

The Effect of Acceleration Voltages on the Preparation of CuInSe₂ Thin Films by Ionized Cluster Beam Technique

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Polycrystalline CuInSe₂ thin films were prepared on Mo-coated soda-lime glass substrates by the ionized cluster beam (ICB) technique, in which Cu, In and Se vapors were ionized and accelerated. The dependence of the film properties on acceleration voltage were studied. The substrate temperature was maintained below 350°C. The films were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), an electron-probe microanalyzer (EPMA) and the Rutherford backscattering spectrometry (RBS). It was found that polycrystalline films with improved grain size and uniformity were obtained when the acceleration voltage exceeded 4 kV, and the acceleration voltage played an important role in the formation of the ternary compound during the crystal growth.

KEYWORDS: CuInSe₂, chalcopyrite-type compounds, ionized cluster beam technique, acceleration voltage, Rutherford backscattering spectrometry, low-temperature deposition, KCN treatment

1. Introduction

The chalcopyrite ternary semiconductor CuInSe₂ has been attracting much attention as a polycrystalline thin-film material for use in high-efficiency solar cells, since the material has a direct energy gap of around 1.0 eV and the highest absorption coefficient, reported so far for any semiconductor.¹⁾ Polycrystalline thin-film heterojunction devices, such as ZnO/CdS/CuInSe₂, achieved a high solar energy conversion efficiency of 16.1%.²⁾

However, most of the deposition techniques, reported so far, require high processing temperatures above 500°C in order to obtain high-quality films,³⁾ a procedure unsuited to use with inexpensive glass substrates. To lower the processing temperature, we have attempted to adopt techniques that use ions in the preparation of CuInSe₂-based films; i.e., the ionized cluster beam (ICB) technique^{4–7)} and the ion plating technique.⁸⁾

In the ICB technique,^{9–11)} the effects of ionized beam bombardment the charge of ionized particles are utilized. The kinetic energy of ionized clusters can be controlled by acceleration voltage, and the migration effect is enhanced with increasing in acceleration voltage. This is one of the characteristics of ICB deposition.

In our previous report,¹²⁾ it was found that the acceleration voltage could change the film quality and an optimum effect on the acceleration voltage of each element existed. However, these conditions existed under 4 kV of acceleration voltage. In the present study we examined higher acceleration voltages and some of the resultant CuInSe₂ thin-film characteristics related to the effects of only the acceleration voltages.

2. Experimental

CuInSe₂ films were prepared on Mo-coated soda-lime glass substrates by simultaneous ICB deposition of Cu, In and Se. The details of ICB apparatus used in this study have appeared in previous reports.^{6,7)} The source materials employed were Cu, In and Se of 99.9999% purity which were ejected from Knudsen-type graphite crucibles. The source temperatures used to obtain Cu-rich films were 1350°C, 950°C and 380°C for Cu, In and Se, respectively. On the other hand, deposition of In-rich films was carried out at source temperatures of

1320°C, 950°C and 380°C for Cu, In and Se, respectively. Thus, the Cu/In ratio was controlled by changing the Cu source temperatures. The Se beams were evaporated in excess. Deposition was carried out according to the two-step process, starting from a Cu-rich composition and ending with an In-rich composition to obtain a larger grain size.

During the film deposition, the substrate temperature was maintained at 350°C by controlling an infrared lamp; substrate temperature was measured using a thermocouple. The acceleration voltage for Cu, In and Se cluster beams was varied between $V_{acc} = 0\text{--}6\text{ kV}$, while the ionization current for the Cu, In and Se clusters was maintained at $I_e = 200\text{ mA}$, 50 mA and 100 mA, respectively. These ionization current conditions were determined from data in a previous report.⁷⁾ The pressure in the vacuum chamber was maintained at less than 1×10^{-5} Torr during deposition. The typical film thickness obtained was approximately 2 μm for a deposition time of 120 min.

Next, the KCN-treatment is described as follows. It is known that Cu(In,Ga)Se₂ films grown with excess copper are subjected to the presence of Cu–Se secondary-phase compounds. It is known that these binary cuprous compounds can be removed by etching in KCN solution.¹³⁾ In our previous report, we showed that the KCN treatment was effective on the films prepared by the low-temperature ICB process as well as the films prepared by the high-temperature process.⁷⁾ We used an aqueous solution of 10% KCN and etching was performed for 3 min to remove Cu–Se secondary-phase compounds.

The characterization of CuInSe₂ films was observed by X-ray diffraction (XRD) for structural analyses, and a scanning electron microscope (SEM) was used for surface-morphology and cross sections analyses. The chemical composition of the samples was determined by an electron-probe microanalyzer (EPMA) and Rutherford backscattering spectrometry (RBS).

3. Results and Discussion

The composition of the obtained CuInSe₂ films was studied using EPMA. It was found that the KCN treatment changed the Cu/In ratio of as-deposited films from a Cu-rich (Cu/In=1.2) composition to a nearly stoichiometric (Cu/In=0.93–1.04) one. This result indicates that the KCN treatment removes the Cu–Se compounds which are sup-

posed to exist at the surface, resulting in nearly stoichiometric CuInSe₂ films.

The phase and crystallographic structure dependence on the acceleration voltages was determined by XRD using Cu-K α radiation. Figure 1 shows the X-ray diffraction patterns of the KCN-treated CuInSe₂ films for different values of accelerating voltage V_{acc} . For the films prepared at 0–6 kV, the 101, 112, 103, 211 and other diffraction lines, characteristic of the chalcopyrite structure, were clearly observed without traces of secondary phases. It was proved that the films prepared in the accelerating voltage range of 0–6 kV had a chalcopyrite structure. The intensity ratio of (112)/(220) increases as V_{acc} increases. Preferential orientation of the (112) axis perpendicular to the film surface appears more clearly as acceleration voltage increases. These effects can be explained with the assumption that the increase in the acceleration voltage enhances adatom migration resulting in promotion of the reaction on the substrate surface and the subsequent growth of preferentially oriented films.

Variations in surface morphology of the obtained films with the acceleration voltage were examined. Figure 2 shows SEM micrographs of the surface morphology of the KCN-treated CuInSe₂ films. SEM observation shows that the surface morphology and the size of the crystal grains are strongly dependent on the acceleration voltage. The sizes of crystal grains increase with an increase in acceleration voltage. In the films deposited at above 4 kV, a remarkable increase in the grain size and uniformity was observed. The observed grain size increased to approximately 1 μ m on an average, and some of the grains as large as 2–3 μ m. In the case of lower acceleration voltages (under 2 kV), there were small voids on the films surface after KCN treatment. On the other hand, no voids were observed on the film surface after KCN treatment when the acceleration voltage exceeded 4 kV. Figure 3 shows a typical surface morphology of CuInSe₂ films prepared with $V_{acc} = 2$ kV: (a) as-deposited film and (b) KCN-treated film. Following KCN treatment, several voids appeared on the surface as shown by arrows. These voids were considered to be formed by the removed Cu–Se compounds. When used in solar cells, these voids cause a short circuit. Thus, formation of

high-quality film with a densely packed top layer is necessary. The cross-sectional micrographs in Fig. 4 also show that in the case of a higher acceleration voltage, the crystals were perfectly columnar with a densely packed structure and adhered tightly to the substrate, whereas in case of a lower acceleration voltage, the crystals did not exhibit such a perfect columnar structures. These results led to the next model of the growth mechanism, a schematic of which is shown in Fig. 5. In films prepared at lower acceleration voltages, Cu_{2–x}Se compounds exist between the grains, some of which reach even the Mo surface. On the other hand, at higher acceleration voltages, Cu_{2–x}Se compounds exist partly to cover the uppermost surface of the CuInSe₂ layer. The CuInSe₂ layer is formed more homogeneously and densely and there is less segregation at the grain boundaries compared with films obtained at lower voltages.

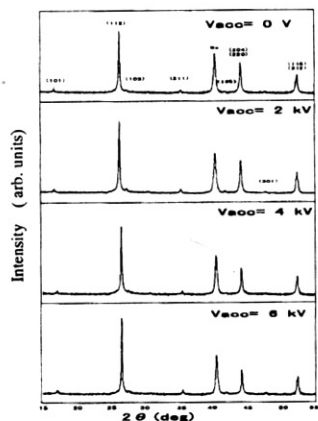


Fig. 1. The acceleration voltage dependence of typical XRD patterns of the KCN-treated CuInSe₂ films.

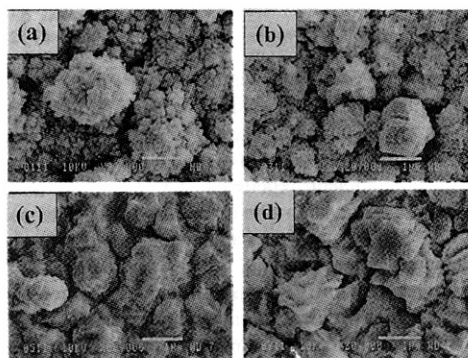


Fig. 2. The SEM micrographs of the surface morphology in the KCN-treated CuInSe₂ films prepared at (a) $V_{acc} = 0$ V, (b) $V_{acc} = 2$ kV, (c) $V_{acc} = 4$ kV and (d) $V_{acc} = 6$ kV.

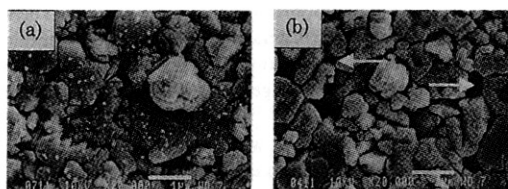


Fig. 3. The SEM micrographs of a typical surface morphology of CuInSe₂ films prepared with $V_{acc} = 2$ kV: (a) as-deposited film and (b) KCN-treated film.

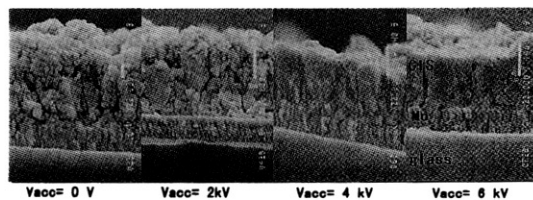


Fig. 4. The SEM micrographs of the cross sections of the KCN-treated CuInSe₂ film.

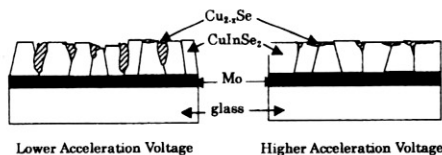
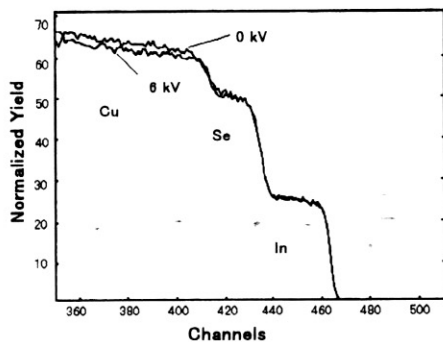


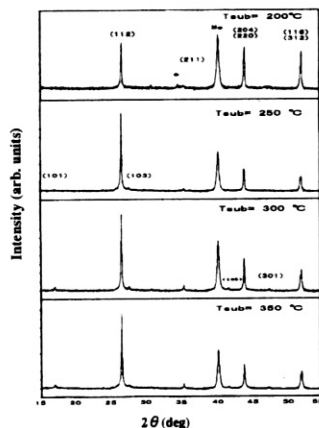
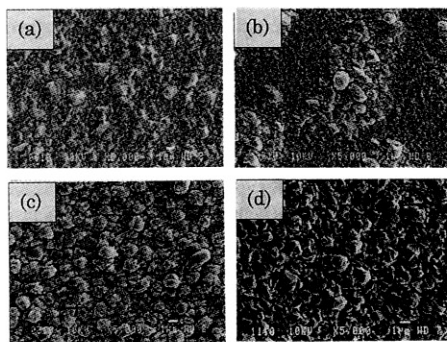
Fig. 5. Model of the growth mechanism.

Fig. 6. RBS spectrum of the KCN-treated CuInSe_2 films at the acceleration voltages of 0 and 6 kV.

Yamada *et al.* reported that in ICB deposition, the effect of adatom migration is enhanced by increasing acceleration voltage.¹¹⁾ Our films deposited at higher acceleration voltages have improved properties because lateral adatom activity is enhanced by higher acceleration voltages resulting in greater homogeneity of films grown.

In order to obtain further information on the compositions, RBS measurements were performed. RBS technique is very useful for observing the surface composition as well as film homogeneity. Figure 6 shows the RBS spectrum of the KCN-treated CuInSe_2 films at acceleration voltages of 0 and 6 kV. The RBS technique made use of a 2.28 MeV He^+ ion beam from an electrostatic accelerator in conjunction with a multichannel energy analyzer. Each spectrum showed that the surface composition of the film was in good agreement with the interior composition. These results suggest that the obtained films have good chemical homogeneity. In-rich films usually have smaller grains than Cu-rich films, however, the 6 kV film showed larger grain size than the nonaccelerated film even though the composition of the former film is more In-rich. These results also indicate that the acceleration voltage is crucial to improve the crystallinity of ICB-grown films.

Next, we investigated the extent to which the substrate temperature can be lowered using the ICB technique. The substrate temperature was varied between 200–350°C. The acceleration voltage was maintained at 6 kV throughout the study. Figure 7 shows the XRD patterns (taken with the $\text{Cu-K}\alpha$ line) of the KCN-treated CuInSe_2 films for different substrate temperatures T_{sub} . For films prepared above 300°C, the 101, 112, 103, 211 and other diffraction lines, characteristic of a chalcopyrite structure, were clearly observed without traces of secondary phases, whereas for films prepared under 250°C, these lines were not clearly observed. Notably,

Fig. 7. Substrate-temperature dependence of typical XRD patterns of the KCN-treated CuInSe_2 films.Fig. 8. SEM micrographs of the surface morphology in the KCN-treated CuInSe_2 films fabricated at (a) 200°C, (b) 250°C, (c) 300°C and (d) 350°C.

the secondary phase was observed at $T_{\text{sub}} = 200^\circ\text{C}$. The intensity ratio of (112)/(220) was approximately 1:1 when $T_{\text{sub}} = 200^\circ\text{C}$ and increased with T_{sub} for higher temperatures. The preferential orientation of (112) axis perpendicular to the film surface seemed more pronounced as the substrate temperature increased.

We examined the temperature dependence of the surface morphology. Figure 8 shows SEM micrographs of the surface morphologies of KCN-treated CuInSe_2 films fabricated at (a) 200°C, (b) 250°C, (c) 300°C and (d) 350°C. A dramatic difference is observed between films deposited under 250°C and above 300°C. SEM observation shows that crystal grains of CuInSe_2 are not very well grown at 200°C and 250°C, while they are sufficiently well grown above 300°C. These results agreed with the results of XRD patterns. The film characteristics are strongly affected by the substrate temperature. It is thus elucidated that by using the ICB technique the ternary compound CuInSe_2 films can be fabricated at temperatures as low as 300°C, with the acceleration voltage at 6 kV.

It is thus concluded that by using the ICB technique the ternary compound CuInSe_2 films can be fabricated at temper-

atures as low as 300°C. In addition, the acceleration of ionized clusters enhances the preferential orientation of the films and the size of crystal grains, suggesting that the growth mode on the Mo substrate is modified by the high kinetic energies gained by accelerated ion beams. These findings clearly show that the use of an accelerated ionized-cluster beam exerts an effect equivalent to or greater than that brought about by thermal energy.

4. Conclusion

CuInSe₂ thin films were prepared by the ICB technique with simultaneous deposition of Cu, In and Se clusters at various acceleration voltages. The migration effect was enhanced by increasing the acceleration voltage. Good-quality films with the chalcopyrite structure were formed at acceleration voltages higher than 4 kV and substrate temperatures of 350°C using the ICB method. Use of the accelerated ionized-cluster beams was found to be effective for lowering the substrate temperature and controlling the morphology and preferential orientation of the films.

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