THIN FILMS OF $CuInSe_2$ AND $CuInS_2$ AND THEIR APPLICATIONS TO $Cd(Zn)S/CuInSe_2$ AND $Cd(Zn)S/CuInS_2$ SOLAR CELLS

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ABSTRACT

$CuInSe_2$ and $CuInS_2$ are direct bandgap I-III-VI_2 semiconductors which have recently received a great deal of attention owing to their remarkable photovoltaic properties. The proposed thesis is devoted to : the preparation of thin films of $CuInSe_2$ and $CuInS_2$ by spray pyrolysis; a study of their structural, optical and electrical properties; and the fabrication of Cd(Zn)S/$CuInSe_2$ and Cd(Zn)S/$CuInS_2$ solar cells by spray pyrolysis.

Thin films of $CuInSe_2$ and $CuInS_2$ were prepared by spraying on to glass substrates aqueous solutions of cupric acetate/CuCl/$CuCl_2$, $InCl_3$ and selenourea or thiourea mixed together in the appropriate stoichiometric proportions. In all, four categories of films were prepared; the (SE-CL-1)-series and (SE-CL-2)-series were $CuInSe_2$ films. The SE-CL-1 films were prepared using CuCl and the SE-CL-2 films by using $CuCl_2$ for the 'Cu' ions. Similarly the S-AC and S-CL-2 series $CuInS_2$ films were prepared using cupric acetate and $CuCl_2$ respectively.

The experimental parameters like substrate temperature, spray rate, ratios of starting materials and their concentrations were optimised against structural, optical and electrical properties of the films. The optimum

substrate temperature was found to be in the range 300-350°C. The compositional and structural properties of the films were studied by X-ray diffraction, TEM (Transmission electron microscopy), SEM (Scanning electron microscopy) and XPS (X-ray photoelectron spectroscopy); optical transmission and reflection spectra were obtained and analysed to study the bandgap properties of the films.

Both $CuInSe_2$ and $CuInS_2$ were positively identified by X-ray diffraction but the chalcopyrite lines were not always clearly evident. Electron diffraction patterns, however, did reveal the presence of the chalcopyrite lines confirming that, for the most part, the $CuInSe_2$ and $CuInS_2$ films had the chalcopyrite structure. The presence of the sphalerite phase along with chalcopyrite cannot, however, be ruled out. The diffraction patterns did not show any lines that could not be assigned to $CuInSe_2$ (or $CuInS_2$). The possibility of $Cu_{2-x}Se$ existing as an additional phase along with $CuInSe_2$ is difficult to disprove by X-ray diffraction alone. XPS studies conducted on a number of sprayed $CuInSe_2$ films showed that they did not contain impurities like Cu_2Se, CuSe, In_2O_3, In_2Se_3, SeO_2, indium or selenium. Thus diffraction studies together with XPS show that the films are single phase $CuInSe_2$. Similarly the $CuInS_2$ films were also found to be single phase.

Optical studies showed that the $CuInSe_2$ and $CuInS_2$ films had a direct bandgap with values around 1.0-1.08 eV for $CuInSe_2$ and 1.4-1.52 eV for $CuInS_2$. The absorption coefficient (near the gap) in $CuInSe_2$ films was generally around 10^5 cm^{-1} and in $CuInS_2$ films between 10^4 and 10^5 cm^{-1}.

TEM and SEM micrographs revealed that the as-grown SE-CL-1 $CuInSe_2$ and S-AC $CuInS_2$ films had a uniform growth but small grain size ($\sim$ 500 Å). Annealing these films in nitrogen for about one hour at 400-500 ^oC improved the grain size, and SEM micrographs revealed grains $\sim$ 0.1-0.5 μm after the anneal. The as grown SE-CL-2 $CuInSe_2$ and S-CL-2 $CuInS_2$ films were however superior and had grains of size 0.5-1 μm.

The sprayed $CuInSe_2$ and $CuInS_2$ films were all p-type and it was found that their resistivity could be controlled by varying the Cu/In ratio in the starting solution. By increasing the Cu/In ratio from 0.9 to 1.2 the resistivity of the films decreased linearly from 1000 ohm-cm to about 1 ohm-cm. We speculate that the acceptors in these films are indium vacancies and/or copper atoms on indium sites. Low temperature measurements indicate that grain boundary scattering is the dominant scattering in these films. The best films were found to have Hall mobilities around 1.5 cm^2/Volt-sec.

A number of $Cd(Zn)S/CuInSe_2$ and $Cd(Zn)S/CuInS_2$ solar cells having efficiencies in the range 2–3 % were prepared by spray pyrolysis. The best cells were a 3.15% $Cd(Zn)S/CuInSe_2$ cell with V_{oc}=0.305 V, J_{sc}=32 mA /cm^2; FF=0.32 and area=0.4 cm^2 and a 2.66 % $Cd(Zn)S/CuInS_2$ cell with V_{oc}=0.44 V, J_{sv}=21.7 mA/cm^2, FF $\simeq$ 0.28 and area=0.38 cm^2, both cells illuminated through the Cd(Zn)S at 100 mW/cm^2.

All the cells were characterized by low V_{oc}s high J_{sc}s and low efficiencies. The best cell was examined by J–V plots and V_{oc} versus T measurements and the following parameters were determined : n(the diode factor) = 1.5; V_{D1}=0.63 eV (in the dark); and $E_{g1}-\Delta E$=0.82 eV.

A model band diagram was drawn for the 3.15 % Cd(Zn)S/ $CuInSe_2$ cell. The reasons for the low V_{oc}s (and thus low efficiencies) in these cells are :

(1) the spreading of the space charge region into the Cd(Zn)S because the condition $n_e >> P$ has not been realised;

(2) the low values of the shunt resistance which decrease the V_{oc} and the fillfactor by an amount $\Delta FF = \frac{V_{mp}}{I_{sc} R_{sh}} = \frac{V_{mp}}{j_{sc} A_1 R_{sh}}$ The low shunt resistances are perhaps due to recombination along the grains and the defects (in $CuInX_2$) which are in large numbers for sprayed films; and

(3) The high values of δ_1 and δ_2, the difference between the Fermi level and the valence and conduction bands respectively in $CuInX_2$ and Cd(Zn)S .

LIST OF PUBLICATIONS.

1. Structural and optical properties of sprayed $CuInS_2$ Films.

   Thin Solid Films, 100 (1983) 111 - 116.

2. Structural and Optical properties of sprayed $CuInSe_2$ Films.

   Thin Solid Films, 102 (1983) 291 - 297.

3. Totally sprayed $CuInSe_2$ - Cd(Zn)S and $CuInS_2$-Cd(Zn)S solar cells.

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