UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, ELECTRICAL, THERMAL AND OPTICAL PROPERTIES OF POLYCRYSTALLINE METAL CHALCOGENIDE COMPOUNDS

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FS 2011 72

STRUCTURAL, ELECTRICAL, THERMAL AND OPTICAL PROPERTIES OF POLYCRYSTALLINE METAL CHALCOGENIDE COMPOUNDS

By

JOSEPHINE LIEW YING CHYI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

September 2011

DEDICATION

To my beloved parents Vincent Liew and Jennifer Tan

for their love and concern……

To my beloved Richard Koo Wee Yeow

for his love, support, understanding and care……

To my friends (too many)

for their wonderful encouragement and support……

To my supervisor PM. Dr. Zainal Abidin Talib

for his guidance, advice, understanding and endless support……

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

STRUCTURAL, ELECTRICAL, THERMAL AND OPTICAL PROPERTIES OF POLYCRYSTALLINE METAL CHALCOGENIDE COMPOUNDS

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Chair: Associate Professor Zainal Abidin Talib, PhD

Faculty: Faculty of Science

Copper selenide (CuSe), tin selenide (SnSe) and copper tin selenide (Cu_2SnSe_3) powder were synthesized by chemical precipitation technique. The concentration, pH, complexing agent, synthesis time and temperature have been optimized to produce very pure CuSe, SnSe and Cu_2SnSe_3 compounds. The optimum condition to prepare CuSe compound was 0.03 mol $CuCl_2 \cdot 2H_2O$ with 0.05 mol Se concentration, SnSe compound was 0.08 – 0.09 mol of $SnCl_2$ prepared in 0.06 mol tartaric acid with Se concentration maintained constant at 0.03 mol, and Cu_2SnSe_3 compound was 0.068 mol $CuCl_2 \cdot 2H_2O$, 0.078 mol $SnCl_2 \cdot 2H_2O$ and 0.025 mol Se concentration with the solution of pH at 1.30.

The structural, compositional, morphological, electrical and thermal properties of the synthesized compounds have been carried out by X-ray diffraction analysis (XRD), energy dispersive X-ray (EDX) analysis, Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM), four point

probe and van der Pauw technique, and Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry **(**DSC) and photoflash technique respectively. Information on the structure and morphology of the synthesized CuSe, SnSe and Cu_2SnSe_3 powder such as the XRD patterns, structural stability, phase transformation, mean crystallite size, compositions, shape of particles and particle size play an important role in understanding and explaining the temperature dependence of its electrical and thermal properties. The observed variation in thermal diffusivity for CuSe was $(1.20 \pm 0.02) \times 10^{-2} - (6.01 \pm 0.02) \times 10^{-3}$ cm^2/s, SnSe was $(3.80 \pm 0.08) \times 10^{-3} - (1.60 \pm 0.01) \times 10^{-3}$ cm^2/s and Cu_2SnSe_3 was $(4.31 \pm 0.09) \times 10^{-3} - (2.97 \pm 0.03) \times 10^{-3}$ cm^2/s. All of the systems displayed similar type of behavior where the thermal diffusivity of the powder decrease exponentially as the temperature increased. Analysis of the data showed the response was ably explained by the phonon scattering mechanisms. The intrinsic and extrinsic scattering at different temperature regions of the synthesized CuSe, SnSe and Cu_2SnSe_3 compound was distinguished through thermal diffusivity and mobility measurement as a function of temperature. The variation of the electrical conductivity in the CuSe was between $(8.24 \pm 0.02) \times 10^2$ to $(10.30 \pm 0.04) \times 10^2$ S/cm, SnSe was between $(15.97 \pm 0.06) \times 10^{-4}$ to (2.25 ± 0.04) S/cm and Cu_2SnSe_3 was between $(5.04 \pm 0.01) \times 10^2$ to $(7.32 \pm 0.03) \times 10^2$ S/cm. The high temperature region showed characteristics of thermionic emission while the variable range hopping was the main mechanism in the lower temperature region.

Single layer and multilayer thin films of CuSe, SnSe and Cu_2SnSe_3 were physically deposited on glass substrate through thermal evaporation technique using powder

that was synthesized from chemical precipitation technique. Various film properties, including the thickness, structure, composition, morphology, surface roughness, average grain size, electrical conductivity, Hall mobility, carrier sheet density, optical band gap and refractive index were studied and discussed in details. The results obtained showed that the physical properties such as the electrical conductivity for CuSe film ($(2.72 \pm 0.03) \times 10^3 - (61.05 \pm 0.03) \times 10^2$) S/cm), SnSe film ($(0.38 \pm 0.01) \times 10^{-2} - (1.08 \pm 0.03) \times 10^{-1}$ S/cm) and Cu_2SnSe_3 film ($(7.93 \pm 0.01) \times 10^1 - (41.48 \pm 0.06) \times 10^2$ S/cm), reflective indices for CuSe film ($(1.468 \pm 0.003) - (3.355 \pm 0.008)$), SnSe film ($(0.994 \pm 0.001) - (2.551 \pm 0.001)$) and Cu_2SnSe_3 film ($(1.569 \pm 0.001) - (3.473 \pm 0.001)$), and optical band gap for CuSe film ($(1.83 \pm 0.04) - (2.58 \pm 0.06)$), SnSe film ($(0.99 \pm 0.01) - (2.45 \pm 0.08)$) and Cu_2SnSe_3 film ($(1.83 \pm 0.05) - (2.37 \pm 0.01)$) were significantly influenced by the thickness (140 – 950 nm), annealing temperature (300 – 673 K) and preparation condition (single layer and multilayer deposition process). Finally, considering the optimization properties of the thin film, multilayer Cu_2SnSe_3 film annealed at temperature below 573 K with thickness not less than 1 μm has been proposed as the most suitable film to be used in photovoltaic devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SIFAT-SIFAT STRUKTUR, ELEKTRIK, TERMA DAN OPTIK UNTUK SEBATIAN POLIHABLUR CHALCOGENIDE LOGAM

Oleh

JOSEPHINE LIEW YING CHYI

September 2011

Pengerusi: Profesor Madya Zainal Abidin Talib, PhD

Fakulti: Fakulti Sains

Serbuk kuprum selenida (CuSe), timah selenida (SnSe) dan kuprum timah selenida (Cu_2SnSe_3) telah disintesis melalui teknik mendakan kimia. Kepekatan, pH, kompleks agen, masa sintesis dan suhu telah dioptimumkan untuk menghasilkan sebatian CuSe, SnSe dan Cu_2SnSe_3 yang sangat tulen. Keadaan optimum untuk menyediakan sebatian CuSe adalah 0.03 mol kepekatan $CuCl_2 \cdot 2H_2O$ dengan 0.05 mol kepekatan Se, sebatian SnSe adalah 0.08 – 0.09 mol $SnCl_2$ yang disediakan dalam 0.06 mol asid tartarik dengan kepekatan Se yang ditetapkan pada 0.03 mol, dan sebatian Cu_2SnSe_3 adalah 0.068 mol $CuCl_2 \cdot 2H_2O$, 0.078 mol $SnCl_2 \cdot 2H_2O$ dan 0.025 mol kepekatan Se dengan larutan pH pada 1.30.

Sifat-sifat struktur, komposisi, morfologi, elektrik dan terma daripada sebatian yang disintesis telah dilaksanakan oleh analisis pembelauan sinar-X (XRD), analisis penyerakan tenaga sinar-X (EDX), mikroskopi medan pancaran pengimbasan elektron (FESEM) dan mikroskopi penghantaran elektron (TEM), kaedah penduga

empat titik dan kaedah van der Pauw, dan analisis permeteran graviti haba (TGA), permeteran kalori pengimbasan kebezaan **(**DSC) dan teknik fotokilat masing-masing. Maklumat pada struktur dan morfologi daripada serbuk CuSe, SnSe dan Cu_2SnSe_3 yang disintesis seperti corak XRD, kestabilan struktur, transformasi fasa, purata saiz kristalit, komposisi, bentuk zarah-zarah dan saiz zarah memainkan peranan penting dalam memahami dan menerangkan kebersandaran suhu terhadap sifat-sifat elektrik dan termanya. Perubahan resapan haba yang diperhatikan untuk CuSe adalah $(1.20 \pm 0.02) \times 10^{-2} - (6.01 \pm 0.02) \times 10^{-3}$ cm^2/s, SnSe adalah $(3.80 \pm 0.08) \times 10^{-3} - (1.60 \pm 0.01) \times 10^{-3}$ cm^2/s dan Cu_2SnSe_3 adalah $(4.31 \pm 0.09) \times 10^{-3} - (2.97 \pm 0.03) \times 10^{-3}$ cm^2/s. Semua sistem menunjukkan tingkah laku yang sama di mana resapan haba daripada serbuk menurun secara exponen apabila suhu meningkat. Data yang dianalisis menunjukkan sambutan tersebut boleh diterangkan oleh mekanisma serakan fonon. Serakan intrinsik dan ekstrinsik di kawasan suhu yang berbeza daripada sebatian CuSe, SnSe dan Cu_2SnSe_3 yang disintesis telah dibezakan melalui pengukuran resapan haba dan kebolehgerakan sebagai fungsi suhu. Perubahan kekonduksian elektrik dalam CuSe adalah di antara $(8.24 \pm 0.02) \times 10^2$ ke $(10.30 \pm 0.04) \times 10^2$ S/cm, SnSe adalah di antara $(15.97 \pm 0.06) \times 10^{-4} - (2.25 \pm 0.04)$ S/cm dan Cu_2SnSe_3 adalah di antara $(5.04 \pm 0.01) \times 10^2 - (7.32 \pm 0.03) \times 10^2$ S/cm. Rantau suhu yang tinggi menunjukkan ciri-ciri daripada pancaran ion haba manakala loncatan pelbagai pembolehubah adalah mekanisma utama di rantau suhu yang lebih rendah.

Lapisan tunggal dan lapisan berbilang filem nipis daripada CuSe, SnSe dan Cu_2SnSe_3 telah dienapkan secara fizikal atas substrak kaca melalui kaedah

penyejatan haba dengan menggunakan serbuk yang disintesis daripada teknik mendakan kimia. Pelbagai sifat filem, termasuk ketebalan, struktur, komposisi, morfologi, kekasaran permukaan, purata saiz bijian, kekonduksian elektrik, kebolehgerakan Hall, pembawa ketumpatan kepingan, jurang jalur optik dan indeks pembiasan telah dipelajari dan dibincangkan dengan teliti. Keputusan yang diperolehi menunjukkan bahawa sifat-sifat fizikal seperti kekonduksian elektrik bagi filem CuSe $((2.72 \pm 0.03) \times 10^{3} - (61.05 \pm 0.03) \times 10^{2})$ S/cm), filem SnSe $((0.38 \pm 0.01) \times 10^{-2} - (1.08 \pm 0.03) \times 10^{-1}$ S/cm) dan filem Cu_2SnSe_3 $((7.93 \pm 0.01) \times 10^{1} - (41.48 \pm 0.06) \times 10^{2}$ S/cm), indeks pembiasan bagi filem CuSe $((1.468 \pm 0.003) - (3.355 \pm 0.008))$, filem SnSe $((0.994 \pm 0.001) - (2.551 \pm 0.001))$ dan filem Cu_2SnSe_3 $((1.569 \pm 0.001) - (3.473 \pm 0.001))$, dan jurang jalur optik untuk filem CuSe $((1.83 \pm 0.04) - (2.58 \pm 0.06))$, filem SnSe $((0.99 \pm 0.01) - (2.45 \pm 0.08))$ dan filem Cu_2SnSe_3 $((1.83 \pm 0.05) - (2.37 \pm 0.01))$ adalah dipengaruhi ketara oleh ketebalan (140 – 950 nm), suhu penyepuhlindapan (300 – 673 K) dan keadaan penyediaan (proses pengenapan lapisan tunggal dan lapisan berbilang). Akhirnya, dengan mengambil kira ciri-ciri pengoptimuman filem nipis, filem Cu_2SnSe_3 lapisan berbilang yang disepuhlindap pada suhu di bawah 573 K dengan ketebalan tidak kurang daripada 1 μm telah dicadangkan sebagai filem yang paling sesuai untuk digunakan dalam peranti fotovolta.

ACKNOWLEDGEMENTS

First of all, I would like to express my deepest praise to God who has allowed and given me all the strength, faith, confidence and patience to complete this project despite all the challenges.

It would be my pleasure to express my most sincere gratitude and highest thanks to my supervisor, PM Dr. Zainal Abidin Talib for his guidance, suggestion, assistance, patience, tremendous support and invaluable advice throughout the duration of this project. I would also like to extend my sincere appreciation to my committee members, Prof. W. Mahmood Mat Yunus, Prof. Zulkarnain Zainal and Prof. Dr. Mohd Maarof bin H.A. Moksin for their advice and helpful discussion during this period of study.

Special thanks are also given to Assoc. Prof. Dr. W. Mohd. Daud W. Yusoff, Assoc. Prof. Dr Zaidan Abdul Wahab, Assoc. Prof. Dr. Mansor Hashim, Prof. Dr. Abdul Halim Shaari, Dr. Lim Kean Pah and Dr. Chen Soo Kean for their advice on sample preparation and characterization. I would also like to thank to all the staff in Physics and Chemistry department especially En. Roslim Mohd, En. Zain Mohd Yusof, En. Razak Harun, Pn. Kamsiah Alias, En. Shaharuddin Hj. Abd. Rahman, Puan Zaidina Mohd Daud, Pn. Choo Chai Syam, En Mohd Shah Ibrahim for their help and co−operation given to me throughout my work. Special thanks is credited to En. Mohd Fairul Sharin bin Abdul Razak and Dr. Saravanan Nagalingam providing guidance on chemical precipitation technique and En. Danail Mohamed at Kulliyyah

of Engnnering (International Islamic University Malaysia), Puan Aminah Jusoh (Institute of Bioscience, UPM) and En. Rafiuz Zaman Haroun (Institute of Bioscience, UPM) for helping me in handling the FESEM, TEM and EDX.

I am gratefully acknowledge the Ministry of Science, Technology and Innovation, Ministry of Higher Education, The Malaysia Academy of Sciences (SAGA 5486512 & RUGS 91756) and TORAY Foundation for their financial support which enable me to undertake this work. Last but not least, my sincere thanks to all my friends, seniors and family members, who involved directly or indirectly towards the success of this project.

I certify that a Thesis Examination Committee has met on 22 September 2011 to conduct the final examination of Josephine Liew Ying Chyi on her thesis entitled "Structural, Electrical, Thermal and Optical Properties of Polycrystalline Metal Chalcogenide Compounds" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

JOSEPHINE LIEW YING CHYI

Date: 22 September 2011

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