UNIVERSITI PUTRA MALAYSIA

ELECTRICAL AND THERMAL PROPERTIES OF THE COMPOSITE SEMICONDUCTORS, (CdSe)_{1-x}(Se)_x AND (CdS)_{1-x}(S)_x

NUR AMALINA MUSTAFFA

FS 2008 43
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By

NUR AMALINA MUSTAFFA

Thesis Submitted to the School of Graduate Study, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2008
DEDICATION

Specially Dedicated to My Beloved Family,

Mustaffa Tupir Mohamed & Che Norlia Abdullah
Mohd. Taufiq Mustaffa
Amal Nabilah Mustaffa
Amal Aqilah Mustaffa

and to My Beloved ONE,

Muhammad Naguib Thasleem Mohd.

for their unconditional support, inspiration, patience and love.
ELECTRICAL AND THERMAL PROPERTIES OF THE COMPOSITE SEMICONDUCTORS, (CdSe)\(_{1-x}(Se)_x\) AND (CdS)\(_{1-x}(S)_x\)

By

NUR AMALINA MUSTAFFA

October 2008

Chairman: Associate Professor Dr. Zainal Abidin Talib, PhD

Faculty: Science

A series of (CdSe)\(_{1-x}(Se)_x\) and (CdS)\(_{1-x}(S)_x\) composite semiconductors were prepared with different stoichiometric compositions of Se and S with x = 0 to x = 0.8 both in the interval of 0.2 by varying the ratio of CdSe:Se and CdS:S in a reaction mixture. The following powder of CdSe, Se and CdS, S were used as the starting materials.

X-ray diffraction analysis was carried out in order to investigate the structural character of the composites obtained. For both samples, analysis of the X-ray diffractogram revealed that the samples were in hexagonal form. Atomic Force Microscopy (AFM) was used for analyzing the surface morphology of the composites samples.

Parallel plate method was used to determine the dc conductivity of all samples in the temperature range of 300 – 460 K. Both samples, (CdSe)\(_{1-x}(Se)_x\) and (CdS)\(_{1-x}(S)_x\), show variation in \(\ln \sigma\) with 1000/T (K\(^{-1}\)) that indicated that there are three distinct
temperature zones with three different characteristic regions. This behaviour suggests that two types of conduction mechanisms were presence. The first region is identified as the extrinsic region, the second region is the intermediate region and the third region is the intrinsic region. For both series of samples, the conductivity obtained for all series of samples shown similar trend, the dc conductivity increased as the temperature increased. For \((\text{CdSe})_{1-x}(\text{Se})_x\) composite where \(x = 0\), the dc conductivity at 300 K is about \(10^{-8}\) S/cm and increase up to \(10^{-5}\) S/cm at 460 K. While for \((\text{CdS})_{1-x}(\text{S})_x\) composite where \(x = 0\), the dc conductivity at 300 K is about \(10^{-10}\) S/cm and increase up to \(10^{-8}\) S/cm at 503 K. The activation energies were calculated from the Arrhenius relation and the values of the activation energy indicated that all the prepared samples were semiconductors.

The ac conductivity properties of polycrystalline \((\text{CdSe})_{1-x}(\text{Se})_x\) and \((\text{CdS})_{1-x}(\text{S})_x\) were studied in temperature range of 300 – 523 K and frequency range of 100 Hz – 1 MHz using Impedance Analyzer. Obtained data of ac conductivity revealed that at low frequency \(\sigma_{AC}(\omega)\) was independent of frequency and proportional to \(\omega^s\) at higher frequency for all samples. The values of the frequency exponent, \(s\) were found to decrease with increasing temperature which suggested that the dominant transport process as Correlated Barrier Hopping (CBH).

Thermal diffusivity values of both \((\text{CdSe})_{1-x}(\text{Se})_x\) and \((\text{CdS})_{1-x}(\text{S})_x\) were investigated using photoflash technique. Thermal diffusivity value decrease as we increase the Se and S compositions in the samples.
Abstrak tesis ini yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SIFAT ELEKTRIK DAN PENGUKURAN PENYERAPAN TERMA BAHAN KOMPOSIT SEMIKONDUKTOR, (CdSe)\(_{1-x}(Se)_x\) DAN (CdS)\(_{1-x}(S)_x\)

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Dalam kajian ini, siri (CdSe)\(_{1-x}(Se)_x\) dan (CdS)\(_{1-x}(S)_x\) komposit semikonduktor telah disediakan dalam pelbagai komposisi stoichiometri Se dan S dengan x = 0 hingga x = 0.8 kedua-duanya, pada selang sebanyak 0.2 dengan mempelbagaikan ratio CdSe :Se dan CdS :S dalam bahan tindak balas. CdSe, Se dan CdS, S digunakan sebagai bahan asas di dalam penyediaan sample.

Belauan sinar-X telah digunakan untuk mengeenal pasti struktur bahan komposit yang telah diperolehi. Bagi kedua-dua bahan, struktur heksagonal diperolehi daripada spektra belauan sinar-X. Mikroskop Daya Atom (AFM) digunakan untuk mengkaji struktur permukaan bahan komposit tersebut.

Kaedah kepingan selari telah digunakan untuk mengkaji kekonduksian dc bagi semua bahan di dalam julat suhu 300 - 460 K. Bagi kedua-dua sample, (CdSe)\(_{1-x}(Se)_x\) dan
(CdS)_{1-x}(S)_x, graf ln σ melawan 1000/T (K^{-1}) menunjukkan, terdapat tiga zon dengan tiga ciri yang berbeza. Ini menunjukkan terdapat dua jenis kekonduksian yang terlibat. Zon pertama merupakan zon yang tidak tulen, zon kedua ialah zon pertengahan, dan zon ketiga merupakan zon yang tulen. Untuk kedua-dua siri sample, didapat kekonduksian dc meningkat apabila suhu meningkat. Bagi (CdSe)_{1-x}(Se)_x apabila x = 0, kekonduksian dc pada suhu 300 K ialah $10^{-8}$ S/cm dan meningkat kepada $10^{-5}$ S/cm pada suhu 460 K. Manakala bagi sample (CdS)_{1-x}(S)_x apabila x = 0 pula, kekonduksian dc meningkat dari $10^{-10}$ S/cm pada suhu 300 K ke $10^{-8}$ S/cm pada suhu 503 K. Tenaga pengaktifan telah dikira daripada persamaan Arrhenius dan nilai-nilainya menunjukkan semua bahan yang telah disediakan merupakan bahan semikonduktor.

Kekonduksian ac bagi bahan (CdSe)_{1-x}(Se)_x and (CdS)_{1-x}(S)_x telah dikaji di dalam julat suhu 300 - 523 K dan julat frekuensi 100 – 1 MHz menggunakan Impedance Analyzer. Data yang telah diperolehi menujukkan pada julat frekuensi yang rendah, $\sigma_{AC}(\omega)$ adalah tidak bergantung pada frekuensi tetapi berkadar pada $\omega^s$ pada frekuensi yang lebih tinggi pada semua sample bahan. Nilai frekuensi exponen, s didapat menurun dengan penurunan suhu. Ini menunjukkan proses kekonduksian di dalam bahan tersebut telah dikenal pasti sebagai Loncatan Halangan Berkaitan (CBH).

Nilai penyerapan terma bagi kedua-dua bahan telah diperolehi daripada kaedah sinaran flash kamera. Nilai penyerapan terma menurun dengan pertambahan Se and S di dalam bahan tersebut.
ACKNOWLEDGEMENTS

First and foremost, I would like to extend my praise to Allah s.w.t that gives me the strength, determination, patience and courage to produce this thesis.

I would like to express my special gratitude to Assoc. Prof. Dr. Zainal Abidin Talib for all he has done for me as a research advisor. Without his assistance, guidance, ideas, supervision and encouragement, I would not be able to complete my graduate studies at Universiti Putra Malaysia. I would also like to extend my sincere appreciation to my co-supervisor, Assoc. Prof. Dr. Wan Mohd. Daud Wan Yusoff for his advice and helpful discussion during my period of study. I would also like to express my gratitude to all the lecturers and staff in Physics Department for providing research facilities and for all their help and cooperation given throughout my study. I gratefully acknowledge the Academy of Sciences Malaysia and MOSTI through SAGA Grant (5486512) for their financial support. I would also like to acknowledge Universiti Teknologi Mara and Ministry of Higher Education for the scholarship that allows me to complete this work.

My sincere thanks to all my friends who have directly or indirectly contributed toward the success of this study. Last but not least, to my beloved parents, siblings, relatives and also to my beloved Naguib, I would like to extend my special thanks for their love, understanding, support, patience and encouragement. Without them, the path to this thesis will be a lonely endeavor. Your love and belief have given me strength to walk through difficulties to achieve success.
I certify that an Examination Committee met on 14th October 2008 to conduct the final examination of Nur Amalina Mustaffa on her Master of Science thesis entitled “Electrical and Thermal Properties of the Composite Semiconductors, \((\text{CdSe})_{1-x}(\text{Se})_x\) and \((\text{CdS})_{1-x}(\text{S})_x\)” in accordance with Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the examination committee are as follows:

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Date: 15th January 2009
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been fully acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

______________________________

NUR AMALINA MUSTAFFA

Date:
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<td>Indium-Tin Oxide</td>
</tr>
<tr>
<td>S</td>
<td>Sulphur</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space Charge Limited Conductivity</td>
</tr>
<tr>
<td>Se</td>
<td>Selenium</td>
</tr>
<tr>
<td>SILAR</td>
<td>Successive Ionic Layer Absorption and Reaction</td>
</tr>
<tr>
<td>SP</td>
<td>Screen Printing</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
</tr>
<tr>
<td>VE</td>
<td>Vacuum Evaporation</td>
</tr>
<tr>
<td>VRH</td>
<td>Variable Range Hopping</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction Analysis</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

\( \rho \)  
Resistivity

\( \sigma \)  
Electrical Conductivity

\( I \)  
Current though the object

\( V \)  
Potential difference across the object

\( R \)  
Resistance of an object

\( L \)  
Thickness of the pellet sample

\( A \)  
Cross sectional area of the object

\( n \)  
Number of the charge carriers in the material

\( q \)  
The charge carrier by each carrier

\( \mu \)  
Mobility of the carrier

\( \omega \)  
Angular frequency

\( E_g \)  
Energy gap

\( E \)  
Electric field

\( W_m \)  
Maximum barrier height

\( s \)  
Frequency exponent

\( k_B \)  
Boltzmann constant

\( \tau_o \)  
Characteristic relaxation time

\( W_H \)  
Effective barrier height

\( \alpha \)  
Thermal Diffusivity

\( t_{0.5} \)  
Time to reach 50% of the maximum

\( G \)  
Conductance
CHAPTER I

INTRODUCTION

1.1 Introduction

The phenomenal growth in research effort devoted to the study of semiconductor, whose conductivity lies between a conductor and an insulator, during the past two decades has resulted in a very large literature on the subject. The first feature used to distinguish semiconductors from electrical conductors was their negative temperature coefficient of resistance which their resistance generally falls as the temperature is raised. This effect has been first notice by Michael Faraday when carrying his experiments on silver sulphide (Smith, 1978).

II-VI compound semiconductors and their alloys have been the subject of extensive research for several decades in both fundamental studies and device applications. The broad range of band gaps and lattice constants, the highly polar nature of these materials and the possibility of incorporating magnetic ions isoelectronically have been key factors that distinguish II-VI materials from their III-V counterparts. Because of this, II-VI semiconductors are particularly attractive for a wide range of applications such as infrared lasers and detectors, blue-green lasers and light emitting diodes (LEDs), nonlinear optical materials, magneto-optical devices and radiation detectors. Such applications have significantly improved photonics, computers, telecommunications as well as many other industries and technologies.
Nevertheless, during 1960s and 1970s II-VI materials did not receive much attention from the semiconductor community due to limitations of growth and doping techniques. Only in the 1980s and 1990s, with the advent of advanced crystal growth techniques such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), did a new surge of research devoted to II-VIs emerge. Presently, with progress along many new directions, including spintronics, nonlinear optical devices and, especially, quantum heterostructures, II-VI materials are beginning to be looked at again.

Among the II-VI materials, Cadmium Selenide (CdSe) and Cadmium Sulphide (CdS) are of great interest because of their potential in many practical applications such as solar cells, optical detectors, field-effect transistors, dosimeters of ionized radiation and optoelectronics devices. CdSe and CdS are very promising for solar cells because of their suitable direct band gap as the band gap for CdS is 2.4 eV (Prabahar and Dhanam, 2005) at 300 K and CdSe is 1.74 eV (Shreekanthan et al. 2003) at 300 K. Furthermore, their optical absorption and good stability also make them ideal and suitable as a medium for solar cells.
1.2 II-VI Semiconductor

For the last five decades, a huge number of research activities have been devoted to the studies of the crystalline structure of binary semiconductor materials, resulting in the fact that this physical property has been well known and documented. Among the types of the crystalline structure, diamond, zinc blende and wurzite are common ones and the semiconductors possessing these structures are of interest for device applications. Depending on growth conditions, one can obtain both the cubic (diamond, zinc blende) and the hexagonal (wurzite) structures for most of II-VI binaries. These crystalline structures are illustrated in Fig. 1.1 below.

![Crystalline structures of the a) diamond and zinc blende (cubic) and b) wurzite (hexagonal) semiconductors](image)

*Figure 1.1: Crystalline structures of the a) diamond and zinc blende (cubic) and b) wurzite (hexagonal) semiconductors*
As mentioned, the crystal structure of a semiconductor depends on growth conditions. During the growth of thin films of the II-VIs, it is common to obtain the cubic and hexagonal phases simultaneously (which is rarely found in bulk materials). Table 1.1 below summarizes the lattice parameters of CdTe and CdSe, II-VI binaries with both zinc blende and wurzite structures.

Table 1.1: Semiconductor crystalline structure

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zinc blende (Å)</th>
<th>Wurzite (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.478</td>
<td>2.805</td>
</tr>
<tr>
<td>CdSe</td>
<td>6.050</td>
<td>2.620</td>
</tr>
</tbody>
</table>

1.3 Cadmium Selenide, CdSe

Cadmium selenide, CdSe is a solid, binary compound of cadmium and selenium. This material is transparent to infra-red (IR) light, and has seen limited use in windows for instruments utilizing IR light. CdSe in its wurzite crystal structure is an important II-VI semiconductor. As a semiconductor CdSe has a band gap of 1.74 eV (Shreekanthan et al. 2003) at 300 K and a n-type semiconductor as reported by Velumani et al (2004). CdSe is also being developed for use in photoconductors, solar cells, thin film transistors, gas sensors, acousto-optic devices, photographic photoreceptors, photoelectrochemical (PEC) cells, non-linear optics, gamma-ray detectors, large-screen liquid crystal display (Velumani et al., 2004).