Abstract

Increasing global energy consumption together with environmental concerns has led to much interest in alternative, cleaner sources of energy such as solar photovoltaic. Researchers in the solar cell community have been looking for ways to reduce costs while maintaining or increasing already high efficiencies. A fundamental understanding of the materials under consideration is essential to rapid development of new technologies. The I-III-VI_2 thin films offer promising systems for achieving high efficiency solar cells at lower costs. In fact, by tailoring the chemistry of the compounds it is possible to change the bandgap of the material in order to collect sunlight more efficiently. First of all, this thesis focuses on absorber layer material preparation and characterization, especially nanocrystalline thin films and consideration of both structural and electrical characteristics of such main cell absorber layer. The thesis examines how different preparation techniques and material usage could affect the properties of the synthesized thin films (absorber layer).

In this study $CuInSe_2$ and $CuInS_2$ thin films were deposited onto ITO glass substrate using the electrodeposition technique in aqueous solution. The electrodeposited films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS). The annealing effects on the electrodeposited precursors were investigated. The chalcopyrite structure of $CuInSe_2$/$CuInS_2$ showed an enhancement of crystallinity after subsequent selenization/sulfurization treatment in Se/S atmosphere, respectively. XRD and SEM studies revealed a dramatic improvement of the crystalline quality of CIS films after annealing treatments. The optical properties of annealed $CuInSe_2$-Se and $CuInSe_2$-S thin films have been studied in order to determine the effect of annealing process in different selenium and sulfur atmosphere. The optical transmittance spectra were measured in the wavelength range 400 - 1000 nm of the visible region. The optical band gap were found to be 1.48 and 1.35 eV, for $CuInSe_2$-Se and $CuInSe_2$-S which is agreement with the reported values of the optical band gap of $CuInSe_2$ and $CuInS_2$ [22], As we notice the difference in annealing temperatures and time also affects the resultant band gap energy in addition to the Se/S percentages in both samples. Mott-Schottky measurements were used to assess the conductivity type of the films and their carrier concentration. The prepared samples underwent an etching process to remove the binary accumulated Cu_{2-x}(Se,S) phases shown in FESEM pictures. This etching process has shown a noticeable decrease in both, the flat band potencial, V_{fb} (V), and the number of acceptors, N_A (cm^{-3}) in selenized $CuInSe_2$ and sulfurized $CuInS_2$ samples.

In the second step we modified copper indium $CuIn_xCr_yGa_{1-x-y}Se_2$ where x=0.4, y= (0.0, 0.1, 0.2, 0.3) superstrate layer by spin coating process. $CuIn_xCr_yGa_{1-x-y}Se_2$ where x=0.4, y= (0.0, 0.1, 0.2, 0.3) nanoparticles have been synthesized firstly using a wet chemical hydrothermal method. This method is based on a non-vacuum thermal process without any additional selenization process. Introducing different metal sources in an autoclave with ethylenediamine as solvent, CIGS nanoparticles were obtained at different temperatures range 190-230°C. The X-ray diffraction (XRD) results confirmed the formation of a tetragonal $CuIn_xCr_yGa_{1-x-y}Se_2$ chalcopyrite structure. The morphology and crystal size of the prepared nanoparticles were determined by field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDS) and high-resolution transmission electron microscopy (HR-TEM). The conductivity of the synthesized nanoparticle samples was measured in a range of temperature between 20 and 200°C by impedance spectroscopy in the frequency interval of $10^{-1} < f < 10^7$ Hz applying a 0.1 V signal amplitude.

Finally, we turned again to the study of the annealing temperature effect on Kesterite materials but this time in those of very low-cost materials and environmentally friendly Cu_2ZnSnS_4. We studied the growth of quaternary Cu_2ZnSnS_4 (CZTS) kesterite thin films by a single step electrochemical deposition followed by annealing at low temperature. The influence of different annealing atmospheres at constant annealing times (t = 45 min) and fixed preparation controlling parameters; i.e., starting materials (precursor metal salts) solution concentration, time of deposition and electrodeposition potential. Structural, compositional, morphological, and optical properties, as well as photoelectrochemical properties were studied. The films, sulfurized during 2 hours, showed a prominent kesterite phase with a nearly stoichiometric composition. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), EDS and UV-VIS-NIR spectrometry. X-ray diffraction and confirmed the formation of pure kesterite CZTS films. SEM shows that films are compact with dense morphology and homogeneous distribution. EDS analyzed the elemental constituents of the quaternary Cu_2ZnSnS_4 with an apparent Cu deficiency and S rich for the sulfurized samples. From optical study, the energy gap was indexed for the sulfurized samples, Eg=1.52 eV. Under illumination sulfurized CZTS films exhibits negative photocurrent and positive photovoltage values confirming the p-type character of the films