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THIN FILM SOLAR CELLS FROM EARTH ABUNDANT MATERIALS

GROWTH AND CHARACTERIZATION OF $Cu_2ZnSn(SSe)_4$ THIN FILMS AND THEIR SOLAR CELLS

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Thin Film Solar Cells from Earth Abundant Materials

Dedicated to My Beloved Parents
Mrs Sampoornamma Kodigala
Mr Sankaraiah Kodigala

Preface

This book describes current status of photovoltaic technology in the process of earth abundant solar cells and deals several things about fabrication and characterization of solar energy materials, including thin film solar cells. The $Cu_2ZnSn(S_{1-x}Se_x)_4$ based solar cells are technologically premature, compared with $CuIn_{1-x}Ga_xSe_2$ (CIGS) based thin film solar cells. Therefore, this book illustrates basic properties of materials and thin film solar cells and has five chapters mainly dealing $Cu_2ZnSn(S_{1-x}Se_x)_4$ system for cell applications.

First chapter deals utilization of renewable energy in many ways for the mankind. To produce electricity by solar energy, the achievements of different companies working in the thin film solar cell industry are emphasized to understand overall situation of the market. The usage of flexible thin film solar cells in the remote areas is explained. The possible earth abundant solar energy materials in the earth crust for low-cost thin film solar cells are mentioned in this chapter. The role of contemporary solar cells, such as Si, CIGS, CdTe, along with Cu_2ZnSnS_4 (CZTS) solar cells are nicely described by providing high priority for the thin film solar cells. The basic working principles of different types of solar cells such as conventional thin film solar cells, quantum dot solar cells, and plasmonic solar cells are quietly illustrated with schematic diagrams. The physics behind the conventional solar cells with bilayer structures is described well to understand. A comparison between CIGS and CZTS thin film solar cells is also exploited.

There are possibilities of generation of secondary phases in the $Cu_2ZnSn(S_{1-x}Se_x)_4$ system while growing it. Therefore, the properties of all secondary phases, which would probably arrive from this compound, such as Cu_2S, SnS, SnS_2, Sn_2S_3, ZnS, ZnSe, Cu_2Se, are distinguished in the second chapter. The growth of these phases by several techniques is cited. In addition, the structural, optical, and electrical properties of the materials are elaborated in this chapter. Some of the binary compounds are useful as absorbers and others as windows for solar cell applications. For example, the Cu_2S and SnS are used as absorbers whilst ZnS and ZnSe are used as window layers in the solar cells that they depend on the basis of their band gaps or other properties. The fabrication processes of Cu_2S and SnS thin film solar cells by different techniques are emphasized. The I–V measurements, stability, efficiencies of the solar cells are described. So far, the SnS-based cells exhibit low efficiency for which the reasons are elaborated. The Cu_2S-based cells show reasonable solar energy conversion efficiency of around 10% but the efficiency decreases with age owing to instability.

Third chapter mainly describes how to grow Cu_2ZnSnS_4 (CZTS) thin films by vacuum and nonvacuum processes because the optimum growth process is very important to have good quality thin film to achieve high efficiency thin film solar cells. The CZTS thin films are grown by different techniques such as chemical solution process, ink jet printing, screen printing, spin coating, spray, thermal vacuum evaporation, reactive sputtering, sputtering, pulsed laser deposition, and electrodeposition techniques. More or less similar techniques are employed to grow $Cu_2ZnSnSe_4$ (CZTSe) or CZTSSe thin films. All the grown metal stacks or semiconductor layers such as CZT, CZTS, or CZTSe are sulfurized or selenized under S or Se atmosphere to obtain device quality thin films for solar cell applications. This postannealing process is well illustrated by pointing optimized conditions.

Fourth chapter contributes a lot of things of characterization techniques, which are highly helpful to assess the quality of the device layers such as absorbers, windows, or other layers. The techniques, which are employed for characterization of the samples, are EDS, XRF, SIMS, ICP, XPS, XRD, Raman, etc. In particular, the EDS, SIMS, and ICP techniques provide how to characterize the samples in detail. The SEM and AFM scan the surface of the samples to determine roughness, grain sizes, etc. that are detailed. The XRD analysis characterizes different kind of samples such as CZTS, CZTSe, and CZTSSe but fails to determine structure of whether kesterite or stannite of them but Raman spectra distinguishes the structures. The defect levels determined by photoluminescence analysis are explicitly illustrated. Based on these characterization results, the CZTS, CZTSe, and CZTSSe samples are analyzed, which determine the quality of the samples that fit well to the solar cells. The characterization results provide compositional, chemical states of compounds, structural, optical properties of the samples. The electrical properties of CZTS, CZTSe, CZTSSe compounds are also given in this chapter.

The fabrication of thin film solar cells using CZTS, CZTSe, and CZTSSe absorbers is explained in the last chapter. The band structures of heterojunctions such as CZTS/CdS and CZTS/ZnS with different orientations of buffer layers are discussed. The cells made with different kinds of techniques are explained with several examples. The I−V characterization of the samples provides efficiency, series resistance, shunt resistance, open circuit voltage, short circuit current, fill factors, etc. The reasons for occurring low and high efficiencies in the thin film solar cells are explained. How the composition of the absorber affects the efficiency of the cells is well described. The annealing recipe on the absorber is one of the important factors to decide photovoltaic parameters. The carrier concentration and resistances of the samples are also play a big role in the thin film solar cells to achieve high efficiency. The cells made with other environment-friendly window layers are explained. The band gaps of absorber, buffer, and window layers can be determined from quantum efficiency measurements.

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Contents

1 Introduction

1.1 Current Trends in Utilization of Solar Energy

The solar, wind, and thermal energies are normally come under the umbrella of the renewable energy, which is one of the alternatives to the conventional energy. The hydro, thermal by coal, and nuclear can be treated as conventional energy sources. The nuclear disasters of Chernobyl and Fukushima are cautioning world about dangers of nuclear plants and consequences to mankind. The nuclear energy shares 7% in world energy and 15% in production of electricity. In order to govern the safety of nuclear power plants, the international energy agency revamps the safety regulations and guidelines. France, Japan, EU, and the United States depend on nuclear power plants for electricity in their energy resources of 75, 30, 28, and 19%, respectively [1,2]. So far, China, Russia, Korea, and Latin America have 28, 11, 5, and 8 nuclear power plants, respectively. A lot of countries promised that they gradually abandon the nuclear power plants in order to reduce risk factor. Capacity of total energy of the world is 4742 GW in which share of the solar energy is 37 GW nothing but 0.78% in 2010. In 2009, the new installation of solar energy is 7.1 GW that is doubled in 2010 as 17.5 GW. The solar energy produced by different countries like Germany, Italy, Czech Republic, Japan, and the United States is 7.5, 3.8, 1.2, 0.8, and 0.8 GW, respectively. In the existing global renewable energy, the production of hydroelectricity is 0.5 TW, tides and ocean currents of 2 TW, geothermal of 12 TW, wind power of 2–4 TW, and solar energy of 120,000 TW. Of all these, the contribution of solar energy is the highest [3].

The top 10 companies such as Q-cells, Sharp, Suntech, Keyocera, First Solar, Motech, Solar World, Jasolar, Yingli, and Sanyo produce solar energy of 9, 8, 8, 5, 5, 4, 4, 3, 3, and 4%, respectively. The remaining 47% is covered by the rest of the world. In fact, the conventional electricity costs around $0.39/kW h or less. In recent years, a lot of efforts have been initiated to develop low-cost thin-film solar cells, which are alternative to high-cost silicon (Si) solar cells. The reduction of cost is easier in non-Si thin-film solar cells than in Si solar cells. We can obviously play as much as alternations in thin solar cells to improve performance of them whereas Si solar cells do not give much room to tailor the parameters to enhance the efficiency. The main drawback with the Si solar cells is that it is an indirect band gap semiconductor and needs a thick layer around 180–300 μm to absorb photons [4]. The band gap of 1.1 eV for Si does not absorb more than 50% of the visible spectrum, i.e., blue and green regions. These factors undermine to reduce the cost of Si solar cells. The low-cost and high-quality chalcogenide-based

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thin-film solar cells have to be developed, which will potentially reduce manufacturing cost of solar energy from \$3−5/W to \$0.60/W. Recently, First Solar Company proclaimed that the current cost of electricity by its CdTe solar panel is \$0.70−0.72/W and aims to develop solar cells at the cost of \$0.6−0.5/W [5].

The search for suitable band gap materials for the applications of solar cells is essential. Therefore, scientists have initiated to fabricate novel and new absorbers by identifying the earth's abundant solar energy materials to reduce the cost of thin-film solar cells. Recently, $Cu(In_{1-y}Ga_y)(S_{1-x}Se_x)_2$ (CIGSS) based thin-film solar cells are technologically developed in which the Zn/Sn replaces In/Ga that reduces cost of the solar panels partially. The replacement changes the system from $Cu(In_{1-y}Ga_y)(S_{1-x}Se_x)_2$ to $Cu_2(ZnSn)(S_{1-x}Se_x)_4$. In every year, the cost of In or Ga doubles its original value owing to high demand in the market. In the earth crust, the existences of Cu, Zn, Sn, S, and Se are 50, 75, 2.2, 260, and 0.05 ppm, respectively whereas availability of In is 0.049 ppm (Figure 1.1) [6,7]. It is learned that 30 tons of In is necessary to produce 1 GW power [8,9,10]. The indium tin oxide (ITO) is one of the main players in the realm of optoelectronic screen displays where In is the prime component to make its oxide layer. On the other hand, the usage of Ga in the light emitting devices is high. Therefore, the optoelectronic industry has high impact for demand of In and Ga. In this context, the search for alternative solar energy materials has to be done in order to reduce the cost. The main objective of the solar industry is to make the laboratory sodalime glass (SLG)/Mo/$Cu_2(ZnSn)S_4$/CdS/ZnO/ZnO:Al thin-film solar cell with the efficiency of >15% and size of less than 1 cm^2 at initial stage that will lead to prototype thin-film solar cell module indicating that the laboratory technology will be translated into industrial scale. The advantage of chosen chalcogenide-based thin-film solar cells is quite profitable to the mankind because it relays on low-cost and abundant $Cu_2(ZnSn)S_4$ absorber. The size of prototype module can then be increased to meter by meter size as an industrial thin-film solar cell panel. The low-cost thin-film solar cell panels with solar to electrical conversion efficiency of

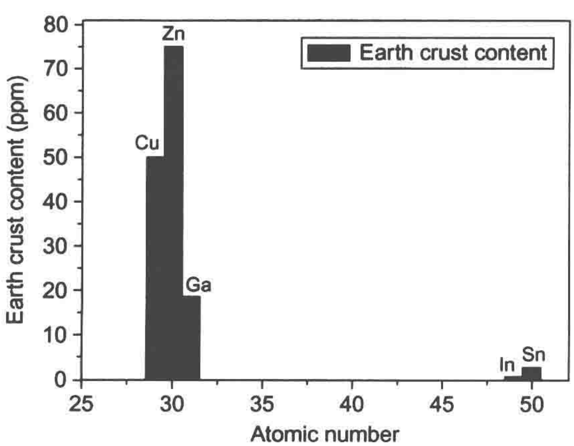

Figure 1.1 Estimated content of Cu, Zn, Sn, In, and Ga in the earth crust.

$\sim$13% or more can adequately be commercialized in the market. The research and development (R & D) supports to grow various stack layers as a sandwich as well as monolithic integration of cells for modules, which is a main constituent to the industry to address the technical problems during the fabrication of thin-film solar cells either in the laboratory or in the industry.

The motto of companies is to develop low-cost solar cells, which potentially mitigate over cost of electricity generated by present Si or $CuIn_{1-x}Ga_xSe_2$ (CIGS) based solar cells. For example, the current cost of electricity >\$1/W by thin-film solar cells is higher than $\sim$\$0.37/kW of conventional electricity. A lot of companies target to reduce solar power cost from present cost of \$1 to 0.60 by 2014. Today, the laboratory CIGS thin-film solar cells lead to the highest efficiencies of 20.3% with an active area of 0.5 cm^2 made by Center for Solar-Energy and Hydrogen Research (ZSW) Company and 18.7% on glass and flexible substrates, respectively, as close to that of Si indicating that understanding of full depth of each layer in the sandwich of thin-film solar cells to some extent has been done [11]. The First Solar company took a decade to develop high-efficiency panel that the giant CdTe thin-film solar cells and their solar panels show efficiencies of 17.3 and 14.4%, respectively [5]. The Germany-based Avancis Company develops monolithically integrated CIGS-based thin-film solar cell panel with size of 30×30 cm^2, which delivers efficiency of 12% and power of 30 W. A number of panels connected in series produce power of 20 MW in Torgau, Germany. The active area cell presumably produces efficiency of 15.5%. The scientists at Empa, the Swiss Federal Laboratories for Materials Science and Technology tout record efficiency of 18.7% on flexible substrates for CIGS by surpassing their own efficiency of 17.6%. Honda Soltec developed 13% efficiency CIGS thin-film solar cell panels. Several companies such as First Solar, Nanosolar, Globalsolar, Muosolar, Solopower, and Solexant have been immensely involving to develop and produce CIGS-based thin-film solar cell and mini-modules to target production of several gigawatt per year range around the world. The Ascent Solar Inc. Company develops CIGS monolithically interconnected thin-film solar cells on flexible plastic substrates with module aperture efficiency of 11.9% and module efficiency of 10.5% while Solopower Company made CIGS thin-film solar cell panel on the metal flexible substrates, which exhibits aperture efficiency of 11%. However, the In and Ga metals used for CIGS cells by these companies are expensive in the international metal markets in London. A brilliant new approach uses Zn and Sn or Ge in the place of In and Ga to mitigate cost of the materials. The energy generated by solar panels is obviously pollution-free whereas the electricity generated by coal thermal power plant or nuclear reactor produces pollution of carbon particles, such as CO_2, as green house effect gases or radiation hazard. Recently, we have learned many lessons from the Fukushima nuclear reactor disorder due to Tsunami in Japan. On the other hand, solar energy creates more jobs and steady economic growth that is why the government and private sectors immensely involve to developing renewable energy at lower cost.

The quaternary p-Cu_2ZnSnS_4 (CZTS) absorber is an excellent semiconductor and a serious candidate for thin-film solar cells owing to suitable band gap of

1.5 eV that matches well to the solar spectrum to acquire most of the intensity photons from the solar radiation. So far, the highest reported efficiency of SLG/Mo/CZTS(Se)/CdS/ZnO:Al thin-film solar cell is 10.1% [12] but industrially neophyte. The efficiency of CZTS-based thin-film solar cells has to be improved, in order to reduce production cost of solar cells. The reason to choose CZTS as an absorber among other semiconductors is that all the elements in the absorber are abundant in the earth crust, nontoxic, and cost-effective whereas the world record efficiency (20.3%) $Cu(InGa)Se_2$ (CIGS)-based thin-film cells contain In and Ga, which are meager in the earth and each year their costs are almost doubling, as mentioned earlier. On the other hand, CZTS is friendly to the environment whereas Ga and Se are mildly toxic. The carrier concentration, mobility, and resistivity of CZTS can be easily varied by changing intrinsic doping concentrations without employing extrinsic dopants, which are needed in the suitable range for thin-film solar cell applications. The lattice mismatch of tetragonal structured CZTS with hexagonal CdS may be acceptable to minimize interface states.

The work on CZTS is limited comparing with outstanding work of CIGS thin-film solar cells. The investigation on new and cheap material is essential to improve efficiency of the cells. We propose to develop CZTS-based thin-film solar cell, which is compatable to CIGS thin film solar cells that the CZTS thin-film absorber will be grown onto Mo-coated glass substrates by radiofrequency (RF) sputtering system using two-stage process employing Cu, ZnS, and SnS targets or combined target in our laboratory. In the first stage, several tests have to be done on the grown CZTS absorber to find out composition grading, surface, structural, optical, and electrical properties. In the second stage, CZTS-based thin-film solar cell will be developed. The CdS as a window by chemical bath deposition technique, i-ZnO and ZnO:Al layers by RF technique will be successively grown onto SLG/Mo/CZTS. Finally, metallic grids will be formed to complete thin-film solar cell structure. The developed SLG/Mo/CZTS/CdS/ZnO/ZnO:Al thin-film solar cell will be tested by conducting several tests, such as current–voltage (I–V) measurements to find out efficiency of the cells. In addition, the photovoltaic parameters such as open circuit voltage (V_{oc}), short current (J_{sc}), and fill factor (FF) will be determined. The capacitance–voltage ($C-V$) measurements allow us to determine carrier concentration of the acceptors in the cell that determines quality of thin-film solar cell. Our main goal is to develop quality CZTS thin-film absorber and efficient CZTS thin-film solar cells. The efficiency of the cell can further be improved.

There are several techniques in developing thin-film solar cells. Vacuum evaporation is one of the well-pioneered techniques among them in growing an absorber layer for thin-film solar cells. For example, the Solibro GmbH Company in Thalheim, Germany, successfully produced CIGS-based modules in megawatt range by coevaporation or physical vapor deposition method on sputter-coated Mo glass substrates. So far, the Company has generated 45 MW modules [13]. The scientists can eventually develop high-quality $Cu_2ZnSn(SeS)_4$ (CZTSSe) thin-film solar cells by vacuum coevaporation at low cost using their expertise in the