UNIVERSITI PUTRA MALAYSIA

DEGRADATION STUDY OF CuInSe2 THIN FILMS

CHANG CHUNG BIN

FS 2013 48

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MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2013

DEGRADATION STUDY OF $CuInSe_2$ 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

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science.

DEGRADATION STUDY OF $CuInSe_2$ THIN FILMS

By

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November 2013

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Faculty: **Science**

The degradation behavior of $CuInSe_2$ 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 $CuInSe_2$ 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/m^2 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 x 10^{-3} to 3.7 x 10^{-3} Ωcm 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 $\Delta\rho=0.4\times10^{-3}\Omega$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 ΔE_g=0.17eV 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 $CuInSe_2$

Oleh

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November 2013

Pengerusi: **Profesor Zainal Abidin bin Talib, PhD**
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Penyahgredan filem nipis $CuInSe_2$ 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 $CuInSe_2$ telah dihasilkan dengan menggunakan kaedah penyejatan haba dan sumber penyejatan telah dihasilkan oleh proses tindak balas unsur-unsur Cu, In dan Se dalam keadaan pepejal. Sampel yang dihasilkan didapati 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/m^2 menunjukan peningkatan dalam saiz kristalit dari 80.90 ke 138.30nm. Filem-filem didapati sensitif 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 kekasaran RMS menurun sedikit dari 14.72 ke 10.64nm selepas pendedahan kepada cahaya dan kekal malar walaupun keamatan cahaya meningkat. Selepas pendedahan cahaya, kerintangan lembaran sampel meningkat untuk semua keamatan cahaya dari 1.3×10^{-3} ke 3.7×10^{-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 kekasaran 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 $\Delta\rho = 0.4x10^{-3}$ Ωcm disebabkan oleh peningkatan kepekatan hidrogen akan mewujudkan lebih kekosongan kuprum dan dengan itu meningkatkan kerintangan. Jurang jalur untuk kedua-dua sampel menurun dengan ΔEg=0.17eV 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.

ACKNOWLEDGEMENTS

First of all, I would like to express my sincere gratitude to my supervisor, Prof. Zainal Abidin Talib for his guidance, suggestion, assistance and support throughout the duration of this project. I would also like to extend my sincere appreciation to Prof. Anuar Kassim for his advice and helpful discussion during this period of study.

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 $CuInSe_2$ 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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LIST OF ABBREVIATIONS

CIS	Copper Indium Diselenide
PVD	Physical vapor deposition
CVD	Chemical vapor deposition
ECD	Electrochemical deposition
PECVD	Plasma enhanced chemical vapor deposition
AM	Air mass
FCC	Face center cubic
CFM	Continuous flow microreactor
AC	Alternating current
DC	Direct current
IQTP	Interim Qualification Tests and Procedures
HF	Humidity-freeze cycle test
SUN	Unit measurement of sun intensity
EQE	External quantum efficiency
DLTS	Deep-level transient spectroscopy
FF	Fill Factor
PPTS	Piezoelectric photo thermal spectroscopy
RF	Radio frequency
ESR	Electron spin resonance
HRTEM	High resolution transmission electron microscope
FWHM	Full width half maximum
JCPDS	Joint Committee on Powder Diffraction Standards
EDX	Energy dispersive x-ray
SEM	Scanning electron microscope
AFM	Atomic force microscope
UV-Vis-NIR	Ultra-violet-visible-near-infrared spectroscopy
XRD	X-ray diffraction
RMS	Root-mean-squared

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_{max}), short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), I_{Pmax}, and V_{Pmax} 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 ingression 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_2SO_4 and HNO_3.

REFERENCES

Agilan, S., Mangalaraj, D., Narayandass, S.K., Mohan Rao, G. 2005. Effect of thickness and substrate temperature on structure and optical band gap of hot wall-deposited $CuInSe_2$ polycrystalline thin films. *Physica B* 365: 93-101

Akaki, Y., Ohryoji, N., Yoshino, K., Kawakita, S., Imaizumi, M., Niki, S., Sakurai, K., Ishizuka, S., Ohshima, T., Ikari, T. 2004. Proton irradiation damages in $CuInSe_2$ thin film solar cell materials by a piezoelectric photothermal spectroscopy. *Solid-State Electronics* 48: 1815-1818

Akl, A.A.S., Ashour, A., Ramadan, A.A., Abd El-Hady, K. 2001. Structural study of flash evaporated $CuInSe_2$ thin films. *Vacuum* 61: 75-84

Ashour, A., Akl, A.A.S., Ramadan, A.A., El-Kadry, N.A., Abd El-ady, K. 2006. Optical manipulation of temperature formation of $CuInSe_2$ thin films. *Materials Science and Engineering B* 134: 63-67

Assi, A., Mohammad Al-Amin, A. 2012. Improving the efficiency of c-Si solar cells through the optimization of emitter profile and low resistance ohmic metal contact. *Procedia Engineering* 50: 246-252

Barett, C.S. 1956. Structure of metals. In *Crystallographic methods, principles and Data*, pp.156. New York: McGraw-Hill.

Bushroa, A.R., Rahbari, R.G., Masjuki, H.H., Muhamad, M.R. 2012. Approximation of crystallite size and microstrain via XRD line broadening analysis in TiSiN thin films. *Vacuum* 86: 1107-1112

Cao, G. 2004. Characterization and properties of nanomaterials. In *Nanostructures & nanomaterials: Synthesis, properties & applications*, pp. 371. London: Imperial College Press.

Champness, C.H. 2003. Diffusion length estimation in $CuInSe_2$-based cells by the photocurrent-capacitance method. *Thin Solid Films* 431-432:172-175

Chandra, N., Sharma, V., Chung, G.Y., Schroder, D.K. 2011. Four-point probe characterization of 4H silicon carbide. *Solid-State Electronics*. 64:73-77

Changshi, L., Feng, L. 2012. Natural path for more precise determination of band gap by optical spectra. *Optics Communications* 285: 2868-2873

Deepa, K.G., Jayakrishnan, R., Vijayakumar, K.P., Sudha Kartha, C., Ganesan, V. 2009. Sub-micrometer thick $CuInSe_2$ films for solar cells using sequential elemental evaporation. *Solar Energy* 83: 964-968

Durisch, W., Lam, K.H., Close, J. 2006. Efficiency and degradation of a copper indium diselenide photovoltaic module and yearly output at a sunny site in Jordan. *Applied Energy* 83: 1339-1350

Fearheiley, M.L., 1986. The phase relations in the Cu,In,Se system and the growth of $CuInSe_2$ single crystal. *Solar Cells* 16:91-100

Fernandez, A.M., Sebastian, P.J., Calixto, M.E., Gamboa, S.A., Solorza, O. 1997. Characterization of co-electrodeposited and selenized CIS ($CuInSe_2$) thin films. *Thin Solid Films* 298: 92-97

Firoz Hasan, S.M., Subhan, M.A., Mannan, K.M. 2000. The optical and electrical properties of copper indium di-selenide thin films. *Optical Materials* 14: 329-336

Graham, R.L., Alers, G.B., Mountsier, T., Shamma, N., Dhuey, S., Cabrini, S., Geiss R.H., Read, D.T., Peddeti, S. 2010. Resistivity dominated by surface scattering in sub-50 nm Cu wires. *Applied Physics Letters* 96: 042116

Gorley, P.M., Khomyak, V.V., Vorobiev, Y.V., Gonzalez-Hernandez, J., Horley, P.P., Galochkina, O.O. 2008. Electron properties of n- and p-$CuInSe_2$. *Solar Energy* 82: 100-105

Igasaki, Y., Maeda, M., Harada, M., Fujiwara, T. 1996. Preparation of $CuInSe_2$ films by hot-wall evaporation technique. *J. Crystal Growth* 167: 769-772

Jayachandran, M., Chockalingam, M.J., Murali, K.R., Lakshmanan A.S. 1993. $CuInSe_2$ for photovoltaics: a critical assessment. *Materials Chemistry and Physics* 34: 1-13

Josephine, L.Y.C. 2011. Structural, electrical, thermal and optical properties of polycrystalline chalcogenide compounds (CuSe, SnSe and Cu_2SnSe_3), PhD Thesis, Universiti Putra Malaysia.

Kasap, S., Capper, P. 2006. Optical properties of Electronic Materials: Fundamentals and Characterization. In *Electronic and Photonic Materials*, pp. 57. New York: Springer.

Kim, C.R., Han, S.Y., Chang, C.H., Lee, T.J., Ryu, S.O. 2010. Synthesis and characterization of $CuInSe_2$ thin films for photovoltaic cells by a solution-based deposition method. *Current Applied Physics* 10: S383-S386

Kindyak, V.V., Kindyak, A.S., Gremenok, V.F., Kutas, A.A. 1994. Optical transitions in laser-evaporated thin $CuInSe_2$ films. *Thin Solid Films* 240:114-115

Kittel, C. 2005. Introduction to Solid State Physics. In *Semiconductor Crystals*, pp. 189-190. USA: John Wiley & Sons.

Klais, J., Moller, H.J., Cahen, D. 2000. Calculation and experimental characterization of the defect physics in $CuInSe_2$. *Thin solid films* 361-362: 446-449

Knight, K.S. 1992. The crystal structures of $CuInSe_2$ and $CuInTe_2$. *Material Research Bulletin* 27:161-167

Kojima, T., Koyanagi, T., Nakamura, K., Yanagisawa, T., Takahisa, K., Nishitani, M., Wada, T. 1998. Stability of Cu(In,Ga)Se_2 solar cells and evaluation by C-V characteristics. *Solar Energy Materials and Solar Cells* 50: 87-95

Kontges, M., Reineke-Koch, R., Nollet, P., Beier, J., Schaffler, R., Parisi, J. 2002. Light induced changes in the electrical behavior of CdTe and Cu(In,Ga)Se_2 solar cells. *Thin Solid Films* 403-404: 280-286

Kotkata, M.F., Kandil, K.M., Al-Kotb, M.S. 1996. Electrical and optical studies on amorphous $CuInSe_2$ films. *Journal of Non-Crystalline Solids* 205-207: 180-183

Lam, K.H., Close, J. and Durisch, W. 2004. Modelling and degradation study on a copper indium diselenide module. *Solar Energy* 77: 121-127

Lee, H.S., Okada, H., Wakahara, A., Yoshida, A., Ohshima, T., Itoh, H., Kawakita, S., Imaizumi, M., Matsuda, S. 2003. Effect of proton irradiation on electrical properties of $CuInSe_2$ thin films. *Solar Energy Materials & Solar Cells* 75: 57-63

Maeda, T., Wada, T. 2009. Characteristics of chemical bond and vacancy formation in chalcopyrite-type $CuInSe_2$ and related compounds. *Physica Status Solidi C* 6: 1312-1316

Malar, P., Damodara Das, V., Kasiviswanathan, S. 2004. Characterization of stepwise flash-evaporated $CuInSe_2$ films. *Vacuum* 75: 39-49

Mehdaoui, S., Benslim, N., Aissaoui, O., Benabdeslem, M., Bechiri, L., Otmani, A., Portier, X., Nouet, G. 2009. Study of the properties of $CuInSe_2$ materials prepared from nanoparticle powder. *Materials Characterization* 60: 451-455

Moharram, A.H., Al-Mekkaway, I.M., Salem, A. 2002. Optical properties and structural changes of thermally co-evaporated CuInSe films. *Applied Surface Science* 191: 85-93

Mudryi, A.V., Gremenok, V.F., Victorov, I.A., Zalesski, V.B., Kurdesov, F.V., Kovalevski, V.I., Yakushev, M.V., Martin, R.W. 2003. Optical characterization of high-quality $CuInSe_2$ thin films synthesized by two-stage selenisation process. Thin Solid Films 431-432: 193-196

Muller, J., Nowoczin, J., Schmitt, H. 2006. Composition, structure and optical properties of sputtered thin films of $CuInSe_2$. Thin Solid Films 496: 364-370

Neumann, H., Perlt, B. 1982. Optical properties of amorphous $CuInSe_2$. *Solid State Communications* 42: 855-856

Nick Dalacu. 2004. Thin-film solar modules with reduced corrosion. *US Patent Application Publication*. US2004/0118445A1

Niki, S., Suzuki, R., Ishibashi, S., Ohdaira, T., Fons, P.J., Yamada, A., Oyanagi, H., Wada, T., Kimura, R., Nakada, T. 2001. Anion vacancies in $CuInSe_2$. *Thin Solid Films* 387: 129-134

Okada, H., Fujita, N., Lee, H.S., Wakahara, A., Yoshida, A., Ohshima, T., Itoh, H. 2003. Deep level transient spectroscopy study of electron-irradiated $CuInSe_2$ thin films. *Journal of Electronic Materials* 32: 5-8

Otte, K., Lippold, G., Hirsch, D., Gebhardt, R.K., Chasse, T. 2001. Conductivity type conversion of p-type $CuInSe_2$ due to hydrogenation. *Applied Surface Science* 179:203-208

Park, S.C., Kwon, S.H., Song, J.S., Ahn, B.T. 1998. Electrical properties of CuInSe2 films prepared by evaporation of Cu2Se and In2Se3 compounds. *Solar Energy Materials and Solar Cells* 50: 43-49

Parkes, J., Tomlinson, R.D., Hampshire, M.J., 1973. The fabrication of p and n type single crystals of $CuInSe_2$. *J. Crystal Growth* 20:315-318

Postnikov, A.V., Yakushev, M.V. 2004. Lattice dynamics and stability of $CuInSe_2$. *Thin Solid Films* 451-452: 141-144

Radue, C., Van Dyk, E.E. 2009. Degradation analysis of thin film photovoltaic modules. *Physica B* 404: 4449-4451

Ramaiah, K.S., Raja, V.S., Bhatnagar, A.K., Juang, F.S., Chang, S.J., Su, Y.K. 2000. Effect of annealing and γ-irradiation on the properties of $CuInSe_2$ thin films. *Materials Letters* 45: 251-261

Rao, A., Krishnan, S., Sanjeev, G., Siddappa, K., Ullal, H.S., Wu, X. 2009. 8MeV electron irradiation studies on electrical characteristics of $Cu(In,Ga)Se_2$ solar cells. *Solar Energy Materials & Solar Cells* 93: 1618-1623

Reger, D.L., Goode, S.R., Ball, D.W. 2010. Chemistry of Hydrogen, Elements in Group 3A through 6A, and the Noble Gases. In Chemistry: Principles and Practice, pp. 882. California: Brooks/Cole.

Repins, I., Beall, C., Vora, N., DeHart, C., Kuciauskas, D., Dippo, P., To, B., Mann, J., Hsu, W.C., Goodrich, A., Noufi, R. 2012. Co-evaporated $Cu_2ZnSnSe_4$ films and devices. *Solar Energy Materials & Solar Cells* 101: 154-159

Rincon, C., Marquez, R. 1999. Defect physics of the $CuInSe_2$ chalcopyrite semiconductor. *Journal of Physics and Chemistry of Solids* 60: 1865-1873

Rincon, C., Sanchez Perez, G. 1984. Influence of the carrier concentration on the optical absorption edge of n- $CuInSe_2$. *Solid State Communications* 50: 899-901

Rincon, C., Sanchez Perez, G. 1986. Degeneracy effect on the optical properties of $CuInSe_2$. *Solar Cells*, 16:363-368

Rockett, A., Abou-Elfotouh, F., Albin, D., Bode, M., Ermer, J., Klenk, R., Lommasson, T., Russell, T.W.F., Tomlison, R.D., Tuttle, J., Stolt, L., Walter, T., Peterson, T.M. 1994. Structure and chemistry of $CuInSe_2$ for solar cell technology: current understanding and recommendations. *Thin Solid Films* 237: 1-11

Sakata, H., Ogawa, H. 2000. Optical and electrical properties of flash-evaporated amorphous $CuInSe_2$ films. *Solar Energy Materials & Solar Cells* 63: 259-265

Satour, F.Z., Zegadi, A. 2012. Xe irradiation-induced defects in $CuInSe_2$ by phase resolved photoacoustic spectroscopy. *Materials Science and Engineering B* 177: 436-440

Schon, J.H., Alberts, V., Bucher, E. 1997. Structural and optical characterization of polycrystalline $CuInSe_2$. *Thin Solid Films* 301:115-121

Senthil, K., Nataraj, D., Prabakar, K., Mangalaraj, D., Narayandass, Sa.K., Udhayakumar, N., Krishnakumar, N. 1999. Conduction studies on copper indium diselenide thin films. *Materials Chemistry and Physics*. 58:221-226

Shah, N.M., Panchal, C.J., Kheraj, V.A., Ray, J.R., Desai, M.S. 2009. Growth, structural and optical properties of copper indium diselenide thin films deposited by thermal evaporation method. *Solar Energy* 83:753-760

Shimura, F. 1989. Basic Semiconductor Physics. In *Semiconductor Silicon Crystal Technology*, pp.82. San Diego: Academic Press.

Swartzendruber, L.J. 1964. Four-point probe measurement of non-uniformities in semiconductor sheet resistivity. *Solid-State Electronics* 7: 413-422

Tanaka, T., Yamaguchi, T., Wakahara, A., Yoshida, A., Taniguchi, R., Matsuda, Y., Masatoshi, F. 2003. Effect of 8 MeV electron irradiation on electrical properties of $CuInSe_2$ thin films. *Solar Energy Materials & Solar Cells* 75: 115-120

Tarrant, D.E., Gay, R.R., Hummel, J.J., Jensen, C., Ramos, A.R. 1991. $CuInSe_2$ module environmental reliability. *Solar Cells* 30:549-557

Valdes, L.B. 1954. Resistivity measurements on germanium for transistors. *Proceedings of the I-R-E* 420-427

Yan, Y., Jones, K.M., Jiang, C.S., Wu, X.Z., Noufi, R., Al-Jassim, M.M. 2007. Understanding the defect physics in polycrystalline photovoltaic materials. *Physica B* 401-402: 25-32

Yanagisawa, T. and Kojima, T. 2003. The stability of the $CuInSe_2$ solar mini-module I-V characteristics under continuous and light/dark irradiation cycle tests. *Microelectronics Reliability* 43: 503-507

Yip, L.S., Shih, I., Champness, C.H. 1993. Method of avoiding ampoule adhesion of ingots in Bridgman growth of $CuInSe_2$. *Journal of Crystal Growth* 129:102-106

Zegadi, A., Slifkin, M.A., Djamin, M., Tomlinson, R.D., Neumann, H. 1992. Photoacoustic spectroscopy of defect states in $CuInSe_2$ single crystals. *Solid State Communications* 83: 587-591

Zhang, S.B., Wei, S.H., Zunger, A., Katayama-Yoshida, H. 1998. Defect physics of the $CuInSe_2$ chalcopyrite semiconductor. *Physical Review B*. 57: 9642-9656