Growth and Characterization of $CuInS_2$ Films grown by Rf Ion-Plating

Ken-ichi KONDO, Susumu NAKAMURA, Hiroyuki SANO, Hiroshi HIRASAWA and Katsuaki SATO[1]

Tsukuba Research Laboratory, Stanley Electric Co., Ltd., 5-9-5 Tokodai, Tsukuba, Ibaraki 300-26, Japan

[1]*Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184*

(Received April 28, 1997; accepted for publication August 21, 1997)

Films of the chalcopyrite semiconductor $CuInS_2$ were grown by rf ion-plating at a relatively low substrate temperature of 400°C, which allows us to use a large size inexpensive glass substrate, for various levels of substrate bias, ranging from $+50$ V 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. There were significant differences in the surface morphology and crystallinity between films prepared under either negatively biased or floating conditions and films prepared under either positively biased or grounded conditions. Single phase $CuInS_2$ films of good quality were obtained when the substrate was subjected to the floating conditions. Cu ions seem to play a very important role in the growth of Cu_xS_y which acts as an accelerator for growing good crystalline $CuInS_2$ at a relatively low temperature.

KEYWORDS: $CuInS_2$, thin film growth, characterization, ion plating, low temperature, crystallinity

1. Introduction

The chalcopyrite semiconductor $CuInS_2$ is one of the most attractive candidates for photovoltaic devices, as its band gap(1.53 eV) is the closest match to the solar spectrum.[1)] Recently, a high power conversion efficiency has been achieved in $CuInS_2$ solar cells,[2–6)] the highest of which was 12%.[3)] To achieve a good conversion efficiency, the quality of $CuInS_2$ is extremely important. Zweigart *et al.*[4)] pointed out that the presence of a secondary CuS phase leads to a complete crystallization of the film. Klenk *et al.*[7)] proposed a model for the growth process in the presence of a copper chalcogenide phase. They pointed out that excess Cu provides a binary copper chalcogenide which acts as "flux" with a high diffusion coefficient for species involved in the growth process. However, these techniques usually require temperatures as high as 600°C, which is not favorable large-size inexpensive glass.

It has been observed from our studies that $CuInSe_2$ films of good quality can be prepared at substrate temperatures as low as 300°C by using ionized cluster beam deposition (ICB) technique.[8,9)] This indicates that the use of an ionized beam is effective for enhancing the sticking and migration of the deposited species. However, the ICB technique is not particularly suited for the preparation of homogeneous films over a large area of the substrate because of its narrow radiant angle of nozzle. We therefore exploited another ion-based method which is capable of the preparation of films with a high productivity. This is the rf-ion plating technique which is used to produce a large size substrate ($400 \times 400\,\mathrm{mm}^2$) with indium tin oxide (ITO) for liquid crystal display (LCD). We employed this technique, since Murayama[10,11)] demonstrated that in the ion plating technique, the role of the ionized particles in the vaporized beam and nucleation sites on the substrate is important for the film formation process. They showed that the temperature for epitaxial growth can be lowered by using the ion-plating technique.

In this paper, we describe the preparation and characterization of $CuInS_2$ films grown by rf ion-plating at relatively low substrate temperatures. We also discuss the role of ions in the growth of films at low substrate temperatures.

2. Experimental

Figure 1 shows the rf ion-plating apparatus in which pure argon gas was introduced into the chamber to produce plasma. $CuInS_2$ films were grown by rf ion-plating on bare and Mo-coated soda lime glass substrates at 400°C in the chamber evacuated to 5×10^{-4} Torr. The rf power for the ion plating was varied between 100 and 400 W. A Pyrex glass tube was set inside the rf coil to prevent contamination from the sputtering coil elements. The Cu and the In compositions were controlled by varying the electron beam power of the Cu_2S and In_2S_3 sources. Cu_2S/In_2S_3 evaporation rate ratio (hereafter referred to as an evaporation ratio) was varied from 2 to 4. The evaporation rate was determined from the thickness of the Cu–S and In–S species measured by two individual sensors of the INFICON IC-4 thickness monitor placed 10 cm above the evaporation sources. We admit that this method does not give an accurate value for

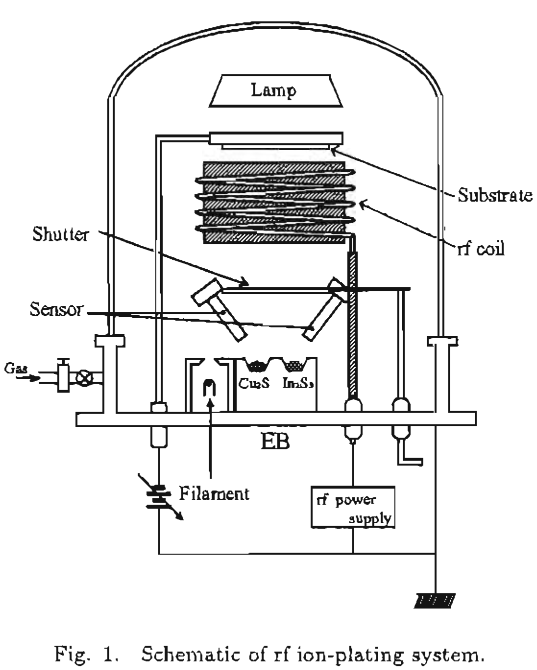


Fig. 1. Schematic of rf ion-plating system.

the flux ratio of Cu_2S and In_2S_3, since they presumably undergo decomposition or deviation from the stoichiometry. Nevertheless we believe that the evaporation ratio can be used as an approximate measure of the flux ratio.

For each growth experiment renewed source materials were used in order to keep the condition constant. Four different conditions of substrate bias were adopted; positively biased with $E_B = +50\,V$ (hereafter referred to as P), grounded (G), floating (F) and negatively biased with $E_B = -50\,V$ (N). The typical thickness of the resulting films was about 2 μm. The films prepared in this work were etched using a 10% KCN solution for 3 min at room temperature and rinsed with deionized water in order to remove the secondary phase, copper sulfides. The films were then characterized by X-ray diffraction (XRD) using the Cu–Kα or Fe–Kα line, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX).

3. Results and Discussion

Figure 2 shows a typical XRD pattern of the films deposited on soda-lime glass substrates with an rf power of 200 W and different Cu_2S/In_2S_3 evaporation ratios (2, 3, and 4). The (104) and (110) of In_2S_3 were observed at 26.3° in the film prepared using an evaporation ratio of 2. With an increase in the evaporation ratio, the XRD peaks due to these extraneous compounds lose their intensity, resulting in a single-phase chalcopyrite structure for films with a ratio exceeding 4. Figure 3 shows the dependence of the XRD peak intensity ratio of $In_2S_3(104)(110)/CuInS_2(112)$ on the Cu/In ratio of as-deposited films grown under 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 a single phase chalcopyrite appeared. This result is in accordance with that reported by Ogawa *et al.*,[5] in which it is described that a large value of the Cu/In ratio in an as-deposited film leads to a good crystallinity in $CuInS_2$, suggesting that a Cu-rich environment is crucial to obtain well-developed crystal grains.

Based on these results, we prepared films for use in solar cells. These films were grown on Mo-coated soda-lime glass substrates at various substrate biases for an evaporation ratio of 4, an rf power of 200 W, and a substrate temperature of 400°C. Significant differences were observed in the surface morphology and crystallinity of films prepared under either N or F conditions and those prepared under either G or P conditions. The SEM mi-

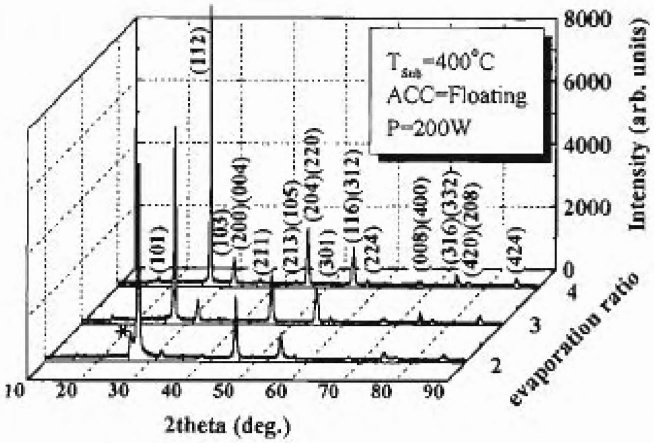


Fig. 2. XRD patterns of films prepared with different evaporation ratio of Cu_2S/In_2S_3. Symbol * indicates peaks due to $In_2S_3(104)(110)$.

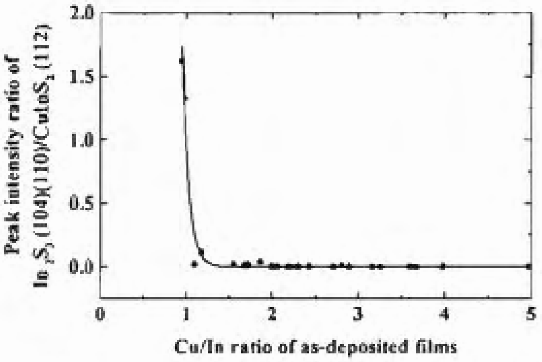


Fig. 3. XRD peak intensity ratio of $In_2S_3(104)(110)/CuInS_2(112)$ versus Cu/In ratio of as-deposited films grown under various conditions.

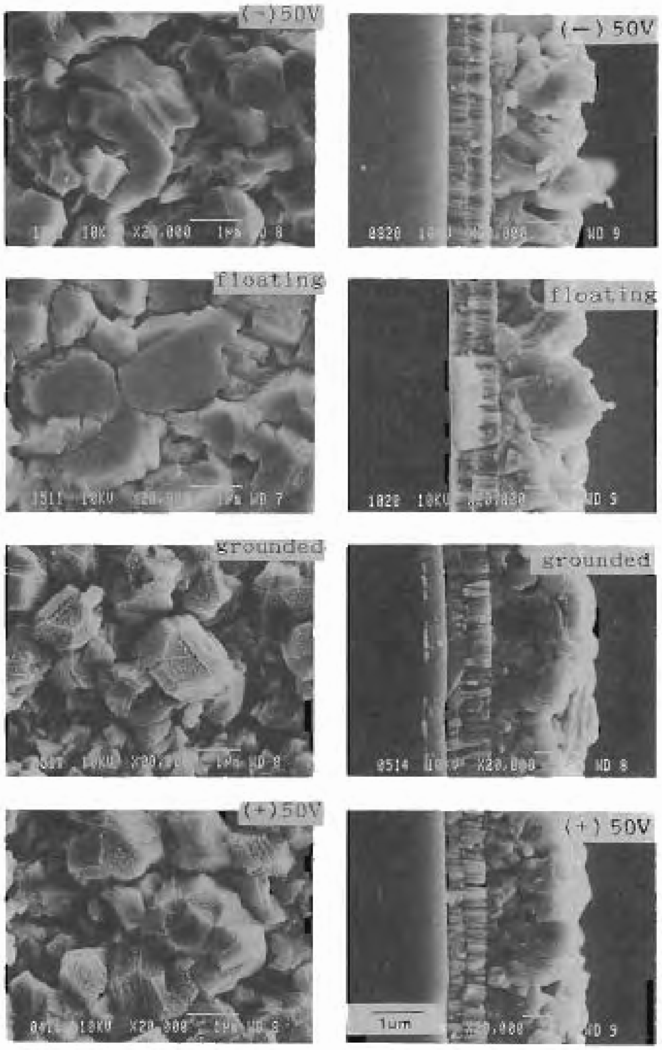
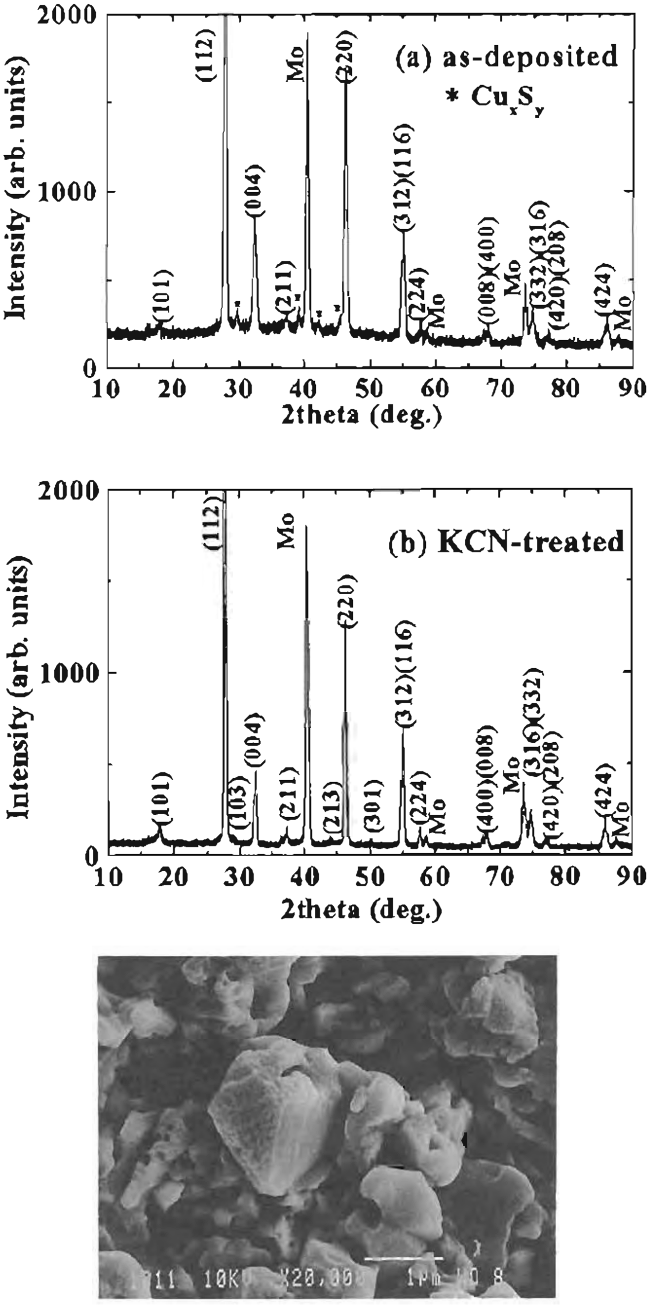


Fig. 4. SEM micrographs of the surface morphology and cross section of as-deposited films for various substrate biases: N (−50 V) F (floating) G (grounded) and P (+50 V).

crographs in Fig. 4 show the surface morphology and cross section of as-deposited films prepared under the N, F, G and P conditions. The grain size was found to be larger than 1 μm in all the films prepared. While the N and F films showed a smooth surface and well-developed grains, the P and G films showed a rough surface and less developed grains. The Cu/In ratio measured in as-deposited P, G, F, and N films was 2.69, 2.40, 4.96, and 2.87, respectively.

Figure 5 shows the XRD patterns in the film prepared under F condition (a) before and (b) after the KCN-treatment. For the KCN-treated film, a SEM photograph is also shown. As observed in Fig. 5(a) a few diffraction lines originating from Cu_xS_y (mainly $Cu_{1.8}S$) are observed in as-deposited films. After the KCN-treatment, these secondary-phase lines disappear and simultaneously the smooth surface was effaced as observed by the SEM photograph shown in Fig. 5. These results suggest that the material with the smooth surface was copper sulfide (Cu_xS_y). Klenk *et al.*[7] also pointed out that the Cu-rich film was covered by $Cu_{2-x}S$. The Cu/In ratio of the P, G, F, and N films after the KCN-treatment was determined as 1.03, 0.98, 1.03, and 0.99, respectively by EDX measurements. On the other hand, the metal/sulfur ratio showed little deviation from unity for all the films investigated.



(c)

Fig. 5. XRD patterns of F(floating) grown (a) as-deposited and (b) KCN-treated films and (c) SEM micrographs of KCN-treated film.

The XRD analysis of the KCN-treated N and F films showed XRD peaks characteristic of the chalcopyrite phase, namely (101), (211), (213), and (301) whereas the P and G films showed weak (101) and (211) peaks. Figure 6 shows the XRD patterns using Fe-Kα of the (116) and (312) peaks in the N, F, G, and P films. Splitting between the (116) and (312) diffraction lines due to tetragonal symmetry, which is characteristic of the chalcopyrite structure and has been used for the evaluation of the crystal quality,[4] is more distinct in the N and F films than in the P and G films. Judging from the appearance of diffraction lines characteristic of the chalcopyrite structure, as well as from the peak splitting due to tetragonality, we found that the optimum bias condition to obtain the best crystallinity is the floating condition.

We have found that (a) a sufficient flux ratio is necessary to obtain a single-phase $CuInS_2$, (b) the XRD peak intensity ratio of $In_2S_3(104)(110)/CuInS_2(112)$ showed a clear dependence on Cu/In ratio of as-deposited films, (c) the flat and smooth surface inherent to Cu_xS_y was observed to cover the $CuInS_2$ of a good quality, and (d) a good crystalline $CuInS_2$ was obtained under the F or N condition at a substrate temperature of 400°C.

Here we discuss the reason why the films of good crystallinity were obtained under the N and F conditions. Because of the difference in mobility between the electrons and ions, the substrate tends to be negatively charged under the floating condition.[12-14] This effect is

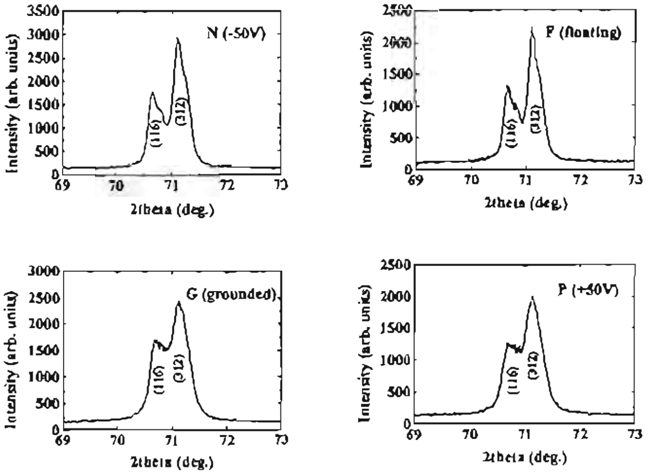


Fig. 6. XRD patterns showing peak splitting of (116) and (312) for substrate bias at N (−50 V), F (floating), G (grounded), and P (+50 V).

known as self-biasing. The sheath potential is considered to be the difference between the plasma potential and the self-bias voltage in the F-condition or the applied voltage in the N-condition. The self-bias voltage between the ground and the substrate holder under the floating condition was measured by the use of a DC voltmeter (Yokogawa 2506A) and was determined as −14 V. The ions are accelerated by this sheath voltage and strike the substrate with a kinetic energy equivalent to the sheath voltage. In our previous study of ICB grown $CuInSe_2$, we reported that the crystalline quality was strongly dependent on the ionization current of Cu-clusters. It was also elucidated that the $CuInSe_2$ films with a large grain size and a good crystalline property were obtained when the ionization current of the Cu-clusters exceeded that of In.[8] It is well known that copper sulfide or selenide play an important role in the growth mechanism of $CuInS_2$ and $CuInSe_2$.[2–5,7] Taking these results into account, we believe that an acceleration by the sheath potential of the Cu-related ions leads to the formation of Cu_xS_y compounds, which in turn work as a solvent for the solution growth of a $CuInS_2$ film at a relatively low substrate temperature. Usually, these Cu_xS_y compounds are observed on the surface of $CuInS_2$ at high substrate temperatures of over 550°C.[2–7] On the other hand, only a small acceleration of ions is expected in the P or G condition.

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 the rf ion-plating and chemical bath deposition techniques, respectively. The thickness of ITO, CdS, $CuInS_2$, and Mo layers was 250 nm, 80 nm, 2 μm and 1 μm, respectively. The solar cells making use of the $CuInS_2$ film prepared under the F condition showed an AM1 conversion efficiency of 1.7% and $V_{oc} = 0.406$ V, $J_{sc} = 11.93$ mA/cm^2, respectively. Although the conversion efficiency of our cell was low, we believe that it can be improved if we optimize the preparation processes.

4. Conclusions

Single-phase $CuInS_2$ films were grown by rf ion plating at 400°C at various levels of the substrate bias. Our results show that the crystalline quality of the films was influenced by the substrate bias: the negative or the floating conditions led to better crystallinity than the positive or the grounded conditions. The best crystallinity was attained in a floating condition. Cu ions seem to play a very important role in achieving a good crystallinity in $CuInS_2$ films grown at low temperatures. From the present study we have elucidated that an rf ion-plating is a promising technique for the preparation of $CuInS_2$ solar-cell films at a relatively low temperature of 400°C, which may enable us to use inexpensive large size glass and may contribute towards minimizing the manufacturing cost because there is no restriction on the size or quality of the glass substrate.

Acknowledgements

The authors would wish to thank Dr. H. Toyotama, M. Yoshida, and Y. Suzuki of Stanley electric Co., Ltd. for their helpful comments and H. Mori for his help in SEM observation.

1) J. L. Shay and J. Wernick: *Ternary Chalcopyrite Semiconductors; Growth, Electronic Properties and Applications* (Pergamon, New York, 1975).
2) R. Scheer, T. Walter, H. W. Schock, M. L. Feaheiley and J. Lewerenz: Appl. Phys. Lett. **63** (1993) 3294.
3) T. Walter, R. Menner, Ch. Köble and H. W. Schock: Proc. 12th EC Photovoltaic Solar Energy Conf, Amsterdam, 1994, p. 1755.
4) S. Zweigart, T. Walter, Ch. Köble, M. S. Sun, U. Rühle and H. W. Schock: 1st WCPEC, Hawaii, 1994, p. 60.
5) Y. Ogawa, A. Jäger-Waldau, Y. Hashimoto and K. Ito: Jpn. J. Appl. Phys. **33** (1994) 1775.
6) D. Braunger, D. Hariskos, T. Walter and H. W. Schock: Sol. Energy Mater. Sol. Cells **40** (1996) 97.
7) R. Klenk, T. Walter, D. Schmid and H. W. Schock: *Proc. 9th Int. Conf. Ternary and Multinary Compounds, Yokohama, 1993*, Jpn. J. Appl. Phys. **32** (1993) Suppl. 32-3, p. 57.
8) H. Sano, S. Katayama, S.-C. Yee, K. Kondo and K. Sato: Proc. 12th Symp. Ion Beam Technology, Hosei Univ., December 1993, pp. 63.
9) H. Sano, S. Nakamura, K. Kondo and K. Sato: 1st WCPEC, Hawaii, 1994, p. 179.
10) Y. Murayama, K. Kashiwagi and M. Matsumoto: Phys. Soc. Jpn. **3** (1971) 2788.
11) Y. Murayama: *Proc. 6th Int. Vacuum Congr, 1974*, Jpn. J. Appl. Phys. (1974) Suppl. 2, Pt. 1, p. 1974.
12) B. N. Chapman: *Glow Discharge Processes* (John Wiley & Sons, New York, 1980) p. 53.
13) K. F. Al-Assadi: Vacuum **43** (1992) 287.
14) I. Ito, I. Kato and H. Ishikawa: *Mater. Res. Soc. Symp. Proc.* **38** (1985) 473.