UNIVERSITI PUTRA MALAYSIA

DEGRADATION STUDY OF CuInSe2 THIN FILMS

CHANG CHUNG BIN

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MASTER OF SCIENCE
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DEGRADATION STUDY OF CuInSe₂ THIN FILMS

By

CHANG CHUNG BIN

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

November 2013
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DEGRADATION STUDY OF CuInSe₂ THIN FILMS

By

CHANG CHUNG BIN

November 2013

Chairman: Professor Zainal Abidin bin Talib, PhD
Faculty: Science

The degradation behavior of CuInSe₂ thin film was studied in this project to understand the effects of high intensity light and corrosive acids on its structural, morphological, electrical and optical properties. Polycrystalline CuInSe₂ thin film has been synthesized using thermal evaporation method and source material was produced by solid state reaction process of Cu, In, Se elements. The samples are in good agreement to the tetragonal structure of JCPDS data (Ref. 98-008-7482). Samples exposed to increasing light irradiance intensity from 250 to 1500W/m² shows increment in crystallite sizes from 80.90 to 138.30nm. It was found out that the films were sensitive to light-induced heat which leads to heating effect and subsequently improves the films quality.

Fine spherical or elliptical grains were observed in the AFM topography for all samples while the RMS roughness of the thin films slightly decreases from 14.72 to 10.64nm after the exposure to light and maintained relatively constant as the increase of light intensity. The sheet resistivity of samples after light exposure at all intensities increased from $1.3 \times 10^{-3}$ to $3.7 \times 10^{-3} \Omega \text{cm}$ with intensity due to the increase of surface scattering effect and the increase of light-induced defects in the films which act as recombination center for electron-hole pair. The direct band gap of the samples increases from 1.52 to 1.59eV with the increasing of light intensity.

For samples degraded in sulfuric acid, the crystal structures and RMS roughness of all samples remain relatively unchanged after the degradation which infers that the ions in sulfuric acid do not affect the crystal structure significantly. Nevertheless, for
samples degraded in nitric acid, the FWHM values increase from 0.8346 to 1.2932 when the concentration of H\(^+\) and (NO\(_3\))\(^-\) ions increases infers that the thin films’ quality degenerates. Both samples degraded in sulfuric and nitric acid shares similar trends in resistivity and band gap results. The resistivity of both samples increased with same magnitude of \(\Delta \rho=0.4 \times 10^3 \Omega \text{cm}\) due to the increase in hydrogen concentration whereby creates more copper vacancies and hence increases resistivity.

The band gap for both samples decreased with a \(\Delta E_g=0.17\text{eV}\) with increasing concentration of hydrogen ions. The decrease of the optical band gap was due to the increase of copper vacancies concentrations. From aforementioned results, all samples subjected to light and acid degradation have an increase of resistivity after exposure. Nevertheless, light exposure dealt greater degradation to the resistivity of thin films than acid exposure with respect to the magnitude. These findings concluded that the effect of light degradations and acid degradations have a significant influence on the morphological, electrical and optical properties of CuInSe\(_2\) thin films and therefore the degradation behavior of CuInSe\(_2\) thin film is understood.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Master Sains

KAJIAN PENYAHGREDAN FILEM NIPIS CuInSe₂

Oleh

CHANG CHUNG BIN

November 2013

Pengerusi: Profesor Zainal Abidin bin Talib, PhD
Fakulti: Sains

Penyahgredan filem nipis CuInSe₂ telah dikaji dalam projek ini untuk memahami kesan cahaya berkeamatan tinggi dan asid menghakis pada struktur, morfologi, sifat elektrik and sifat optik sampel. Filem nipis polihablur CuInSe₂ telah dihasilkan dengan menggunakan kaedah penyejatan haba dan sumber penyejatan telah dihasilkan oleh proses tindak balas balas unsur-unsur Cu, In dan Se dalam keadaan pepejal. Sampel yang dihasilkan didapat mempunyai struktur tetragon yang sepadan dengan data JCPDS (Ref. 98-008-7482). Sampel yang didedahkan kepada sinaran cahaya dengan keamatan yang meningkat dari 250 ke 1500W/m² menunjukan peningkatan dalam saiz kristalit dari 80.90 ke 138.30nm. Filem-filem didapat sensitive kepada haba diaruh cahaya dan kualiti filem-filem tersebut meningkat disebabkan oleh kesan pemanasan cahaya.

Butiran bulat atau elips dapat diperhati dalam topografi AFM untuk semua sampel manakala keakuratan RMS menurun sedikit dari 14.72 ke 10.64nm selepas pendedahan kepada cahaya dan kekal malar walaupun keamatan cahaya meningkat. Selépas pendedahan cahaya, kerintangan lebaran sampel meningkat untuk semua keamatan cahaya dari 1.3 x 10⁻³ ke 3.7 x 10⁻³ disebabkan oleh kesan penyebaran permukaan dan kecacatan ringan dalam filem-filem yang bertindak sebagai pusat pengabungan semula untuk pasangan elektron-lubang. Jurang jalur langsung sampel meningkat dari 1.52 ke 1.59eV apabila keamatan cahaya meningkat.

Untuk sampel yang direndam di dalam asid sulfurik, struktur kristal dan keakuratan RMS semua sampel kekal tidak berubah. Ini menyimpulkan bahawa ion dalam asid sulfurik tidak menjejaskan struktur kristal dengan ketara. Walau bagaimanapun, bagi...
sampel yang direndam di dalam asid nitrik, nilai FWHM meningkat dari 0.8346 ke 1.2932 apabila kepekatan H\(^+\) dan (NO\(_3\))\(^-\) ion menaik. Ini menyimpulkan bahawa kualiti filem-filem nipis tersebut telah menyahgred. Kedua-dua sampel yang direndam di dalam asid sulfurik dan asid nitrik mempunyai perkembangan rentetan yang sama dalam keputusan kerintangan dan juga jurang jalur. Kerintangan kedua-dua sampel meningkat dengan magnitud of \(\Delta \rho = 0.4 \times 10^{-3} \ \Omega \text{cm}\) disebabkan oleh peningkatan kepekatan hidrogen akan mewujudkan lebih kekosongan kuprum dan dengan itu meningkatkan kerintangan. Jurang jalur untuk kedua-dua sampel menurun dengan \(\Delta E_g=0.17 \text{eV}\) dengan peningkatan kepekatan ion hidrogen.

Pengurangan jurang jalur optik adalah disebabkan oleh peningkatan kepekatan kekosongan kuprum. Daripada keputusan di atas, semua sampel yang didedah pada cahaya dan asid meningkatkan kerintangan selepas pendedahan. Walau bagaimanapun, pendedahan cahaya mengakibatkan penyahgredan yang lebih besar kepada kerintangan filem nipis daripada pendedahan asid dari segi magnitud. Ini menunjukkan bahawa kesan penyahgredan cahaya dan penyahgredan asid mempunyai pengaruh yang besar ke atas morfologi, sifat elektrik dan optik dalam filem nipis CuInSe\(_2\) dan oleh itu sifat penyahgredan filem nipis CuInSe\(_2\) dapat difahami.
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I am gratefully acknowledge the Faculty of Science and Universiti Putra Malaysia for their support in terms of research facilities and staff who has assisted me to take on the challenge of this project.
I certify that a Thesis Examination Committee has met on xxxx 2013 to conduct the final examination of Chang Chung Bin on his master thesis entitled “Degradation studies of CuInSe₂ thin films” 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 Master degree. Members of the Thesis Examination Committee were as follows:

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Name and Matric No.: CHANG CHUNG BIN, GS26944
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<td>Copper Indium Diselenide</td>
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<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>ECD</td>
<td>Electrochemical deposition</td>
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<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapor deposition</td>
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<td>AM</td>
<td>Air mass</td>
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<td>FCC</td>
<td>Face center cubic</td>
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<td>CFM</td>
<td>Continuous flow microreactor</td>
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<td>EQE</td>
<td>External quantum efficiency</td>
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<td>DLTS</td>
<td>Deep-level transient spectroscopy</td>
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<td>FF</td>
<td>Fill Factor</td>
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<td>PPTS</td>
<td>Piezoelectric photo thermal spectroscopy</td>
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<td>RF</td>
<td>Radio frequency</td>
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<td>ESR</td>
<td>Electron spin resonance</td>
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<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscope</td>
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<td>FWHM</td>
<td>Full width half maximum</td>
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<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
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<td>EDX</td>
<td>Energy dispersive x-ray</td>
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<td>SEM</td>
<td>Scanning electron microscope</td>
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<td>AFM</td>
<td>Atomic force microscope</td>
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<td>UV-Vis-NIR</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction

The world’s population reaches 7 billion people in 2011 and will continue to grow exponentially to a predicted 8 billion people in 2025. This infers that the world’s energy consumption will increase exponentially too, and poses us a threat that our energy consumption will overwhelm Earth’s carrying capacity and bring our civilization to a collapse. Generations of scientists observed the threat and spend decades to research on renewable energy technologies with the hope of solving the energy crisis instead of relying on fossil fuel as our sole energy source.

Apart from surmounting the energy crisis, renewable energy technologies are also essential as they contribute in reducing emissions of greenhouse gases such as carbon dioxide, methane and nitrous oxide from fossil fuel power plants and of great importance in developing an environment which is more sustainable to Earth’s ecosystem. However, most of the renewable energy sources such as wind-power energy are considered as low-density energy sources. Otherwise stated, a large coal or nuclear power plant can produce hundred-fold megawatts of electricity more than renewable energy power plant’s capacity.

Nevertheless, renewable energy such as solar energy is a very promising candidate to solve the energy crisis as it is environmentally benign and is more versatile to be built in diverse location such as building roof top and walls compared to conventional power plants. This allows the solar power plants to generate a substantial amount of electricity meant for the usage of the locality. Furthermore, it is more likely for the people to install solar photovoltaic generators on their homes and offices than to allow a coal or a nuclear power plant in their neighborhood.

Good desirable photovoltaic systems need to have high energy conversion efficiencies (>15%) and stability (30 years) (Jayachandran et al. 1993). To achieve high efficiencies, a solar cell material must have an appropriate optical band gap wherein to effectively absorb the solar spectrum. Good stability and reliability of the solar panels are also important for cost reduction such as to decrease the frequency of maintenance needed after installation of the systems.
Though conventional solar cells such as mono-crystalline silicon solar cells has a high solar conversion efficiency about 17.5% (Assi et al. 2012), thin-film solar photovoltaic cells such as CIS module have a reasonable efficiency of 11.6% (Durisch et al. 2006) with the advantage of large-scale production capabilities. Thin film solar cell provides layering characteristics wherein it enhances the absorption of solar spectrum with multi-layer solar cells makes them a fair alternative for conventional silicon solar cell. Thin film solar cells are also suitable for large-area automated fabrication and continuous production as it can be deposited on flexible substrate such as long polymer roll.

Thin-film devices are generally based on amorphous silicon while other thin-film devices utilize polycrystalline materials. The fabrication of a thin-film solar cell involves depositing a layer of semiconductor material (such as amorphous silicon, copper indium diselenide, or cadmium telluride) on a low-cost substrate, such as glass, metal, or polymer. Deposition techniques presently used are physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical deposition (ECD), plasma enhanced chemical vapor deposition (PECVD) or some combination of them.

### 1.2 Copper Indium Diselenide

Copper Indium Diselenide (CIS) is a p-type semiconductor suitable for thin film solar cells due to its high absorption coefficient (~10^5 cm\(^{-1}\)) and its optimum band gap (1.01eV) for solar spectrum absorption (Firoz Hasan et al. 2000). The high absorption coefficient of CuInSe\(_2\) allows a uniform 70-80% quantum efficiency in the range of 550nm to 1250nm of the air mass AM 1.5 solar spectrum (Jayachandran et al. 1993). Moreover, CdS forms an ideal hetero-junction with CuInSe\(_2\) as the surface of CuInSe\(_2\) matches with the surface of CdS with low lattice mismatch of 1.16%.

CuInSe\(_2\) belong to the semiconducting I-III-VI\(_2\) materials which has a chalcopyrite lattice structure similar to a copper pyrite. The chalcopyrite lattice has the same characteristic with zinc blende lattice where each atom has fourfold bonding around it. The Se atoms are situated at FCC sub-lattice and the sites connected to the FCC sub-lattice are equally occupied by Cu and In atoms. The electrical conductivity type of the films is determined by the (Cu+In)/Se atomic ratio. The film is p-type when the ratio is less than one and Se excess, and n-type when Se deficiency.
1.3 Degradation of CuInSe$_2$

As a solar cell module is exposed to high intensity sunlight and potentially severe weather conditions, an exact evaluation for reliability is required. Several studies to ascertain the stability of the commercial CuInSe$_2$ modules have been conducted.

For example, Yanagisawa and Kojima (2003) studied on the behavior of a commercial CuInSe$_2$ module (1~2cm$^2$) properties with time under various light irradiation conditions. A light irradiation/dark state cycle test and continuous light irradiation test were carried out using xenon lamp at 200W/m$^2$. The cell characteristics such as maximum power ($P_{\text{max}}$), short circuit current ($I_{\text{sc}}$), open circuit voltage ($V_{\text{oc}}$), fill factor (FF), $I_{P_{\text{max}}}$, and $V_{P_{\text{max}}}$ at initial state and after each cycle were monitored. Under both test conditions, the maximum power was improved during early cycles and then gradually degenerated. A good correlation between the decrease of maximum power and the increase in internal defect were established.

Another researcher Lam et al. (2004) studied the dependency of the cell properties on light irradiance and weather condition under real operating conditions such as under the sunlight. A commercial 40W CuInSe$_2$ module was setup on a roof and environmental parameters such as global solar irradiance, cell temperature, air mass and cell efficiency were recorded before and after one year of sunlight exposure. The efficiency of the solar module decreased from 11.57% to 10.54% after one year of exposure to sunlight and weather conditions due to the increase of series resistance in the module due to degradation of materials.

1.4 Problem Statement

Significant studies on the stability of CuInSe$_2$ based solar cell module have been done (Yanagisawa et al. 2003, Lam et al. 2004, Rao et al. 2009). Although devices are generally encapsulated for protection from aggressive environment, the issues associated with the absorber layer alone can also impact the performance of a solar cell device (Rockett et al. 1994).

For example, glass can be affected by the combined effect of moisture and high temperature despite glass is generally regarded as corrosion-proof (Nick, 2004). The moisture in air would ingress into the glass pores after a certain time of exposure. Thereafter the alkali in the glass will be leach out and subsequently creates more hydrated pores. These pores in glass substrates will hasten acid ingestion into the thin film and result in performance reduction.
Therefore, the behaviors such as resistivity and optical coefficient of bare-thin film to high intensity light irradiance such as sunlight, high temperature, and corrosive degradation from acid rain are critical studies to understand the degradation modes of CuInSe$_2$ solar cell which affects its stability.

1.5 Objective of the study

The objectives of the present work are summarized as follow:

1. to synthesize the polycrystalline CuInSe$_2$ powder through solid state reaction method.

2. to fabricate the CuInSe$_2$ metal chalcogenide thin films using the synthesized powder through thermal evaporation technique.

3. to characterize CuInSe$_2$ thin film of its structural, morphological, electrical, and optical properties; before and after degradation cause by thermal-light cycles; by chemical attacks of H$_2$SO$_4$ and HNO$_3$. 
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