OPTICAL AND ELECTRICAL CHARACTERISTICS OF E-BEAM EVAPORATED ZnS_xSe_{1-x} THIN FILMS

By
KHEDR MOHAMED MOSTAFA ABO-HASSAN



A thesis submitted for the degree of Doctor of Philosophy

At the Institute of Postgraduate Studies and Research

University of Malaya

Kuala Lumpur

December, 1997
Perpustakaan Universiti Malaya

Dimikrofiskan pada 19.01 . 2000

HAMSIAH BT. MOHAMAD ZAHARI IPR UNIT REPROGRAFI PERPUSTAKAAN UTAMA

ACKNOWLEDGEMENT

To the Almighty Allah I give thanks for giving me the help and strength to complete this research. I would also like to express my sincere gratitude to both of my supervisors: Professor Dr. S. Radhakrishna and Professor Dr. Muhamad Rasat Muhamad whose guidance, advice, patience and assistance provided me the impetus to begin and complete this work.

I am indebted to Mrs Vijaya Lakshmi from I. P. S. P., University of Malaya for her great effort in obtaining SEM micrographs and EDX spectra.

My thanks are also due to the staff members in Physics Department, especially in the Solid State Laboratory, for allowing me to use the equipment and facilities during the experimental part of this work.

To my friends and colleagues in I. P. S. P. and in Material Science Laboratory, especially Mr. S. Anandan, I express my deep appreciation for constructive discussion.

I am grateful to Miss Habibah binti Shaari in the office of the Department of Physics, and Miss Zubaidah binti Yusup in the office of I. P. S. P. for their assistance. My special thanks are registered to Miss Teoh Mei Lin for her encouragement and assistance in reading the draft of this thesis.

I would like to acknowledge here that this work has been supported by Physics Department, IRPA 09-02-03-0138. My gratitude and appreciation also go to Public Service Department Malaysia for awarding me a scholarship under the Malaysian Technical Cooperation Programme (MTCP) during the course of this work.

I would like to express my profound gratitude to the Arab Student Aid International for awarding me a scholarship loan during this study.

Finally, this work would not have been possible without the encouragement of my beloved parents, Mohamed and Zarifa, four brothers and five sisters and their families who prayed for my success and gave me every kind of support I need.

Contents

ACKNOWLEDGEMENT	ii
CONTENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vii
ABSTRACT	xii
ABSTRAK	χv
CHAPTER ONE: INTRODUCTION AND THEORETICAL REVIEW	1
1.1 Introduction	1
1.2 Methods of thin film preparation	3
1.3 Crystallographic properties of II-VI materials	8
1.3.1 Zincblende structure	8
1.3.2 Wurtzite structure	9
1.3.3 Zinc sulphide (ZnS)	11
1.3.4 Zinc selenide (ZnSe)	12
1.3.5 zinc sulpho-selenide (ZnS-ZnSe)	12
1.4 Band structure and optical properties	12
1.4.1 Band structure	12
1.4.2 Fundamental absorption.	18
1.5 Electrical properties.	20
1.5.1 Energy band models.	22
1.5.2 Temperature dependence of dc-conductivity	25
CHAPTER TWO: EXPERIMENTAL TECHNIQUES	29
2.1 Electron beam apparatus.	29
2.2 Sample preparation	30
2.3 EDX and SEM	34
2.4 X-ray diffraction.	37
2.5 UV-VIS-Spectrophotometer	38

CHAPTER THREE: CALCULATION OF THICKNESS AND OPTICAL PARAMETERS OF THIN FILM BY USING OPTICAL TRANSMISSION DATA
DATA
3.1 Introduction
3.2 Theory
3.3 The proposed method of calculation. 47
3.5 The proposed memory of constitution.
3.3.1 Calculation of thickness
3.3.2 Calculation of <i>n</i> and <i>k</i>
3.4 The envelope method
CHAPTER FOUR: STRUCTURAL ANALYSIS
4.1 Introduction
4.2 Results and Discussion
•
CHAPTER FIVE: OPTICAL CHARACTERISTICS
5.1 Introduction
5.2 Optical transmission
5.3 Refractive index and dielectric function
5.4 Absorption coefficient and the fundamental energy gap
CHAPTER SIX: ELECTRICAL PROPERTIES OF ZnS, Se _{1-x} THIN FILMS 112
6.1 Introduction
6.2 Current-Voltage (I-V) characteristics
6.3 Temperature dependence of dc-conductivity
6.4 The effect of film structure on the dc-conductivity
CHAPTER SEVEN: CONCLUSION AND SUGGESTIONS FOR FURTHER
į
WORK 139

LIST OF TABLES

- Table 1.1(a): X-ray diffraction data for cubic zinc sulphide (β-ZnS) [65].
- Table 1.1(b): X-ray diffraction data for hexagonal zinc sulphide (α-ZnS) [65].
- Table 1.2: X-ray diffraction data for cubic zinc selenide (ZnSe) [65].
- Table 3.1: Values of M, t and n for $\lambda_1 = 1530$ nm and $\lambda_2 = 1318$ nm obtained from the proposed method.
- Table 4.1: Film thickness and deposition rate for $Z_{NS_x}S_{C_{1:x}}$ films grown by electron beam evaporation onto glass substrates at 60 °C.
- Table 4.2: Atomic and weight percentages of Zn, Se and S, as observed in EDX, for ZnS_xSe_{1-x} samples prepared by electron beam evaporation onto glass substrates at 60 °C.
- Table 4.3: x values and the excess S (AT%) as calculated according to procedure (I), atomic and weight percentages of Zn, Se and S according to equation 4.1 by assuming $W_1 = 9$ and $Y_1 = 4$.
- Table 4.4: x values and the excess Se (AT%) as calculated according to procedure (II), atomic and weight percentages of Zn, Se and S according to equation 4.7 by assuming $W_2 = 16$ and $Y_2 = 5$.
- Table 4.5 (a): x values and the excess S (AT%) as calculated according to procedure (I), atomic and weight percentages of Zn, Se and S according to equation 4.1 by assuming $W_1 = 9$ and $Y_1 = 4$.
- Table 4.5 (b): x values and the excess Se (AT%) as calculated according to procedure

 (II), atomic and weight percentages of Zn, Se and S according to equation

 4.7 by assuming W₂= 16 and Y₂= 5.

- Table 4.5 (c): x values and the excess SSe (AT%) as calculated according to procedure (III), atomic and weight percentages of Zn, Se and S according to equation 4.10 by assuming $W_3 = 26$ and $Y_3 = 5$.
- Table 4.6: x, 2θ , $\Delta d/d$, B, B_m, B_g and D values for $ZnS_xSe_{1:x}$ thin films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Table 4.7: Elastic compliances S_{ij} and elastic stiffnesses C_{ij} for ZnS [95] and ZnSe [26] cubic crystals, S_{ij} values are deduced from C_{ij} values using equations (4.16-4.18), C_0 values and the reduced stiffnesses C_{ij} for ZnS and ZnSe single crystals.
- **Table 4.8:** x and strain (Δa_0 %) for ZnS_xSe_{1-x} thin films, C_0 values, C_{ij} and S_{ij} for ZnS_xSe_{1-x} single crystals and stress SS for the films.
- Table 5.1: dispersion parameters for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Table 5.2: Deformation potentials of ZnS [6, 118] and ZnSe [119] materials.
- Table 5.3: Deformation potentials, shift in E_g caused by the stress $(\delta E_H$ and $\delta E_{<111}>$), reduced effective mass, shift in E_g caused by grain size effect (ΔE_g) and the estimated crystal energy gap for ZnS_xSe_{1-x} materials.
- Table 5.4: γ_0/KT^* parameters and optical phonon energies for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Table 6.1: The experimentally determined values of β for ZnS_{0.41}Se_{0.59} and ZnS samples at high temperatures and the corresponding high-frequency dielectric constants ϵ^*_{PF} , ϵ^*_{PF} and ϵ^* , according to the Pooe-Frenkel and Schottky effects, respectively.

Table 6.2: The radius (α_0^{-1}) and density of localized states near the Fermi energy level $N(E_{\rm F})$, as estimated according to the variable range hopping model, for ${\rm ZnS_xSe_{1:x}}$ thin films, t is film thickness and D is the grain size in the film.

LIST OF FIGURES

- Figure 1.1: Geometry and processes of electron-beam evaporation [58].
- Figure 1.2: Zincblende. The arrangement of metal atoms and non-metal atoms in zincblende, the cubic form of ZnS [3].
- Figure 1.3: Wurtzite. The arrangement of metal atoms and non-metal atoms in wurtzite, the hexagonal from of ZnS [3].
- Figure 1.4: (a) Brillouin zone of the zincblende lattice and (b) double Brillouin zone of the wurtzite lattice [1].
- Figure 1.5: A schematic drawing of the band structures at the Γ -point for (a) zincblende (T_d -symmetry) and (b) wurtzite (C_{6V} -symmetry) [1].
- Figure 1.6: Band structure of ZnSe calculated by non-local pseudo-potential method

 [69].
- Figure 1.7: Band structure of cubic ZnS (a) and hexagonal ZnS (b) calculated using local pseudo-potential method [69].
- Figure 1.8: Sketch of Mott-CFO model for covalent semiconductors having three dimensional cross-linked network structure [71].
- Figure 1.9: Density of states g(E) suggested by Davis and Mott [79].
- Figure 1.10: Density of states g(E) suggested by Marshal and Owen for As₂Se₃ [71].
- Figure 2.1: Component parts of the six-position electron beam source (plane view) [73].
- Figure 2.2: Schematic diagram of a scanning electron microscope [77].
- Figure 2.3: Schematic diagram for the goniometer x-ray path [78].
- Figure 2.4: The schematic diagram of the UV-3101 PC optical system [79].

- Figure 2.5: (a) A cross sectional view of the chamber used in the deposition of the electrodes and (b) a plane and a cross section views of the deposited electrodes on the film.
- Figure 2.6: Schematic diagram for closed cycle refrigerator cryostat [80].
- Figure 3.1: Reflection and transmission of light by a single film.
- Figure 3.2: Transmittance spectrum for ZnS_{0.9}Se_{0.1} film prepared by electron beam evaporation onto glass substrate at 60 °C.
- Figure 3.3: Dispersions of n (a) and k (b) for ZnS_{0.9}Se_{0.1} film as calculated using the proposed and the envelope methods.
- Figure 3.4: Transmittance and reflectance spectra for ZnS_{0.9}Se_{0.1} thin film.
- Figure 4.1: EDX profiles for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 4.2: Scanning electron microscope photographs for polycrystalline ZnS_xSe_{1-x} thin films grown by electron beam evaporation onto glass substrates at 60 °C.
- Figure 4.3: X-ray diffraction patterns for polycrystalline ZnS_xSe_{1-x} thin films grown by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 4.4: The < 111 > inter-planar spacing d versus x for ZnS_xSe_{1.x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C, x values are determined according to procedures I, II and III.
- Figure 4.5: The lattice constant a_0 versus x for $ZnS_xSe_{1:x}$ thin films prepared by electron beam evaporation onto glass substrates at 60 ° C, x values are determined according to procedure I, II and III.

- Figure 4.6: d versus x for ZnS_xSe_{1-x} single crystals and thin films prepared by electron beam evaporation onto glass substrates at 60 0 C.
- Figure 4.7: a_0 versus x for ZnS_xSe_{1-x} single crystals and thin films prepared by electron beam evaporation onto glass substrates at 60 0 C.
- Figure 5.1: Transmission spectra, T_f %, versus the incident photon wavelength, λ , for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 5.2: Transmission spectra, T_t %, versus the incident photon wavelength, λ , for $ZnS_xSe_{1:x}$ thin films prepared by electron beam evaporation onto glass substrates at 60 $^{\circ}$ C.
- Figure 5.3: Dispersion of refractive index n (a) and extinction coefficient k (b) for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 5.4: Static refractive index n(0) versus x (a) for ZnS_xSe_{1-x} thin films and versus t (b) for $ZnS_0 gSe_{0.1}$ thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 5.5: Real part ϵ_1 (a) and imaginary part ϵ_2 (b) of the dielectric function versus E for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 5.6: Average energy gap \vec{E}_g versus x for ZnS_xSe_{1-x} films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 5.7: Covalent and ionic energy gaps, E_h and C, versus x for ZnS_xSe_{1-x} films prepared by electron beam e. vaporation onto glass substrates at 60 °C.

- Figure 5.8: Ln (E_h) versus $\ln(a_0)$ for ZnS_xSe_{1-x} films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 5.9: $1/(n^2-1)$ versus E^2 for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 5.10: Absorption coefficient versus photon energy for $ZnS_xSe_{1:x}$ thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 5.11: $(\alpha nE)^2$ (a) and $(\alpha nE)^{2/3}$ (b) versus E for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C with.
- Figure 5.12: Fundamental optical energy gap E_g versus x for ZnS_xSe_{1-x} thin films.
- Figure 15.13: Energy gap versus micro-crystallite diameter for ZnS_{0.9}Se _{0.1} thin films prepared by electron beam evaporation onto glass substrates at 60 °C.
- Figure 5.14: $Ln(\alpha)$ versus E, in the exponential part of the absorption coefficient, for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 0 C.
- Figure 5.15: $(\alpha E n)^{1/2}$ versus E for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 5.16: $(\omega n E)^{1/2}$ versus E for $ZnS_{0.12}Se_{0.88}$ thin film prepared by electron beam evaporation onto glass substrate at 60 ° C.
- Figure 6.1: I-V characteristics at different temperatures for ZnS_xSe_{1-x} thin films, prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 6.2: I-V characteristics at different temperatures for ZnS_xSe_{1-x} thin films, prepared by electron beam evaporation onto glass substrates at 60 °C.

- Figure 6.3: $\ln(\sigma)$ in $(\Omega.cm)^{-1}$ versus $F^{-1/2}$ in $(V/cm)^{-1/2}$ for ZnS_xSe_{1-x} films at different temperatures.
- Figure 6.4: $\ln(\sigma)$ in $(\Omega.cm)^{-1}$ versus $F^{1/2}$ in $(V/cm)^{1/2}$ for ZnS_xSe_{1-x} films at different temperatures.
- Figure 6.5: $ln(\sigma)$ versus (1000/*T*) for ZnS_{0.41}Se_{0.49} and ZnS films prepared by electron beam evaporation onto glass substrates at 60 0 C.
- Figure 6.6: ln (σ), versus 1000/T for ZnS_{0.78}Se_{0.22} thin film prepared by electron beam evaporation onto glass substrate at 60 ° C.
- Figure 6.7: $\ln(\sigma)$ versus 1000/T for $Z_{\rm IS}_{\rm x}S_{\rm el.x}$ thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 6.8 (a): $\ln (\sigma)$ versus 1000/T for ZnS_xSe_{1-x} thin films prepared by electron beam evaporation onto glass substrates at 60 ° C.
- Figure 6.9: Electrical conductivity σ versus temperature T for ZnS_xSe_{1-x} films.
- Figure 6.10: Variation of activation energies ($\Delta E_1 \Delta E_1$ and ΔW_2) with sulphur concentration x in ZnS.Se_{1.x} films.
- Figure 6.11: Variation of pre-exponential factors (σ_0 , σ_1 and σ_2) with sulphur concentration x in ZnS_xSe_{1-x} films.
- Figure 6.12: Variation of activation energies (ΔE , ΔE_1 and ΔW_2) with film thickness t (a) and grain size D (b) for $ZnS_{0.9}Se_{0.1}$ films.
- Figure 6.13: Variation of pre-exponential factors $(\sigma_0, \sigma_1 \text{ and } \sigma_2)$ with film thickness t(a) and grain size D (b) for $ZnS_{0.9}Se_{0.1}$ films.
- Figure 6.14: $\ln \sigma$ versus x for ZnS_xSe_{1-x} thin films at different temperatures.
- Figure 6.15: $\ln \sigma$ versus t and D for $\text{ZnS}_{0.9}\text{Se}_{0.1}$ thin films at different temperatures.

ABSTRACT

Thin films of ZnS_xSe_{1-x} ($0 \le x \le 1$) were prepared by electron beam (e-beam) evaporation technique. The films were deposited onto glass substrates held at about 60 °C and were fixed horizontally 15 cm above the source material. The vacuum chamber base pressure was about 2×10^{-5} torr during the deposition process. The atomic percentage of the film constituents obtained from an energy dispersive x-ray analyzer (EDX) has shown that zinc (Zn) contributes with almost 40 % of the atomic parcentage to the film composition. Sulphur (S) compositional fraction (x) has been estimated from the atomic percentages of sulphur and selenium (Se) in the individual film. The results indicated that films with x between 0.12 and 1.0 have been obtained. Scanning electron micrographs of film morphology have shown that the films exhibit smooth surfaces with relatively large grains embedded in a matrix of finer grains. The analysis of the pronounced diffraction peaks detected by x-ray diffraction (XRD) technique indicates that the films are polycrystalline with cubic structure growing preferentially along <111> axis. The grain diameter has been estimated from the broadening of the diffraction peak and is found to be in the range of 158 - 662 Å. The cubic lattice parameter a_0 has been found to vary linearly with x following Vegard's law. However, the difference between ao values for thin film and single crystal of ZnS_xSe_{1-x} materials has been used to estimate the stress experienced inside the films. Most of the films exhibit tensile stress with values in the range of 0.51-17 × 109 dynes/cm2 with exception of six samples which exhibit compressive stress in the range of -4.6 to -0.05×10^9 dynes/cm².

A new method has been developed to estimate the thickness and the optical parameters of the films by using the experimental values of the transmission spectrum. The results of this method have been found to be in a good agreement when compared with the values obtained from the well-known envelope method. The empirical relations in the dielectric theory have been used to estimate the characteristic energies such as Penn energy gap, plasma energy, Fermi energy, the average energy of the valence electrons, the energy of the effective dispersion oscillator and the dispersion energy. The absorption edge shows three distinct regions, the high-absorption region ($\alpha > 10^{-4}$ cm⁻¹), the exponential part and the weak-absorption tail. Depending on the film composition the direct optical energy gap E_g has been determined to be in the range of 2.58-3.73 eV. The variation of E_g with x has been found to be in a reasonable agreement with the results previously reported by other workers. The effect of the uniaxial stress and the grain size on the energy gap has been studied and the shift produced in E_g from these effects has been estimated.

The electrical dc-conductivity of the films has been investigated. The ohmic behaviour of the current - voltage (I - V) characteristics indicates a good electrical contact between the metal electrodes and the sample. The model proposed by Mott and Davis has been employed in order to explain the variation of conductivity with temperature in the range of 20 - 475 K. The effects of various parameters such as sulphur concentration, film thickness and grain size on the activation energy and the conductivity of ZnS_xSe_{1-x} films have been investigated. It was found that, as in the other II - VI compounds the impurities and native defects, which might be unintentionally introduced into the films during their preparation, have a significant contribution to the dc - conductivity.

ABSTRAK

Filem-filem nipis ZnS_xSe_{1-x} (0 $\leq x \leq 1$) telah di sediakan dengan menggunakan penyejatan alur elektron. Filem-filem ini telah dimendapkan ke atas substrat kaca pada suhu 60 °C dan diletakkan melintang 15 cm di atas sumber bahan tersebut yang berada pada tekanan 2 × 10⁻⁵ torr ketika proses pemendapan. Peratus atom kandungan filem yang diperolehi dari suatu pengalisis sebaran sinar - X (EDX) menunjukkan bahawa zink (Zn) menyumbangkan hampir 40 % daripada atom kepada komposisi filem. Pecahan komposisi (x) sulfur (S) telah dianggarkan dari peratusan atom sulfur dan seleneum (Se) dalam filem individu dan keputusannya menunjukkan bahawa filem-filem yang diperolehi mempunyai nilai x antara 0,12 dan 1.0. Mikrografs mikroskop imbasan elektron (SEM) yang diambil pada permukaan filem menunjukkan bahawa filem-filem ini mempamirkan permukaan yang rata dengan hablur bersaiz besar ditabur dalam matrik yang lebih halus. Analisis corak interferens dari kesan belauan sinar - X (XRD) menunjukkan bahawa filem-filem itu adalah polihablur dengan struktur kubus yang tumbuh berorientasikan arah < 111 >. Garis pusat hablur yang diukur dari pelebaran corak interferens dianggarkan diantara 15.8 - 66.2 nm. Pemalar kekisi a₀ didapati berubah secara linear dengan x mengikut Hukum Vegard. Seterusnya, perbezaan antara nilai untuk filem nipis dan hablur tunggal bahan ZnSxSel.x digunakan untuk mengukur tegasan yang telah dihasilkan di dalam filem-filem itu. Kebanyakan filem itu menunjukkan bahawa ia mengalami tegasan tensil dengan nilai dalam lingkungan $0.51-17 \times 10^{-19}$

dynes/cm sementara enam sampel menunjukkan bahawa ia mengalami tegasan mampatan dalam lingkungan $-4.6 \text{ ke} - 0.05 \times 10^{19} \text{ dynes/cm}$.

Satu kaedah baru telah dicadangkan untuk mengukur ketebalan dan pemalar optik filem-filem dengan mengunakan nilai spektrum transmisi yang diukur. Keputusan yang diperolehi dengan cara ini didapati sama tepat dengan yang diperolehi dari kaedah bungkusan. Hubungan empirik dalam teori dielekrik telah digunakan untuk mengukur sifat sifat tenaga valen, cirian jurang tenaga Penn, tenaga plasma, tenaga Fermi, tenaga purata elektron, tenaga sebaran penggetar berkesan dan tenaga sebaran. Spektrum pekali serapan α menunjukkan tiga kawasan yang berlainan; kawasan penyerapan tinggi $(\alpha>10^4~{\rm cm}^{-1})$, bahagian eksponen dan ekor penyerapan lemah. Bergantung kepada komposisi filem jurang tenaga optik terus E_g didapati berada dalam lingkungan 2.58 - 3.73 eV. Perbezaan E_g dengan x didapati bersetuju dengan keputusan yang diperolehi terdahulu. Kesan tekanan unipaksi dan saiz hablur kepada jurang tenaga dikaji dan perubahan yang dihasilkan pada E_g dari kesan-kesan ini telah diukur.

Sifat elektrik filem-filem diselidik melalui pengkonduksian arus terus (dc). Perlakuan ohm pada ciri arus – voltan (I-V) menunjukkan pengkonduksian baik antara elektod logam dan permukaan sampel tersebut. Model yang dikemukakan oleh Mott dan Davis telah digunakan untuk menerangkan perbezaan pengkonduksian dengan suhu pada julat 20 - 475 K. Kesan-kesan struktur filem, seperti kepekatan sulfur, ketebalan filem dan saiz hablur kepada tenaga pengaktifan dan pengkonduksian ZnS_xSe_{1-x} filem dikajikan. Adalah didapati bahawa seperti dalam semua sebatian II-VI, kecacatan dan pengdopan yang mungkin diperkenalkan secara tak sengaja ke dalam filem-filem itu semasa proses pemendapan, boleh mempengaruhi pengkonduksian arus terus.