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Preparation of Oriented $CuInSe_2$ Thin Films at Low Substrate Temperature

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$CuInSe_2$ thin films have been prepared by vacuum evaporation on glass substrate using Cu_2Se and In_2Se_3 powder as evaporation sources.[1] In general, preparation of $CuInSe_2$ thin films requires substrate temperature of 400-500°C. We have obtained highly preferred oriented $CuInSe_2$ thin films at substrate temperature above 400°C without assistance of rf plasma. Moreover, we have succeeded to obtain $CuInSe_2$ thin films at substrate temperature of 300°C with assistance of radio frequency (rf) plasma.

1.INTRODUCTION

$CuInSe_2$ is one of I-III-VI_2 ternary chalcopylite structured compound semiconductors, and that has attracted interest recently as the absorption material of high efficiency thin film solar cells due to its large optical absorption coefficient and direct energy band gap about 1eV. As techniques for the preparation of $CuInSe_2$ thin films[2], three sources co-evaporation,[3,4] selenization of metal layers,[5,6] sputtering,[7] laser abration,[8] chemical spray pyrolysis[9] and electro-deposition[10] are known. The former two methods are advantageous from the viewpoint of development of high efficiency solar cells. Accordingly most studies have focused on these two methods recently.

After consideration of social needs such as low cost development and large area deposition, we prepared $CuInSe_2$ thin films by vacuum evaporation method on glass substrate using Cu_2Se and In_2Se_3 powder as evaporation sources. This method requires no complicated equipment and is hopeful for large area deposition. Moreover, Cu/In ratio in thin films can be controlled by adjustment of ratio of weight of two evaporation sources. By this method, highly preferred oriented $CuInSe_2$ thin films were obtained. And we have succeeded to prepare preferred oriented films with assistance of rf plasma at relatively low substrate temperature of 300°C.

2.EXPERIMENTAL

The schematic diagram of equipment is shown in Fig.1. $CuInSe_2$ thin films were prepared by vacuum evaporation method under gas pressure less than $3x10^{-5}$[Torr]. Substrate was Corning7059 glass cleaned with acetone in ultrasonic cleaner and set 21cm above evaporation sources, and was heated varied up to 600°C.

The helical electrode in chamber was set only when using rf plasma. Ar gas was used as plasma production gas at pressure of $5x10^{-4}$[Torr]. The rf power was varied up to 600W.

As evaporation sources, Cu_2Se and In_2Se_3 binary powder were used. We put these binaries into molybdenum (Mo) evaporation boat and covered with Mo lids with several holes. Electric current was supplied to Mo boats about 360A. Such large current is necessary to avoid evaporation of metal elements and Se with time difference. Evaporation of two

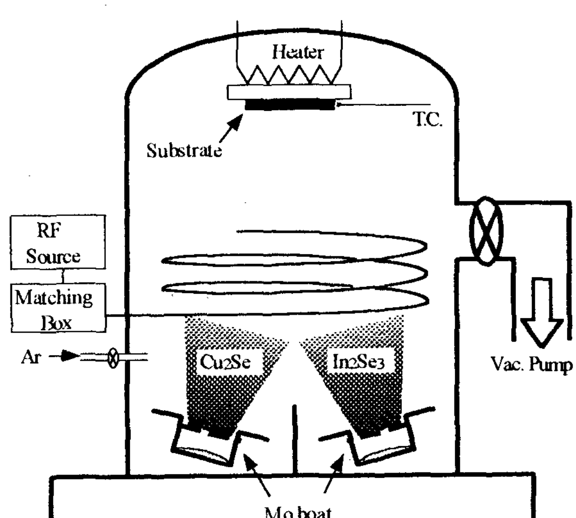


Fig. 1 Schematic diagram of equipment for preparation of $CuInSe_2$ thin films

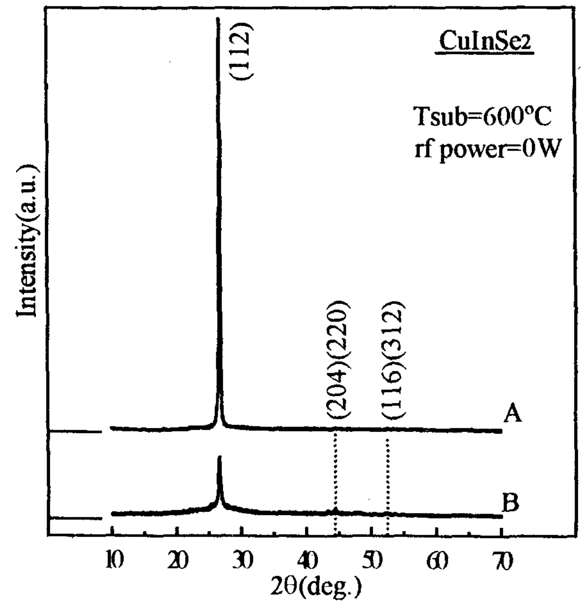


Fig. 2 XRD patterns of films prepared by different evaporation orders
A: Cu_2Se first and In_2Se_3 second
B: In_2Se_3 first and Cu_2Se second

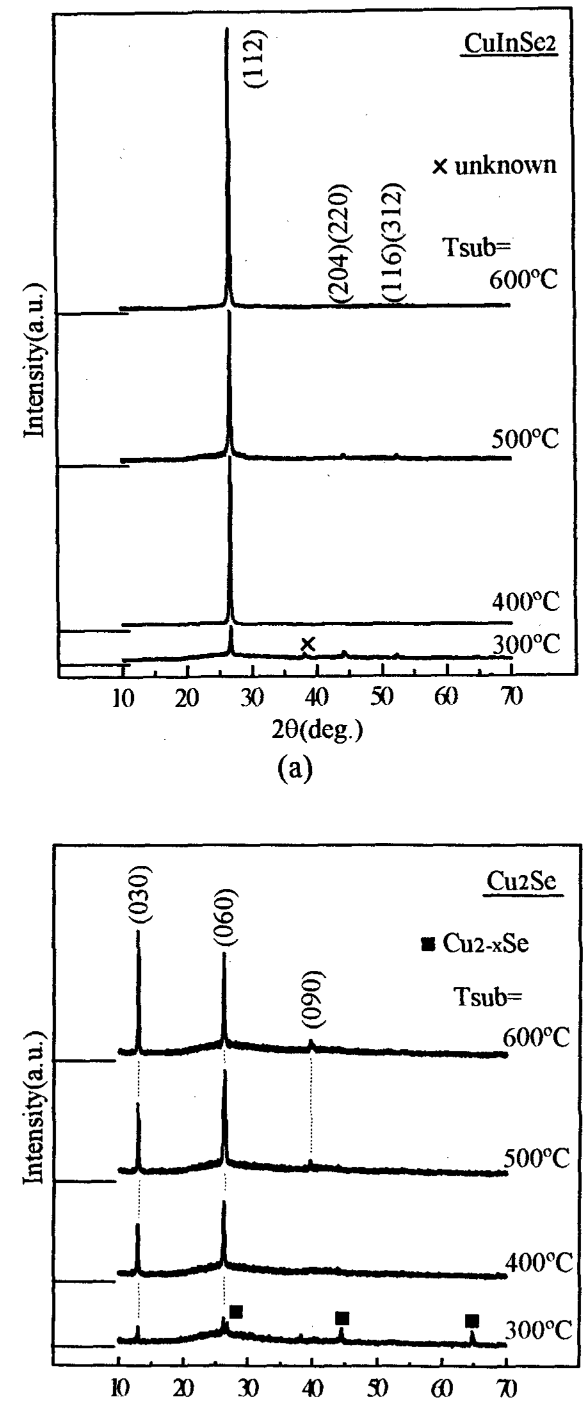


Fig.3 XRD patterns of films prepared at the substrate temperature of 300-600°C by evaporating of (a) Cu_2Se and In_2Se_3 (b) Cu_2Se only

sources are not simultaneously but sequentially. Evaporation order of them was chose by comparing the difference of X-ray diffraction(XRD) patterns of films prepared by both evaporation orders. XRD patterns of them are shown in Fig.2. For example, XRD patterns of films prepared at substrate temperature of 600°C without assistance of rf plasma are shown. XRD pattern of film prepared in order of In_2Se_3 first and Cu_2Se second (A) includes not only peaks from $CuInSe_2$ but also that unknown. On the other hand, pattern of film prepared in the reverse order (B) includes no peak other than that from $CuInSe_2$ and shows preferred orientation to (112) of $CuInSe_2$. This result is also obtained in other deposition conditions. Therefore evaporation order of them was Cu_2Se first and In_2Se_3 second.

3.RESULTS AND DISCUSSION

3.1 The cause that influences degree of preferred orientation of $CuInSe_2$ thin films

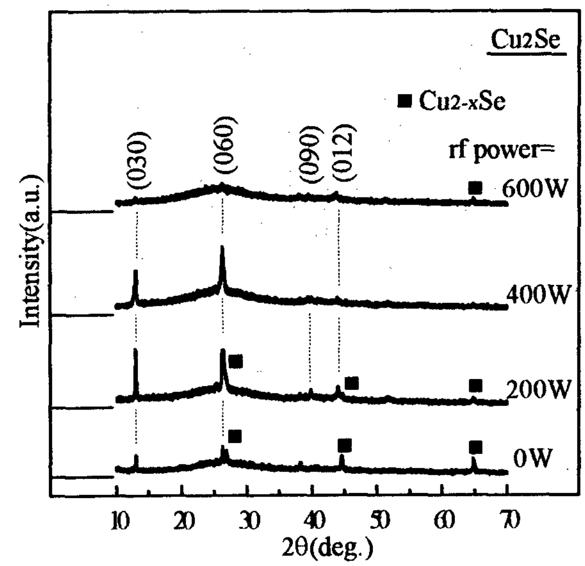
XRD patterns of films prepared at the substrate temperature of 300-600°C without assistance of rf plasma are shown in Fig.3(a). Patterns of films prepared at substrate temperatures above 400°C include no peak other than those from $CuInSe_2$ and indicate highly preferred orientation to (112) of $CuInSe_2$. On the other hand, pattern of film prepared at 300°C includes not only peaks from $CuInSe_2$ but also that from unknown and degree of preferred orientation is inferior to those of films prepared above 400°C.

And we prepared films by evaporating of each binaries, Cu_2Se and In_2Se_3, individually under the same deposition conditions that for preparation of $CuInSe_2$ thin films. From XRD patterns of these films, it is observed that films prepared by evaporation of In_2Se_3 did not crystallize, on the other hand, those of Cu_2Se crystallized. XRD patterns of films prepared by evaporation of Cu_2Se under the same conditions of $CuInSe_2$ in Fig.3(a) are shown in Fig.3(b). Pattern of film prepared at 300°C includes peaks from both of Cu_2Se and $Cu_{2-x}Se$, but pattern of film prepared at 600°C shows highly preferred orientation to (030) of Cu_2Se. This tendency of preferred orientation is very similar to that of Fig.3(a). Therefore, we consider that degree of preferred orientation of $CuInSe_2$ thin films depends on that of Cu_2Se thin films.

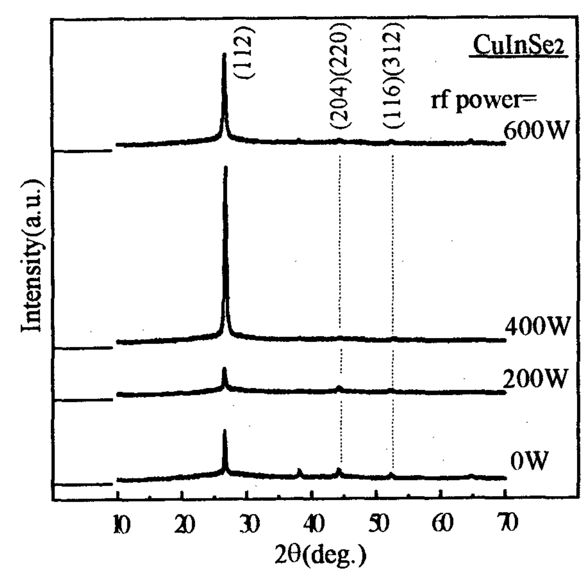
3.2 Lowering substrate temperature for preparation of $CuInSe_2$ thin films

From the results described above, we employed rf plasma during evaporation of both binary sources to improve degree of preferred orientation of Cu_2Se thin films at 300°C in order to improve that of $CuInSe_2$ thin films. XRD patterns of films prepared by evaporating of Cu_2Se at 300°C with assistance of rf plasma are shown in Fig.4(a). Cu_2Se thin film which indicates preferred orientation is obtained at 300°C with assistance of rf plasma at power of 400W. And XRD patterns of films prepared by evaporating of Cu_2Se and In_2Se_3 at 300°C with assistance of rf plasma are shown in Fig.4(b). Preferred orientated $CuInSe_2$ thin film was obtained at 400W. From this results, it is clear that use of rf plasma during evaporation is very effective to improve degree of orientation of $CuInSe_2$ thin films. The scanning electron microscope (SEM, HITACHI S-4500) image of thin film is shown in Fig.5. The structure with large grains tightly arranged is observed.

As the method to improve degree of orientation of $CuInSe_2$ thin films at low substrate temperature, we prepared $CuInSe_2$ thin films by setting interval between evaporation of Cu_2Se and In_2Se_3 in order to obtain preferred orientated Cu_2Se thin films at lower substrate temperature. XRD pattern of film prepared at the substrate temperature of 200°C with interval of



(a)



(b)

Fig.4 XRD patterns of films prepared with assistance of rf plasma by evaporating of (a)Cu_2Se only (b)Cu_2Se and In_2Se_3

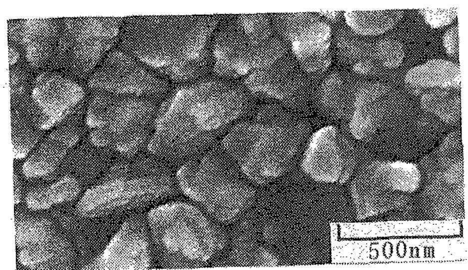


Fig.5 SEM image of $CuInSe_2$ thin film prepared at 300°C with assistance of rf plasma at 400W

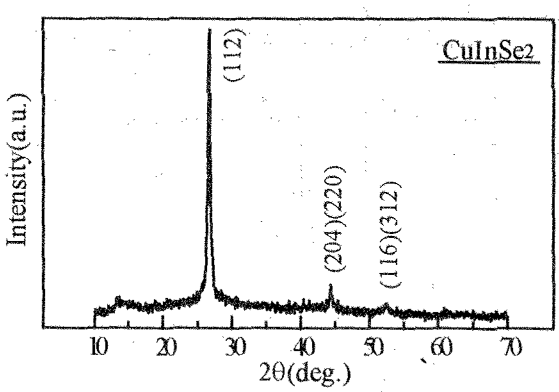


Fig.6 XRD pattern of film prepared at 200°C with interval of 4min.

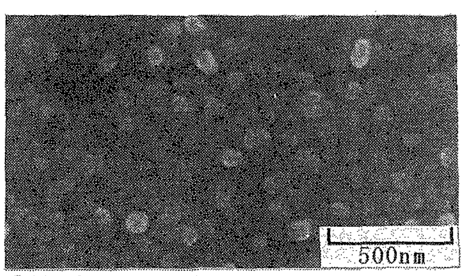


Fig.7 SEM image of $CuInSe_2$ thin film prepared at 200°C with interval of 4min.

4min. between evaporation of two sources without assistance of rf plasma is shown in Fig.6. This pattern includes only peaks from $CuInSe_2$, and indicates preferred orientation to (112) of $CuInSe_2$. By this method, highly orientated $CuInSe_2$ thin film have been obtained at such a low substrate temperature as 200°C. The SEM image of this film is shown in Fig.7. The structure with smaller grains than the film prepared at 300°C with assistance of rf plasma at 400W is observed.

4.CONCLUSION

Highly orientated $CuInSe_2$ thin films were prepared at substrate temperature of 300°C with assistance of rf plasma at power of 400W by using the result that degree of preferred orientation of $CuInSe_2$ thin films depends on that of Cu_2Se thin films. The structure with large grains tightly arranged is observed. By setting interval between evaporation of two sources, preferred orientated $CuInSe_2$ thin film was obtained at substrate temperature of 200°C with small grains.

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