SPRAY-PYROLYSED COPPER INDIUM SULPHIDE FILMS FOR PHOTOVOLTAIC APPLICATIONS

By

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DEDICATED TO

MY PARENTS

AND

AUNTY & UNCLE

CERTIFICATE

I am satisfied that the Thesis presented by A.N. Tiwari is worthy of consideration for the award of the Degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or full to any other university or institute for award of any degree/diploma.

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ABSTRACT

Uniform, homogeneous and adherent thin films of $CuInS_2$ have been deposited on various substrates using spray pyrolysis technique. The substrate temperature, composition of spray solution (i.e. Cu/In and S/Cu ratios) and its pH have been identified as the important parameters controlling the crystallographic structure, presence of impurity phases, if any, and electrical resistivity of the film. Deposition conditions have been optimized and the regimes have been established to obtain single phase $CuInS_2$ (pure) and mixed phase ($CuInS_2$ + binary sulfide and/or oxide of Cu and/or In as impurity phase) material. For obtaining single phase $CuInS_2$ films, it is essential to keep the $[S]/[Cu] \geqslant 4$ and excess Cu (with respect to In) in the range of +15 to -5% (In excess) in spray solution. The solution pH should be more than 3. At pH = 3.2, the as-deposited $CuInS_2$ (on glass substrates), deposited at a typical substrate temperature of $\sim$575 K with spray $\sim$ 10 ml.min possesses sphalerite structure which transforms to chalcopyrite structure on annealing at 675 K for 120 min. However, the chalcopyrite $CuInS_2$ is obtained in as-deposited conditions using spray solution of pH = 4.2. Also, the $CuInS_2$ films deposited with spray solution of pH = 3.2 on crystalline substrates (like CdS, ZnO, SnO_x:F, etc.) have chalcopyrite structure in as-deposited conditions, while the structure is sphalerite when amorphous substrates (glass, a-Si, etc.) are used. These films have (112) preferred orientation and the

grain size is $\backsim$ 500 A°. Films sprayed beyond the above described conditions are mixed phase films. Films sprayed with > 20% excess Cu and $\geqslant$ 10% excess In in spray solution have Cu_xS and In_xS_y impurity phases, respectively.

Analyses of transmittance and reflectance spectra have been used to establish the purity of deposited material, in particular to identify the presence of Cu_xS impurity phase which is otherwise difficult to distinguish from $CuInS_2$ using X-ray and electron diffraction techniques. Single phase $CuInS_2$ films (both chalcopyrite and sphalerite) show a sharp direct absorption edge at $\simeq$ 1.38 eV. Another direct transition at 1.32 eV corresponding to the transition from copper vacancy level to the conduction band has also been identified. For mixed phase ($CuInS_2$+Cu_xS) films, an additional direct transition at $\simeq$ 1.2 eV corresponding to Cu_xS is observed. Spectroscopic ellipsometry has been used to evaluate the optical constants of these films in high energy region. The interband transitions have been identified in the ε spectra of pure $CuInS_2$ film. It is observed that presence of any impurity phase (Cu_xS or In_xS_y) affects the ε spectra, and the optical transitions.

The sprayed films have p-type conductivity with a hole mobility of $\backsim 10^{-4}$ $m^2V^{-1}S^{-1}$. The electrical resistivity is found to depend on substrate temperature, excess Cu (or In) in spray solution and its pH. The resistivity of single phase films can be varied from 10^3 to 10^{-2} ohm-meter by varying the excess Cu from -5 to +15% in spray solution. The films deposited with 10% In excess, having In_xS_y impurity phase, show resistivity $\backsim 10^4$ ohm-meter, whereas those deposited with $\geqslant$30% excess Cu, having Cu_xS impurity phase, show resistivity $\backsim 10^{-4}$ ohm-meter. Photoconductivity has been observed in the films sprayed with excess Cu upto 7%. The photoconductivity gain depends on Cu/In ratio in the spray solution. The In at Cu vacancy site acting as donor level is most probably responsible for the photoconductivity.

The feasibility of making all sprayed heterojunction solar cells of $CuInS_2$ with transparent conductors has been demonstrated. Various parameters have been optimized to obtain 3% efficient $CuInS_2/SnO_x$:F and 2% efficient $CuInS_2$/ZnO solar cells. Post-deposition annealing is found to improve the junction formation and solar cell performance. The current transport across the junction is due to multistep tunnelling and recombination through the states in the interface region.

Solar cells of sprayed $CuInS_2$ with evaporated CdS have been made in front-wall and back-wall configuration with efficiencies of 2.5 and 1.2%, respectively. Optical losses in these configurations have been estimated. The use of $Cd_{1-x}Zn_xS$ (with x = 0.20) in back-wall configuration is found to increase the cell efficiency. The generation-recombination mechanism governs the carrier transport across $CuInS_2$/CdS junction. The junction analyses indicate that the behaviour of $CuInS_2$/CdS junction is similar to the Cu_xS/CdS junction.

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