UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Manufacturing Engineering

SYNTHESIS AND CHARACTERIZATION OF ELECTRODEPOSITED NICKEL CHALCOGENIDES FOR PHOTOELECTROCHEMICAL / SOLAR CELL APPLICATION

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Master of Science in Manufacturing Engineering

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SYNTHESIS AND CHARACTERIZATION OF ELECTRODEPOSITED NICKEL CHALCOGENIDES FOR PHOTOELECTROCHEMICAL / SOLAR CELL APPLICATION

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A thesis submitted
in fulfillment of the requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "Synthesis and Characterization of Electrodeposited Nickel Chalcogenides for Photoelectrochemical / Solar Cell Application" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:	....
Name	:	....
Date	:	....

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

Signature	:……………..
Supervisor Name	:……………………… ....
Date	:…………………….......................................

DEDICATION

To my beloved supervisor, family and friends.

A wonderful teacher, understood me so well,

Helped me up, whenever I fell.

Even when I made a big mistake,

You said, we learn, the more we make.

Family and friends always been there,

making sure I was o.k.

The one that helped me be,

the kind of person I am today.

A simple thank you can turn a negative into a positive,

I find a way to be thankful to all of you,

Thank you! *For being my blessings.*

-Marelisa Fabrega

ABSTRACT

Nickel chalcogenides, NiX_2(X=S,Se) thin films were successfully electrodeposited on indium-tin-oxide (ITO)-coated glass substrates. The deposition time for the thin films were set at 10 minutes to 30 minutes with an interval of 5 minutes. The thin films were characterized for their structural, morphological and compositional characteristics. Their optical and semiconducting parameters were also analyzed in order to determine the suitability of the thin films for photoelectrochemical (PEC) / solar cell applications. Films were well adherent to the subtrates and grew up to thickness of ≈ 1.5μm. Structural analysis via X-Ray Diffraction (XRD) analysis reveals that films are polycrystalline with increasing intensity of XRD peaks in thicker films. Preferred orientation of (2 2 0) plane in NiS_2 and (2 1 1) plane in $NiSe_2$ was observed as the highest peak in spectrum. The surface morphology of the films determined by Scanning Electron Microscope (SEM) showed the growth of the films to be uniform and well covered for thinner films. However, at longer deposition times, the structure of the films start to break into grains (flakes) due to maximum grain stress point. Compositional analysis via Energy Dispersive X-ray (EDX) technique confirmed the presence of Ni, S, and Se elements in the films synthesized. The optical bandgap energy of the films fit into the range (1-3eV) for a PEC / solar cell materials and decreases as the deposition time of the films increases. Bandgap energy of 1.12 eV and 1.15 eV was obtained for NiS_2 and $NiSe_2$ films deposited at 30 minutes and 25 minutes, respectively. Results on the semiconductor parameters analysis of the films showed that the nature of the Mott-Schottky plots indicates that the films obtained are of p-type material. All values come in the range of many other transition metal chalcogenides and this has proven that NiX_2(X=S,Se) thin films are capable as a solar / PEC cell material

ABSTRAK

Filem nipis Nikel Kalkogenida, NiX_2(X=S,Se) berjaya dielektrodeposisikan pada substrat kaca yang bersalutkan indium-timah-oksida (ITO). Masa deposisi untuk filem-filem nipis telah ditetapkan pada 10 minit hingga 30 minit dengan selang masa 5 minit. Filem-filem nipis telah disintesis untuk menentukan ciri-ciri struktur, morfologi dan komposisi. Parameter optik dan semikonduktor juga dianalisis untuk menentukan kesesuaian filem nipis untuk aplikasi fotovolta (PEC)/ sel solar. Film nipis melekat pada substrat dengan baik dan ketebalan filem bertambah kepada ≈1.5µm. Analisis struktur melalui pembelauan sinar-X (XRD) mendedahkan bahawa filem berpolihablur mempunyai peningkatan pada intensiti puncak pada filem yang tebal. Orientasi pilihan bagi filem NiS_2 adalah (2 2 0) manakala $NiSe_2$ adalah (2 1 1). Morfologi permukaan filem-filem ditentukan dengan mikroskop pengimbasan elektron (SEM) dan ia diperlihatkan bahawa film dideposisikan dengan seragam dan juga meliputi seluruh permukaan substrat dengan film nipis. Walau bagaimanapun, pada masa deposisi yang lebih panjang, struktur filem-filem mula berpecah dan berbentuk kepingan. Analisis komposisi filem melalui teknik tenaga serakan sinar-X (EDX) mengesahkan kehadiran elemen-elemen Ni, S, dan Se dalam filem-filem yang disintesis. Nilai jurang tenaga optik perlu berada dalam julat (1-3eV) untuk aplikasi fotovolta /sel solar dan nilai tersebut akan berkurangan dengan masa deposisi filem yang bertambah. Nilai jurang tenaga sebanyak 1.12 eV dan 1.15 eV telah diperolehi bagi filem NiS_2 dan $NiSe_2$ yang dideposisi pada 30minit dan 25minit. Dapatan daripada analisis parameter semikonduktor melalui plot Mott-Schottky menunjukkan bahawa filem- filem adalah daripada semikonduktor jenis-p. Semua nilai yang diperoleh adalah serupa dengan bahan kalkogenida logam peralihan yang lain dan ini telah membuktikan bahawa NiX_2(X=S,Se) filem nipis mampu berfungsi sebagai bahan PEC/ sel solar

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Rajes a/p K.M. Rajan
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LIST OF ABBREVIATIONS AND SYMBOLS

(i) Abbreviations

CVD	Chemical Vapour Deposition
CE	Counter Electrode
CIGS	Copper Indium Gallium Selenide
EDX	Energy Dispersive X-Ray
E_g	Energy gap
FWHM	Full width at half maximum
ITO	Indium-Tin-Oxide
LCR	Inductance-Capacitance-Resistance
N	Doping density
N_A	Acceptor impurities density
N_c	Density of states in conduction band
PEC	Photoelectrochemical
PV	Photovoltaics
PVD	Physical Vapour Deposition
RE	Reference Electrode
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscope
TMC	Transition Metal Chalcogenide
UV-Vis	Ultraviolet-Visible
V_b	Band bending
V_{fb}	Flat band potential
WE	Working Electrode

(ii) Symbols

ε	Dielectric constant
α	photon energy
λ	wavelength of X-Ray
β	Full width half maximum
θ	Bragg's angle

LIST OF PUBLICATIONS

(i) Conference

Parts of this thesis have been presented in:

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(ii) Journal

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(a) Joseph Sahaya Anand, **Rajes K.M Rajan** and Abdul Aziz Mohd Zaidan, 2013. Electrosynthesized NiS_2 Thin Films and Their Optical and Semiconductor Studies. *Reports in Electrochemistry*, 3, pp. 25-29.

(b) T. Joseph Sahaya Anand and **Rajes K.M. Rajan**, 2014. Synthesis and Characterization of Electrodeposited NiX_2(X=S,Se) Thin Films for Solar Energy Conversion. *Materials and Manufacturing Processes* (under revision).

(c) T. Joseph Sahaya Anand and **Rajes K.M. Rajan**, 2014. Characterization of the Surface Properties of $NiSe_2$ Thin Films: Influence of Deposition Time. *Thin Solid Films* (Submitted).

(d) Joseph Sahaya Anand, Mohd Zaidan Abdul Aziz, Shariza Sharir, **Rajes K.M.Rajan**, Chua, 2014.Electrochemical Studies of $NiSe_2$ Thin Films: Growth and Analysis of TEA and EDTA Additives. *Thermochemica Acta* (Submitted).

CHAPTER 1

INTRODUCTION

1.1 Background

Growing fuel prices and fast depleting conventional energy source has led to findings on sustainable and efficient energy source. Hence, renewable energy has been suggested as a viable approach for this particular energy crisis. Presently, many research group has focused on solar energy as the most promising renewable energy to cater the future energy demand due to its abundancy and inexhaustibility (Hennayaka and Lee, 2013).

Photoelectrochemical (PEC) is a solar device which is fabricated with semiconductor electrolyte interface. Being an advanced microelectronic technology, PEC can be applied for electrochemical energy conversion and energy storage (Yadav and Masumdar, 2010). At present, the mainstream of solar technology is based on crystalline silicon (c-Si) wafers (Aberle, 2009). The c-Si wafers require large amount of materials for the PEC fabrication. Thus, the c-Si wafers are extremely expensive for large scale production (Anuar *et al.*, 2007). Prior to the high material consumption and high cost in wafer technology, researchers have focused on other possible alternative technology and materials to develop solar device (Moheimani and Parlevliet, 2013).

Concurrently, thin film technology has been introduced as the cutting edge in developing a solar device. Thin-film is a successive thin layers, in thickness of 1μm to 4μm deposited onto a substrate such as glass, polymer, or metal (Gangopadhyay *et al.*, 2013). This technology significantly use less material than bulk crystalline solar cells. This makes the thin film technology more efficient in terms of material consumption (Moheimani and

Parlevliet, 2013). Hence, thin film technology can be considered as an engineering breakthrough in solar technology.

Research is being carried out extensively in finding new materials for energy conversion for reasonable cost by not compromising their efficiency (Duchatelet *et al.*, 2013). For energy conversion, the most suitable band gap energy is about 1.0-1.6eV. However, not all semiconductor materials are suitable for solar cells (Moheimani and Parlevliet, 2013). Owing to this efforts in finding new materials, Transition Metal Chalcogenides (TMC) are proposed as the most satisfactory semiconductor materials for PEC application. TMC, is combinatorial of transition metal and chalcogenide, MX_2 (M: Cd, Mo, Zn; X: S, Se and Te). TMC posseses excellent optical, electrical and semiconductor properties, especially in the thin film form (Anand and Shariza, 2012). Hence, TMC materials are under limelight for PEC fabrication by adopting thin film technology. At present, Cadmium Telluride, CdTe is the most ideal TMC material for thin film with its narrow and direct band gap ~1.5eV (Yang *et al.*, 2010). Apart from CdTe, Cadmium Sulphide, CdS (Yadav and Masumdar, 2011), Cadmium Selenide, CdSe (Hankare *et al.*, 2011), Zinc Sulphide, ZnS (Luque *et al.*, 2013), and Tin Sulphide, SnS (Jain and Arun, 2013) thin films are also developed for PEC application. It is evident that cadmium chalcogenides are the most widely used TMC material for energy conversion purpose due to its significant photoconversion efficiency (Hankare *et al.*, 2003). However, Cd is very toxicative and harmfull to the environment (Aberle, 2009).

Correspondingly, in a recent study, Nickel has been found to be potential candidate to substitute Cadmium in thin film chalcogenide as a material with better electrical properties to meet solar cell expectations. According to the investigation, Ni^{2+} has a standard ionic radius of 0.069nm, which is slightly less than Cd^{2+} (0.097nm) and higher electronegativity of 1.91 Pauling compared to Cd^{2+} (1.61 Pauling) (Rmili *et al.*, 2013).

Hence, with smaller ionic radius, nickel chalcogenides could form stronger ionic bonds with higher electronegativity that makes it attracts electrons effectively. Apart from this, nickel transition metal has longer life time with better functionality due its physical properties of high melting point 1453°C and high anti corrosive and resistivity. Ultimately, nickel is also >60% recyclable. Thus, it contributes to longer product cycle and prevents source depletion (Mistry, 2012). On the other hand, the chalcogens sulphide and selenium (X=S,Se), are non-metal while Tellurium (Te) is a metalloid in an alkaline. Hence, chemical behavior and reaction of sulphide and selenium are reported similar which are in contrast to Telluride (Mathur *et al*., 1995). In this regard, NiX_2(X=S,Se) films were investigated for a comprehensive study of their suitability for PEC application.

Nickel chalcogenides can be synthesized by spray pyrolisis, electrochemical deposition and sputtering (Yadav and Masumdar, 2010a) (Kokate *et al*., 2006) (Volobujeva *et al*., 2009). One of the most attractive methods for producing nickel chalcogenide thin film, owing to the possibility of large area deposition at low cost is the potentiostate electrodeposition method. This method is relatively accurate and yields good quality films due to the potential reduction at the working electrode (Yang *et al*., 2010). Correspondingly, it requires presence of reagents that act as a source of chalcogenide and complexion of metal ions that forms via 'ion-by-ion' growth mechanism (Hankare *et al*., 2010).

This research work aims on NiX_2(X=S,Se) thin film and the studies include the observations on growth kinetics, structural, morphological, compositional, optical and semiconducting parameters. This film is expected to contribute on the advantageous and limitations stated in synthesizing the transition metal chalcogenide thin films, whitout compromising its functionality and properties.

1.2 Problem Statement

Fossil fuels are non-renewable. This resource is limited and expected to deplete by 2046. This indicates that in the year 2046, there will be almost no liquid fuel (Moheimani and Parlevliet, 2013). On the other hand, the world energy consumption is reported increasing at 10 Terawatts (TW) annually and by 2050 it is projected to be about 30 TW (Razykov *et al*., 2011). Fossil fuels are depleting very fast and is becoming expensive day by day (Aloney *et al.*, 2009). Despite the fact expensive, fossil fuel exploitation is also contributing in environmental pollution and climate change (Tseng *et al*., 2012). Clearly, decline of fossil fuel resource is not able to support the increasing energy demand at the long run. Therefore, alternate renewable energy, namely solar energy has been suggested to meet the future energy demand (Tyagi *et al*., 2013). Correspondingly, photoelectrochemical solar cell is gaining popularity in compliance to its usage in energy conversion and energy storage. Consequently, PEC is being fabricated and investigated largely in order to improve their performance in solar energy conversion efficiency (Yadav and Masumdar, 2011).

At current market scenario, crystalline silicon (c-Si) dominates solar cell application due to its higher effciencies of 24.7% (Moheimani and Parlevliet, 2013). Prior to wafer technology, c-Si consumes large amount of materials (Parida *et al*., 2011). High production cost of solar cell comprises the cost of materials, technology used and material consumption (Borja *et al*., 2011). Hence, c-Si usage seemed to be impossible to achieve PV module production cost below $1/W and contemporarily restricts wafer technology in solar cell fabrication (Razykov *et al*., 2011). Meanwhile, indium and gallium are expensive elements and therefore makes the popular Copper Indium Gallium Selenide (CIGS) solar device with efficiency 20.3% (Zhou *et al*., 2013) costly and commercially limited (Rath *et al*., 2012).

Another challenge in solar cell is employing a suitable fabrication method which cost effective and suitable for large scale production. Contemporarily, the fabrication method is expected to yield a high quality thin film for solar cell application (Kaupmees *et al*., 2007). Prior to cost competition, many researchers are in the effort of replacing vacuum usage in the fabrication method with cost efficient fabrication method (Todorov *et al.,* 2011). This is also supported by Kim *et al*., (2005) claiming that the adopted fabrication method must be cost effective without compromising its efficiency.

Several toxic substances applied in solar cells claimed to be toxicative to the environment during production process, namely Cadmium Sulphide, CdS(Zhou *et al*., 2011) (Lekiket and Aida., 2013). Hence, it limits the use of CdS as photoelectrode material for solar cell (Patil and Singh, 2010). Prompted by environmental underlying issues, a clean and renewable alternative energy solution is imperatively needed to sustain energy supply in the long run (Bhaskar *et al*., 2013).

In summary, a sustainable energy supply can be explored efficiently by resolving the limitations. Thus, more thorough investigations should be made regarding solar energy as a realistic measure to find sustainable and clean energy. It is important to note that, to the best of our knowledge, the first report on nickel chalcogenides (NiS and NiSe) thin film prepared via solution growth technique was published in 1986 (Pramanik and Biswas, 1986) and followed by several reports after nearly two decades (Zhuang *et al*., 2005) (Anuar *et al*., 2004). Thus, this investigation of NiX_2(X=S,Se) thin film is expected to provide feasible study to discover the suitability of the material for PEC application.

1.3 Research Objectives

Based on the problem statements, this research is designed to accomplish the following specific objectives :

i) To synthesize stoichiometry NiX_2(X=S,Se) thin films via electrodeposition technique.

ii) To characterize the thin films for their structural, morphological and compositional studies for various deposition time and potential.

iii) To analyze the optical properties of these thin films by determination of energy band gap.

iv) To analyze the film semiconductor parameters that influences the suitability for energy conversion application.

1.4 Significance of the Research

This research contributes to the efforts in finding new material for PEC application. Owing to the contribution, the present study incorporates analytical tools, namely, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Optical and Mott-Schottky. The analytical tools were adopted to determine the possibility of structural, morphological, optical and semiconductor properties of NiX_2(X=S,Se) film to be used for solar energy conversion. Thus, the results are expected to reflect the suitability of NiX_2 (X=S,Se) film to fulfill the requirements as efficient solar cell material

1.5 Structure of the Thesis

The current chapter 1 introduces the context of the research covering issues such as the background, objectives and significance in order to give an overview on this research.