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Growth of $CuInS_2$ films by rf ion plating and their characterization

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Abstract

Films of the chalcopyrite semiconductor $CuInS_2$ were grown by rf ion plating at low substrate temperature of 400°C for various levels of substrate bias, ranging from + 50 to − 50 V. The Cu and In compositions were controlled by varying the electron beam power of the Cu_2S and In_2S_3 sources. The crystalline quality was influenced by the level of the substrate bias. There were significant differences in surface morphology and crystallinity between films prepared under either negatively biased or floating conditions and those prepared under either positively biased or grounded conditions. Single-phase $CuInS_2$ films of the best quality were obtained when the substrate was subjected to the floating condition. Such substrate bias dependence of crystalline quality clearly demonstrates the critical rolė that ions play in films prepared at low temperature.

Keywords: $CuInS_2$; rf ion plating; Growth; Characterization; Low temperature

1. Introduction

The chalcopyrite semiconductor $CuInS_2$ is one of the most attractive candidates for photovoltaic devices, because its band gap (1.53 eV) is the closest match to the solar spectrum [1]. Recently, high-power conversion efficiency has been achieved in $CuInS_2$ solar cells, [2–5] the highest of which was 12% [3]. However, the growth method used

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for the films in such cells included a high-temperature annealing process over 550°C, thereby restricting the size and quality of the glass substrate. Making use of ionized beams, we have succeeded in obtaining chalcopyrite semiconductors at low temperature (400°C), which allows us to use inexpensive large soda-lime glass substrates and inexpensive manufacturing equipment and thus, minimizing manufacturing costs [6]. In this paper, we describe the preparation and characterization of $CuInS_2$ films grown by rf ion plating, which is known to have high productivity [7].

2. Experimental

$CuInS_2$ films were grown by rf ion plating on uncoated and Mo-coated soda-lime glass substrates at 400°C in a chamber evacuated to 5×10^{-4} Torr. Fig. 1 shows the rf ion plating apparatus in which pure argon gas was introduced into the chamber to produce plasma at various levels of rf power for ionization, from 100 to 400 W. The Cu and In compositions were controlled by varying the electron beam power of the

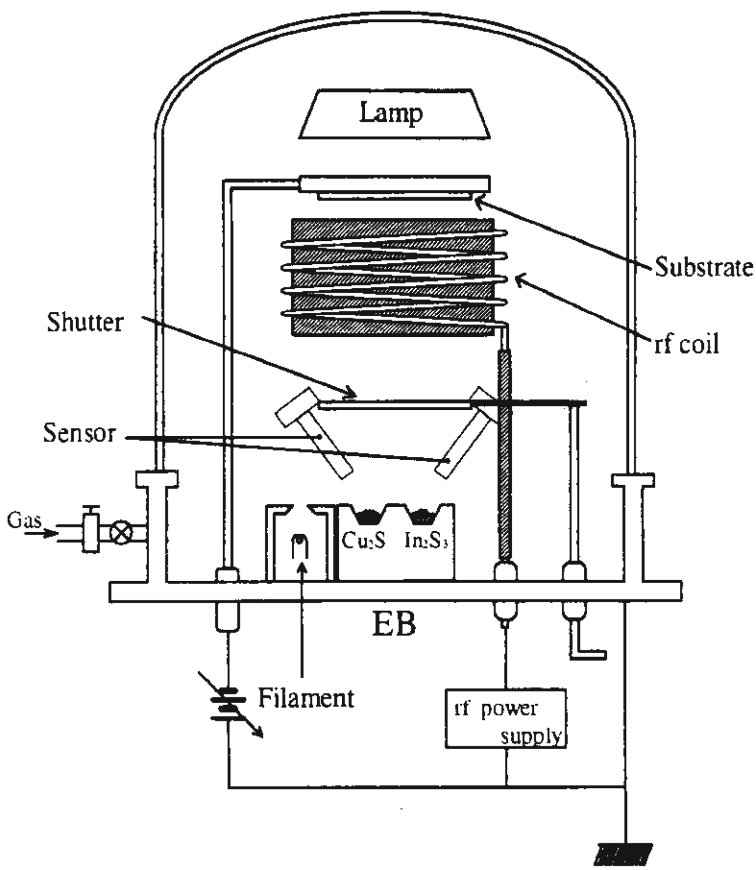


Fig. 1. Schematical illustration of rf ion plating system.

Cu_2S and In_2S_3 sources. Cu_2S/In_2S_3 flux ratio (hereafter called flux ratio) was varied from 2 : 1 to 4 : 1. The substrate was either positively biased at + 50 V (hereafter called P), grounded (G), floating with floating potential of − 14 V (F) or negatively biased at − 50 V (N). The thickness of resulting films was about 2 μm. To remove copper sulfides, films prepared in this work were etched by a 10% KCN solution for 3 min at room temperature and rinsed with deionized water. The films were then characterized using X-ray diffraction (XRD) with Cu-K_α or Fe-K_α line, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) and inductively coupled plasma optical emission spectroscopy (ICP).

3. Result and discussion

Fig. 2 shows typical XRD patterns of the films deposited on uncoated soda-lime glass substrates with an rf power of 200 W and different flux ratios (2, 3, and 4). An XRD peak due to In_2S_3 (1 0 4, 1 1 0) was observed at 26.3° in the film prepared using a flux ratio of 2. With an increase of the flux ratio, such extraneous peaks lost their intensity and become to have single-phase chalcopyrite structure for flux ratio of 4. This is more clearly observed in the plot of XRD peak intensity ratio of In_2S_3 (1 0 4, 1 1 0)/$CuInS_2$ (1 1 2) versus flux ratio in Fig. 3, in which rapid decrease of the peak intensity ratio with flux ratio is observed for films prepared with low rf power. Fig. 4 shows the dependence of the XRD peak intensity ratio of In_2S_3 (1 0 4, 1 1 0)/$CuInS_2$ (1 1 2) on Cu/In ratio of as-deposited films grown at various conditions. The Cu/In ratio was determined by EDX. A distinct threshold of the Cu/In ratio (in as-deposited films) was observed in the plot, above which single-phase chalcopyrite appeared.

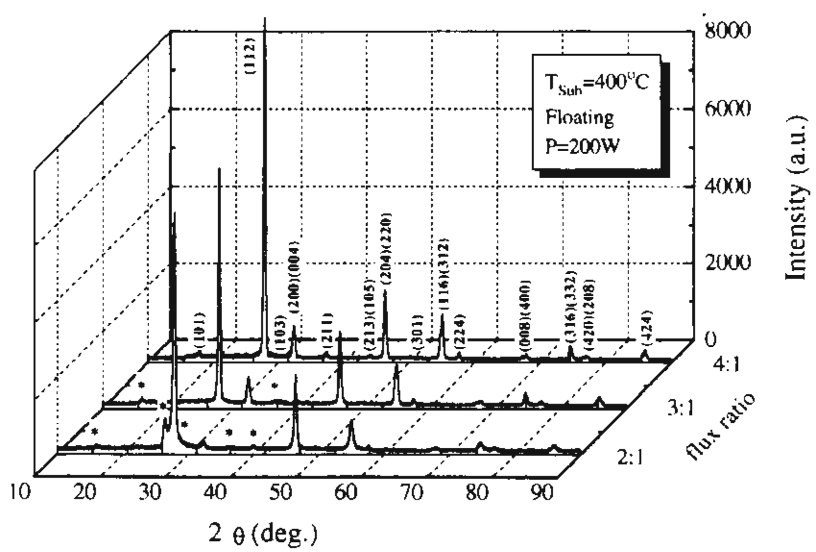


Fig. 2. XRD patterns of films prepared with different flux (i.e., Cu_2S/In_2S_3) ratios.

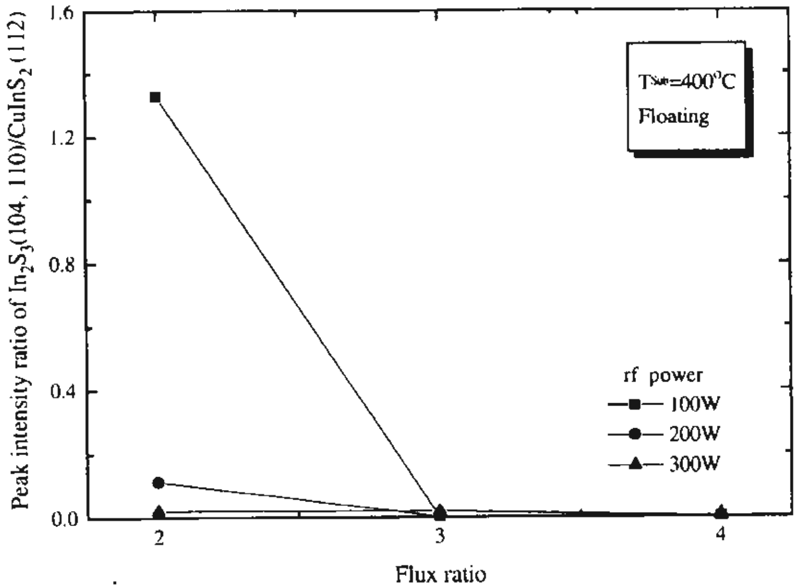


Fig. 3. Plot of XRD peak intensity ratio of In_2S_3(1 0 4,1 1 0)/$CuInS_2$(1 1 2) versus flux ratio for various rf power, after KCN-treatment.

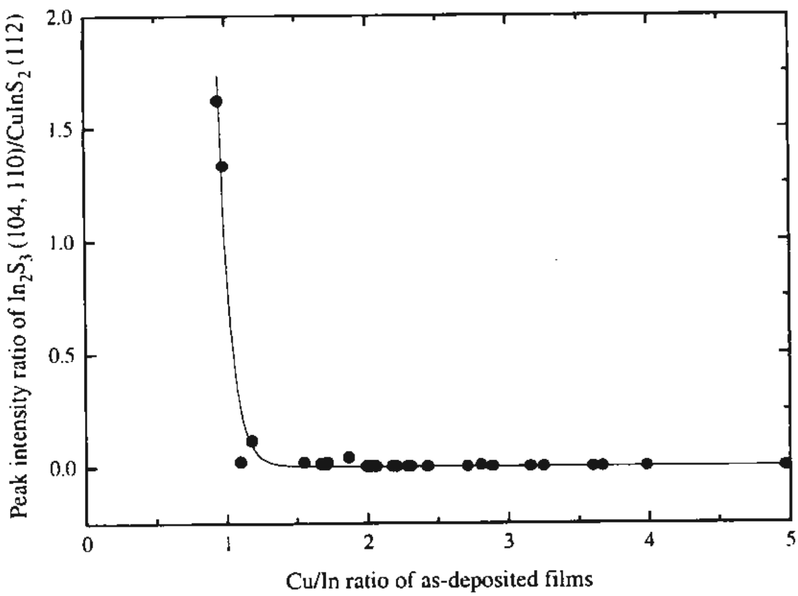


Fig. 4. Plot of XRD peak intensity ratio of In_2S_3(1 0 4, 1 1 0)/$CuInS_2$(1 1 2) versus Cu/In ratio of as-deposited films grown at various conditions.

Ogawa et al. [5] reported that high value of Cu/In ratio in as-deposited films is important in order to get good crystallinity of $CuInS_2$. These results suggest that Cu-rich environment is very important in the growth of good crystalline $CuInS_2$.

Then we prepared films for solar cells with rf ion plating $CuInS_2$ films. For this purpose, we adopted the flux ratio of 4 according to the above results. Other conditions were as follows: The substrates were Mo-coated soda-lime glass, substrate temperature was 400°C and the rf power was 200 W. The substrates bias were varied from − 50 to + 50 V. Significant differences in surface morphology and crystallinity were observed between films prepared under either N or F conditions and those prepared under either G or P conditions. Fig. 5 shows SEM micrographs showing the surface morphology of as-deposited films prepared under N, F, G and P conditions. In all the films, the grain size was greater than 1 μm. The N and F films showed a smooth surface, whereas the P and G films a rough surface.

Fig. 6 shows XRD patterns of an as-deposited film and a KCN-treated film together with the SEM photograph of a KCN-treated film, grown under F conditions. The as-deposited film showed lines originated from Cu_xS_y (mainly $Cu_{1.8}S$). After KCN treatment, the Cu_xS_y phases vanished, corresponding to the SEM observation in which smooth surface disappeared. From these results, the materials with the smooth surface may be assigned to some kind of copper sulfides (Cu_xS_y). The Cu/In ratio of these films after KCN-treatments, measured by EDX was nearly stoichiometric. This result is also supported by ICP analysis in which Cu/In ratio was determined as 0.98 in the F-grown KCN-etched film. In the XRD analysis of the KCN-treated films, the N and F films showed characteristic XRD peaks of the chalcopyrite phase, namely, (1 0 1), (2 1 1), (2 1 3), and (3 0 1), whereas the P and G films showed weak (1 0 1) and (2 1 1) peaks.

Fig. 7 shows the XRD patterns of (1 1 6) and (3 1 2) peaks in the N, F, G, and P films obtained with Fe–K_α line. Peak splitting between (1 1 6) and (3 1 2) diffraction lines is more distinct in the N and F films than in the P and G films. The splitting is characteristic of the chalcopyrite structure and has been used for evaluation of crystalline quality [4]. The best crystallinity (judged from the characteristic XRD peaks and the peak splitting) was attained for the F-grown film.

We have found that (a) a sufficient flux ratio is necessary to obtain single-phase $CuInS_2$, (b) the XRD peak intensity ratio of In_2S_3(1 0 4, 1 1 0)/$CuInS_2$ (1 1 2) showed clear dependence on rf power, (c) flat and smooth surface inherent to Cu_xS_y was observed to cover the $CuInS_2$ of a good quality, and (d) good crystalline $CuInS_2$ was obtained under F or N condition. We, therefore, consider that ionization of Cu enhances the activity of Cu_xS_y compounds. Zweigart et al. [4] pointed out that the presence of a secondary CuS phase leads to a complete crystallization of the film.

Using the films, we fabricated solar cells with ITO/CdS(CBD)/$CuInS_2$/Mo-coated soda-lime glass structure, in which ITO and CdS films were prepared by rf ion plating and chemical bath deposition techniques, respectively. The thickness of ITO, CdS, $CuInS_2$, and Mo were 250 nm, 80 nm, 2 μm and 1 μm, respectively. The solar cells whose absorption layer was prepared under the F condition showed an AM1 conversion efficiency of 1.7%. Although the conversion efficiency of our cell was low, we

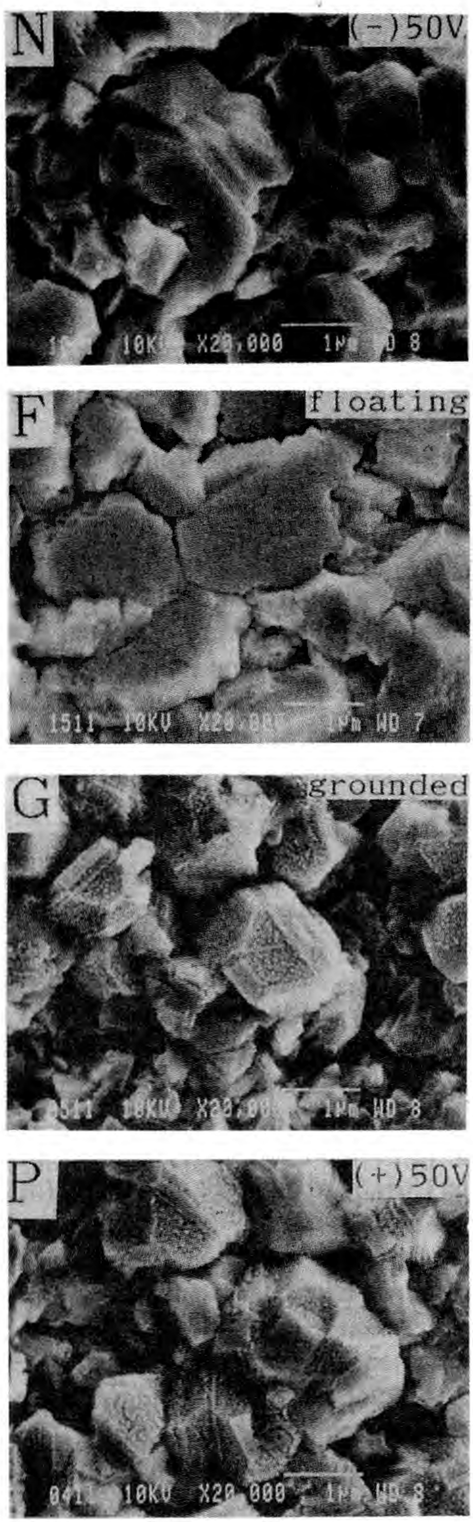
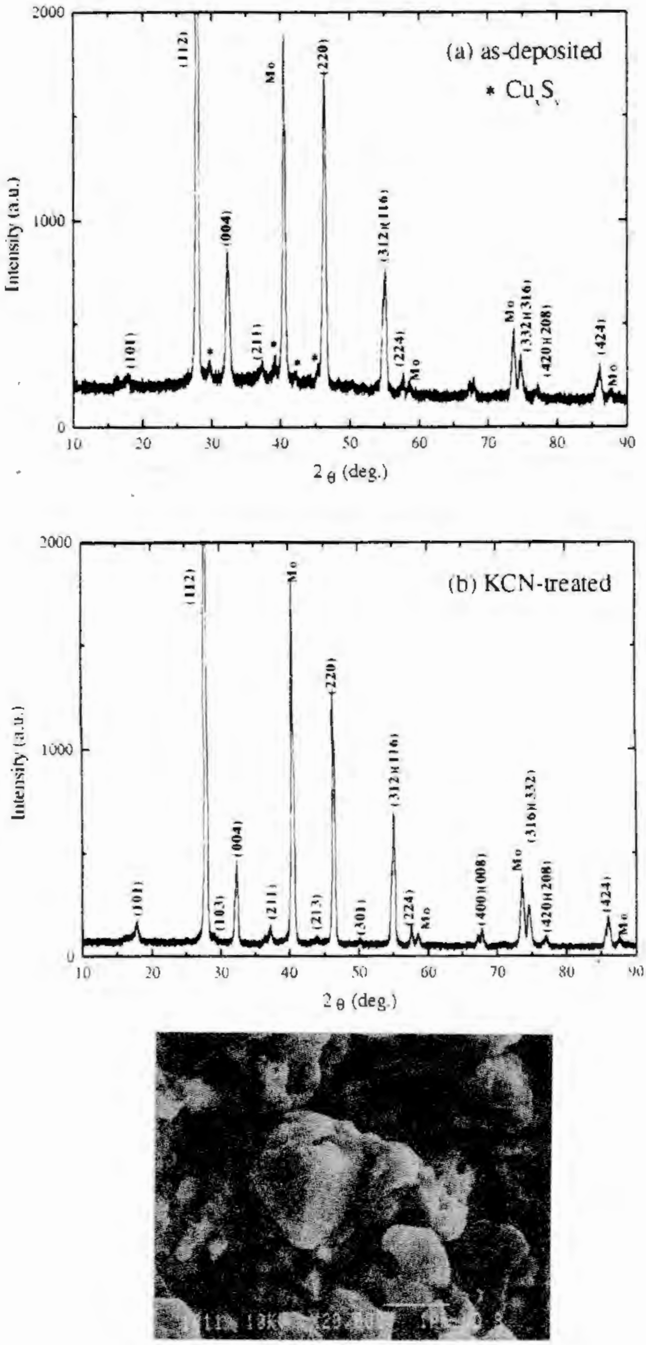


Fig. 5. SEM micrographs showing surface morphology of as-deposited films for various substrate biases: N (− 50 V), F (floating), G (grounded), and P (+ 50 V).



SEM micrographs of KCN-treated film

Fig. 6. XRD patterns of (a) as-deposited and (b) KCN-treated films and SEM micrograph of KCN-treated film grown with the floating (F) condition.

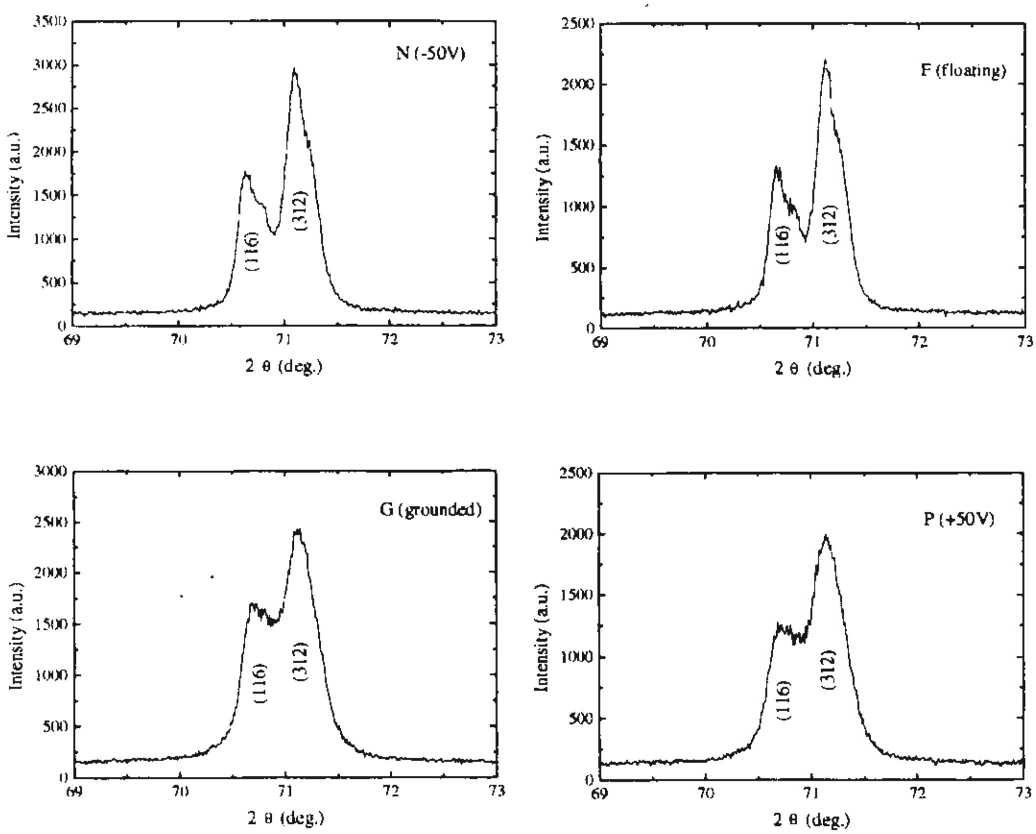


Fig. 7. XRD patterns showing peak splitting of (1 1 6) and (3 1 2) for substrate biases of N (− 50 V), F (floating), G (grounded), and P (+ 50 V).

believe it can be improved if we optimize the preparation processes to form the OVC phases and to introduce sodium into the $CuInS_2$ films [8, 9]. To confirm this, we are currently working on the growth of OVC by changing the flux ratio in two steps. We will report these results elsewhere.

4. Conclusions

Single-phase $CuInS_2$ films were grown by rf ion plating at 400°C at various levels of substrate bias. Our results show that the crystalline quality of the films was influenced by the substrate bias; the N and F films had better crystallinity than the P and G films. The best crystallinity was attained for the floating condition. Cu ions seem to play a very important role in achieving good crystallinity in $CuInS_2$ films grown at low temperature. These results suggest that rf ion plating is an attractive technique for minimizing the manufacturing-costs, because there is no restriction on the size or quality of the glass substrate.

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