7	0	0	6

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