

**Study of Electrodeposited Cu_2O , CuInS_2 and ZnSe for
Applications in Thin Film Solar Cells**

Loku Balasuriyage Don Ruwan Palitha Wijesundera

A Thesis presented for the Degree of Master of Philosophy

**Department of Physics
University of Kelaniya
Sri Lanka**

April – 2001

Abstract

In this study, preparation of Cu_2O , CuInS_2 and ZnSe thin films for fabrication of $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ and $\text{CuInS}_2/\text{ZnSe}$ heterojunction solar cells are presented. A general discussion of the history and theoretical background of solar cells are also made. The experimental study deals with growth and characterisation of electrodeposited Cu_2O , growth and characterisation of CuInS_2 , potentiostatic electrodeposition of ZnSe , characterisation of ZnSe and fabrication and characterisation of thin film $\text{ITO}/\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Metal}$ and $\text{Ti}/\text{CuInS}_2/\text{ZnSe}/\text{Metal}$ heterostructure solar cells. Cu_2O films of $\sim 0.8 \mu\text{m}$ thickness were potentiostatically electrodeposited on ITO/glass substrates using previously determined parameters. X-ray diffraction, X-ray fluorescence, scanning electron microscopy, optical absorption and reflectance, C-V measurements were used to study the material. The deposited Cu_2O is of high purity having a polycrystalline structure with a grain size of $\sim (1-2) \mu\text{m}$. It has a direct band gap of 2 eV. As deposited Cu_2O was n-type in conductivity and the doping density of the material was of the order of 10^{18} cm^{-3} . Sulphurisation of Cu-In alloy prepared by one step electrodeposition and sequential electrodeposition was investigated to obtain CuInS_2 films. Both methods were successful in producing CuInS_2 thin films. Current-potential scan was carried out to establish the deposition parameters for potentiostatic electrodeposition of Cu-In alloy. X-ray diffraction, X-ray fluorescence, scanning electron microscopy, optical reflectance, C-V measurements and photoelectrochemical characterisation were used to study the material. The Cu^{2+} to In^{3+} ionic ratios in the Cu-In alloy deposition bath or the Cu/In atomic ratios of the initial Cu and In layers played a major role in determining the composition of the CuInS_2 films. Both methods produced single phase polycrystalline chalcopyrite

structure CuInS_2 having a direct band gap of 1.5 eV. As deposited CuInS_2 was found to be n-type in conductivity and the doping density of the material was of the order of 10^{17} cm^{-3} . The best CuInS_2 films produced V_{oc} of $\sim 300 \text{ mV}$ and $\sim J_{sc}$ of 6 mA/cm^2 in a PEC containing polysulphide as the electrolyte. Current-potential scans were determined in an aqueous solution containing ZnSO_4 and SeO_2 in order to establish the deposition parameters for potentiostatic electrodeposition of ZnSe. ZnSe films of $\sim 0.4 \mu\text{m}$ thickness were potentiostatically electrodeposited on glass/ITO substrate. X-ray diffraction, X-ray fluorescence, optical absorption and reflectance, C-V measurements and photoelectrochemical characterisation were used to study the material. The deposited material was amorphous. As deposited ZnSe was found to be p-type in conductivity and the doping density of the material was of the order of 10^{16} cm^{-3} . Antimony was a good p-type dopant for ZnSe and doped ZnSe films exhibited a doping density of the order of 10^{17} cm^{-3} . A glass/ITO/n- Cu_2O /p- Cu_xS /Al heterostructure solar cell was fabricated by partial sulphidation of Cu_2O . Current-voltage characteristics and spectral response of the devices were studied. The spectral response of the cell was observed to be limited to shorter wavelengths. The best $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ cell exhibited V_{oc} of 255 mV, J_{sc} of 1.62 mA/cm^2 and FF of 0.34 under AM1 artificial illumination. A Ti/ CuInS_2 /ZnSe/ITO heterostructure solar cell was fabricated by electrodepositing very thin ($\sim 0.2 \mu\text{m}$) p-doped ZnSe film on CuInS_2/Ti . Current-voltage and capacitance-voltage characteristics and spectral response of the devices were studied. The best $\text{CuInS}_2/\text{ZnSe}$ cell exhibited V_{oc} of 335 mV, J_{sc} of 2 mA/cm^2 and FF of 0.263 under AM1 artificial illumination. The study reveals the possibility of utilising ITO/ $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}/\text{Metal}$ and Ti/ $\text{CuInS}_2/\text{ZnSe}/\text{Metal}$ heterostructures in developing low-cost thin film solar cells. Further enhancements of the efficiencies of $\text{Cu}_2\text{O}/\text{Cu}_x\text{S}$ and $\text{CuInS}_2/\text{ZnSe}$ solar cells are suggested.