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Structural Properties of $CuGa_xIn_{1-x}Se_2$ Thin Films Deposited by Spray Pyrolysis

Thin films of $CuGa_xIn_{1-x}Se_2$ (x=0.0-1.0) have been prepared by spray pyrolysis onto soda-lime glass substrates heated to a temperature of 325°C. The structure, crystal orientations, lattice parameters and grain size of the experimental films have been studied using the X-ray diffraction and scanning electron microscopy. All the deposited films were polycrystalline and showed single phase with an intense (112) orientation. The lattice parameters, a and c of the films vary linearly with the change of gallium composition. The grain size of the films decrease with the increase of gallium content.

Keywords: $CuGa_xIn_{1-x}Se_2$, Thin films, Spray pyrolysis, Structural properties

1. Introduction

The ternary chalcopyrite semiconductors of the I-III-VI_2 group have attracted considerable attention over the last two decades because of their potential application in the opto-electronic devices, particularly in solar cells. Among the several materials of this group, $CuInSe_2$ and $CuGaSe_2$ have proved to be effective and stable light absorbers for the fabrication of heterojunction solar cells [Nadenau et al, Tuttle et al]. However, the band gap of $CuInSe_2$ (1.04 eV) is well below the optimum value suitable of efficient energy conversion. Incorporation of gallium into $CuInSe_2$ has demonstrated to shift the band gap towards a better match with the incident solar spectrum leading to higher conversion efficiencies. Although thin films of $CuGa_xIn_{1-x}Se_2$ have been grown by a variety of techniques, devices fabricated using multisource elemental evaporation have shown better efficiencies compared to the layers prepared by the other deposition techniques [Tuttle et al]. However, this method is not suitable for the economic production of these layers on large scale due to the conflicting requirements associated with the simultaneous deposition of the different elements. It is therefore interesting to develop a new technique for the growth of high quality $CuGa_xIn_{1-x}Se_2$ films which should be simple and suitable for large scale production of the layers over a greater area. Spray pyrolysis is a simple and economic technique viable for large area production of the films. This technique is currently used for the deposition of II-VI and I-III-VI_2 compounds. Though there are reports on the deposition

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of $CuInSe_2$ films by this technique, there is no detailed study on the preparation of $CuGa_xIn_{1-x}Se_2$ layers with different Ga/In ratios using this method. In our earlier studies, we are successful in synthesising $CuGa_xIn_{1-x}Se_2$ films by spray pyrolysis and some of the results on the physical properties of $CuGa_{0.5}In_{0.5}Se_2$ and $CuGaSe_2$ thin films were reported earlier [REDDY, CHALAPATHY, CHALAPATHY, REDDY]. In this note, we report on the structural properties of $CuGa_xIn_{1-x}Se_2$ thin films with the change of gallium composition, x in the grown layers.

2. Experimental

The copper gallium indium diselenide thin films with different gallium to indium ratios were prepared by spray pyrolysis described earlier [CHALAPATHY, REDDY]. In literature there are reports on the preparation of other ternary films by spray pyrolysis [BOUGNOT et al., TIWARI et al., SUBBARAMAIAH et al]. Aqueous solutions containing copper chloride ($CuCl_2.2H_2O$), gallium trichloride ($GaCl_3$), indium trichloride ($InCl_3$) and n,n-dimethyl selenourea (all are analar grade from Aldrich, USA) were used as the starting solutions. The Cu:(Ga+In):Se atomic ratio in the solution was maintained as 1:1:3.5. An excess of dimethyl selenourea was taken in the starting solution in order to compensate the loss of selenium during the deposition due to its high vapour pressure. The concentrations of $CuCl_2$ and $GaCl_3/InCl_3$ were maintained at 0.0015 M while that of selenourea was 0.0055 M. The relative concentrations of $GaCl_3$ and $InCl_3$ were varied appropriately to achieve the desired Ga/In ratio in the films while their total concentration in the solution was kept constant. The solutions were sprayed onto soda-lime glass substrates kept at a temperature of 325°C with an accuracy of + 5°C measured using Eurotherm Model 840 temperature controller. The solution was sprayed at a flow rate of 4 ml min^{-1}. Compressed and filtered air was used as the carrier gas at a flow rate of 6 l min^{-1}. The source to substrate distance was maintained as 25 cm. The entire process of deposition was carried out in dark to avoid the dissociation of selenourea into elemental selenium. About 200 ml of the solution was sprayed and the thickness of the deposited films was about 0.5 - 0.7 µm. The structural characterisation of the deposited $CuGa_xIn_{1-x}Se_2$ films was carried out using a Siemens D-5000 X-ray diffractometer with Cu K_α radiation (λ=1.542 A°). The XRD spectra were recorded in the scanning range 20° - 60°. The surface morphology of the films was examined by a Hitachi S-2400 scanning electron microscope. The chemical composition of the films was analysed by Energy Dispersive Analysis of X-rays (EDAX) using a Linc exL 6065 energy analyser attached to the scanning electron microscope.

3. Results and discussion

The structural properties of $CuGa_xIn_{1-x}Se_2$ films are found to be greatly influenced by the Ga/(Ga+In) composition ratio. The EDAX elemental analysis showed that all the deposited films were nearly stoichiometric in composition. The evaluated Ga/(Ga+In) ratio in the different alloy films is nearly equal to that of the ratio maintained in the starting solution.

The selenium content in the $CuGa_xIn_{1-x}Se_2$ films was nearly equal to its stoichiometric value in the compound, although an excess of selenium was taken in the starting solution. This may be because of the re-evaporation of selenium from the film surface after the deposition due to its high vapour pressure as the layers were formed at a temperature of 325°C.

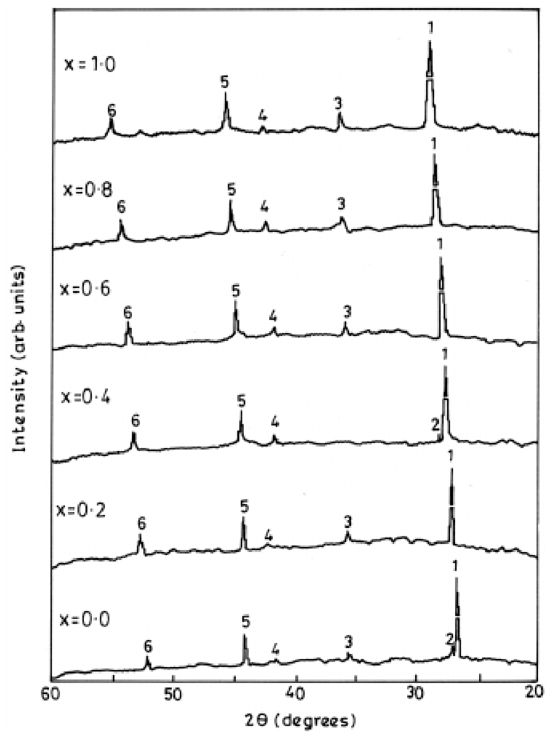

Fig.1. XRD spectra of $CuGa_xIn_{1-x}Se_2$ films with various gallium compositions, x.
1 - (112),
2 - (103),
3 - (211),
4 - (105),
5 - (220)/(204),
6 - (116)/(312)

The X-ray diffraction spectra showed that all the deposited films were polycrystalline and single phase. Fig.1 shows the X-ray diffraction spectra of $CuGa_xIn_{1-x}Se_2$ films with different gallium concentrations deposited in the present investigation. The films exhibited an intense peak oriented along the (112) lattice plane parallel to the substrate. The other strong peaks observed from the XRD spectra correspond to the (220)/(204) and (116)/(312) orientations. In addition to these lattice planes, one or more peaks corresponding to (103), (211) and (105) planes were also seen in the films which exhibit the presence of chalcopyrite structure. The peaks observed in the present study are in good agreement with the reported results on single crystals [REZAVIDI; LAM, SHIH] and polycrystalline films [GREMENOK et al]. The high resolution XRD scans indicated a clear tetragonal splitting of the (220)/(204) and (116)/(312) peaks which is a characteristic of the chalcopyrite structure. With the increase of gallium content in the films, the positions of the diffraction peaks shift towards higher angles, the behaviour similar to that observed in sputtered $CuGa_xIn_{1-x}Se_2$ films [YAMAGUCHI et al]. Fig.2 shows the variation of lattice parameters, a and c with the gallium content, x in the films, deduced from the X-ray diffraction spectra.

The figure also includes the lattice constants of $CuGa_xIn_{1-x}Se_2$ films prepared by sputtering and laser ablation. The variation of a and c with x for the films deposited in the present study is almost linear following the usual Vegard's behaviour over the entire gallium composition investigated. The values of c/a also vary linearly in the range, 1.97 - 2.00 with the change of gallium concentration. The observed slight deviation in the respective values with the reported data is probably due to the change in the deposition methods. The surface topography of the films was found to be uniform with densely packed crystallites. The grain size of the $CuGa_xIn_{1-x}Se_2$ films was obtained from the SEM micrographs (Fig.3) and also calculated from the XRD spectra using the Scherrer relation [SCHERRER]. The grain size determined by both methods was nearly equal. It was found that the grain size decreased with the increase of gallium composition in the films which can be clearly seen by the broadening of the (112) diffraction peak with the increase of x. The decrease in grain size with the increase of gallium composition in the films is similar to the behaviour reported on $CuGa_xIn_{1-x}Se_2$ films deposited by other techniques [ALBIN et al., GREMENOK et al.]. The $CuInSe_2$ films showed well faceted crystal structure with a grain size of about 650 nm while the $CuGaSe_2$ films exhibited compact nodular morphology and the evaluated grain size is 200 nm.

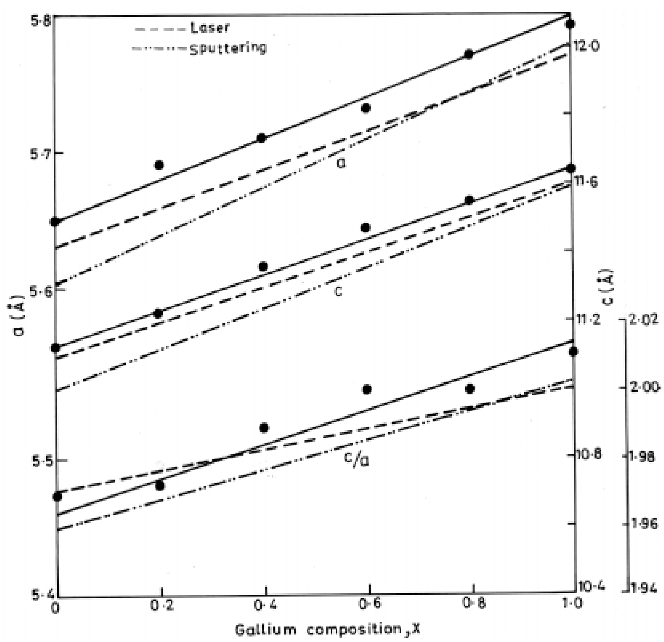

Fig.2. Variation of lattice constants and their ratio with gallium content. x in $CuGa_xIn_{1-x}Se_2$ films.

4. Conclusions

$CuGa_xIn_{1-x}Se_2$ thin films have been synthesised by spray pyrolysis using the aqueous solutions of the constituent compounds and the structural properties have been studied. All the deposited films were polycrystalline and single phase; exhibited the chalcopyrite structure with a strong (112) orientation. The lattice parameters, a and c have been found to vary linearly with the gallium composition, x in the films. The grain size of the films was highly influenced by the gallium content in the films and it decreased with the increase of x. The present study demonstrated that $CuGa_xIn_{1-x}Se_2$ layers with different gallium contents can be grown by spray pyrolysis which may be useful for solar cell application due to the simplicity of the technique.

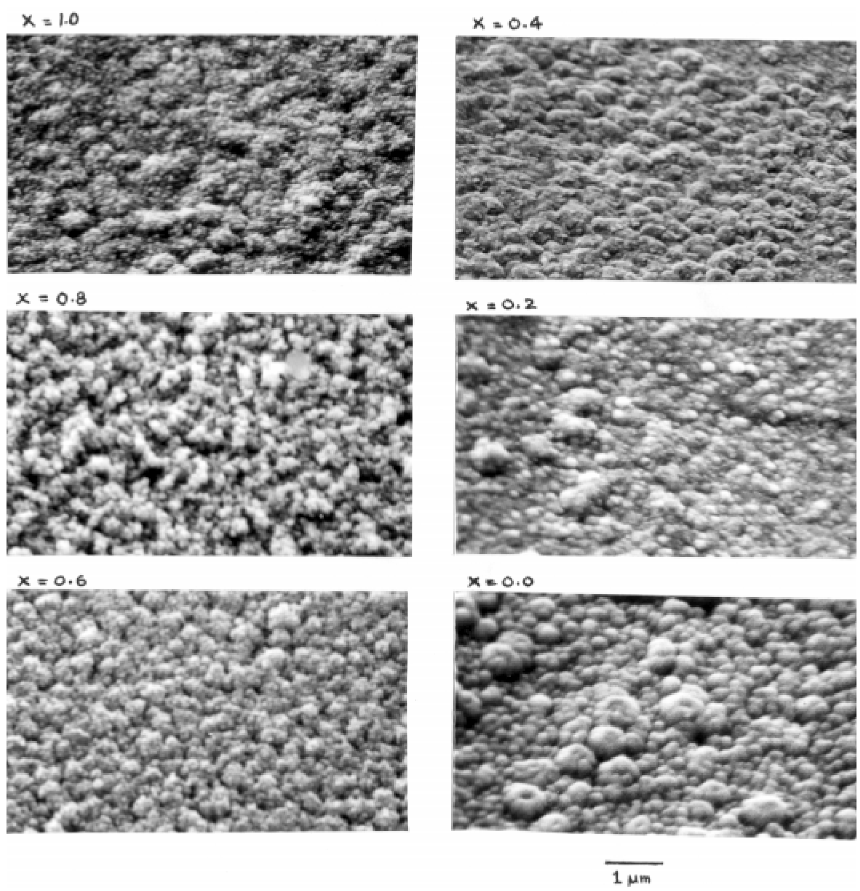

Fig.3. Scanning electron micrographs of $CuGa_xIn_{1-x}Se_2$ thin films.

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