Influence of degree of vacuum during deposition on properties of $Cu(In,Ga)S_2$ absorber film and Mo back contact film

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Abstract. We have prepared the $Cu(In,Ga)S_2$ absorber film and the Mo back contact film of thin film solar cell with changing degree of vacuum during deposition, and investigated the orientation, the internal stresses, and the exfoliation. The (112) X-ray diffraction peak was the strongest in $Cu(In,Ga)S_2$ films deposited under 0.07Pa. $Cu(In,Ga)S_2$ films deposited over 0.07Pa have (204) orientation. Mo films which deposited at narrow region of degree of vacuum from 0.5Pa to 0.6Pa have (211) orientation on tension condition, other Mo films have (110) orientation on compression condition. We have found that $Cu(In,Ga)S_2$ film prepared on Mo film under tension condition are easily exfoliated from Mo film.

Introduction

Thin film solar cells based on chalcopyrite absorbers are promising candidates for next generation photovoltaic modules. They have the highest efficiencies of all thin-film solar cells [1], excellent stability and radiation hardness together with competitive projected production costs. Furthermore the flexible solar cell is practicable on flexible substrate like polyimide [2]. $CuInS_2$ has a band gap of about 1.5eV suitable for optimum conversion efficiency, a lower toxicity than Se-containing chalcopyrites, and it can be prepared by simple, extremely fast sequential (two-step) processes [3,4]. Since $Cu(In,Ga)S_2$ solid solutions can have band gaps from 1.5eV to 2.43eV depending on the ratio of Ga/In, we can employ $Cu(In,Ga)S_2$ absorber for the top cell of the tandem configuration with wide band gap[5-7]. The highest efficiency of chalcopyrite sulphide-based (Se-free) $Cu(In,Ga)S_2$ thin film solar cells is 12.3 % (independently confirmed total area measurements) [8].

We know that $Cu(In,Ga)S_2$ film on Cu-rich condition has (112) orientation(112 plane is parallel to substrate) and that on Cu-poor condition has (204) orientation (204 plane is parallel to substrate) [8]. It was reported that orientation of other materials (such as $(Ba,Sr)TiO_3$[9], AlN[10]) dependent on degree of vacuum during deposition. The relation between the orientation of $Cu(In,Ga)S_2$ film and degree of vacuum during deposition have not been studied in detail so far.

$Cu(In,Ga)S_2$ solar cell has the substrate / Mo Back contact / $Cu(In,Ga)S_2$ / CdS / ZnO structure. We occasionally encounter a exfoliation problem of $Cu(In,Ga)S_2$ film from Mo film[11-13]. Although the exfoliation is great problem for yield, the origin of exfoliation problem has been not clarified yet. It has been known that the internal stresses of Mo films are affected by degree of vacuum during deposition [14]. There are possibility that internal stresses are dependent on a exfoliation of $Cu(In,Ga)S_2$ film from Mo film.

In this study, we have prepared the $Cu(In,Ga)S_2$ film on soda-lime glass(SLG) with changing degree of vacuum during deposition, and investigated the orientation. Furthermore we have prepared the $Cu(In,Ga)S_2$ film on polyimide covered with Mo back contact and investigated the relations between the internal stresses and the exfoliation.

Experimental

A multi-source 2-stage evaporation has been employed using an EL10 evaporator manufactured by Eiko engineering. In, Ga, Cu, and S were deposited by means of four Knudsen cells. In the first stage, In-Ga-Cu-S precursor layers were deposited at 250°C onto SLG (12.5mm×50mm×1mm). The (Ga+In):Cu ratio was 1:0.9. In the next stage, the substrate was heated to 580°C, and Cu and S were deposited onto the precursor layer. The conversion from Cu-deficiency to Cu-excess is accompanied by a change in the film's emissivity. We have used this effect for *in-situ* monitoring by observing the substrate and heater temperature with separate thermocouples. The nominal Cu-excess in the film has been adjusted to 10% by continuing stage 2 evaporation for a certain time after detection of the stoichiometry transition. A total evaporation period closes to 1.0 hour. Degree of vacuum during deposition is accidentally different every evaporation, furthermore hydrogen gas was introduce for the purpose of intentional change the degree of vacuum during deposition. In order to investigate exfoliation and stress, $Cu(In,Ga)S_2$ films were deposited on polyimide substrate(12.5mm×50mm×0.125mm) by 2-stage evaporation(substrate temperature in second stage is at 425°C). Compression or tension stresses were estimated from warping of polyimide substrates.

Mo films were deposited on polyimide substrates using RF-magnetron sputtering methods flowing Ar. Degree of vacuum during deposition was changed by adjustment of Ar flow.

X-ray diffraction (XRD) spectra have been recorded using Cu-K_α radiation. The thickness of the films was estimated from scanning electron microscopy (SEM) cross section images and stylus profiling. The Ga/(In+Ga) and Cu/(In+Ga) ratios were measured using Wavelength Dispersive X-ray Spectrometry (WDS) in the Electron Probe Micro Analyzer (EPMA). Resulting films have been analyzed by SEM and optical microscope.

Results and Discussion

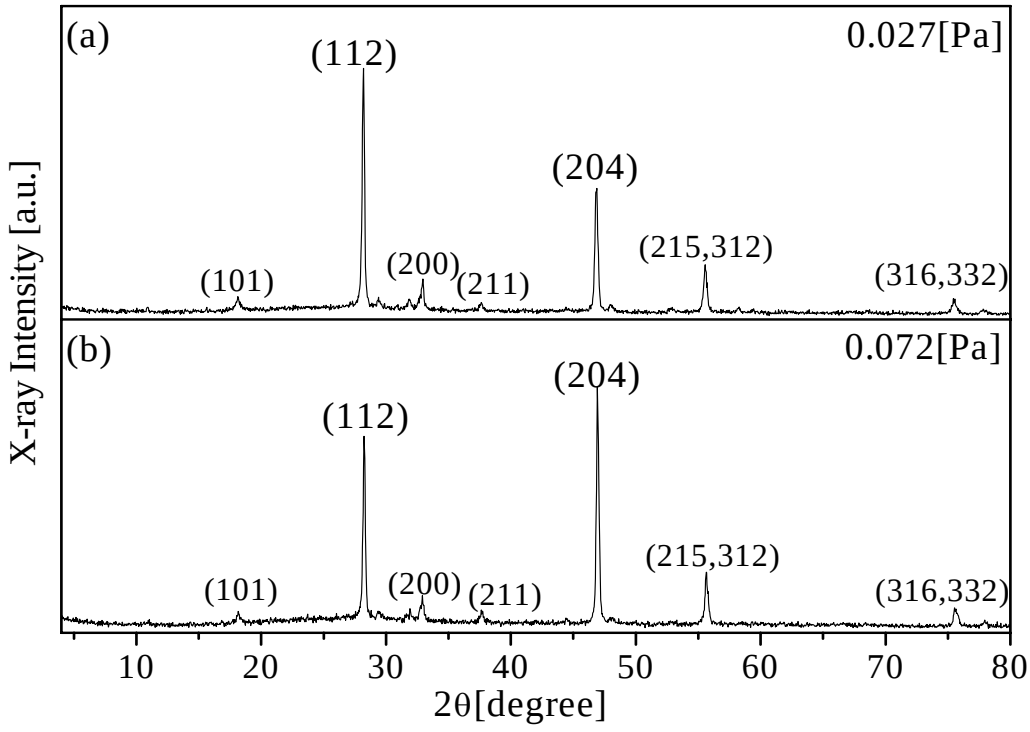

Fig.1 XRD pattern of $Cu(In,Ga)S_2$ films prepared in degree of vacuum (a) 0.027Pa and (b) 0.072 Pa during deposition

Thickness of $Cu(In,Ga)S_2$ and Mo films are 1.7μm and 1.0μm, respectively. Ga/(In+Ga) of all $Cu(In,Ga)S_2$ thin film are 0.2. Band gap is estimated at 1.69eV. Figure 1 shows XRD pattern of $Cu(In,Ga)S_2$ film prepared in degree of vacuum 0.027Pa(a) and 0.072Pa(b) during deposition. In the case of $Cu(In,Ga)S_2$ film prepared in 0.027Pa, the (112) diffraction peak was the strongest. On the other hand, in the case of $Cu(In,Ga)S_2$ film prepared in 0.072Pa, the (204) diffraction peak was the strongest, which indicates that $Cu(In,Ga)S_2$ thin film was oriented along the (204) plane parallel to the substrate. Relative intensities of powder diffraction of (204) and (112) are 25 and 100, respectively (JCPDS 27-159).

Figure 2 shows that (204) XRD intensity of $Cu(In,Ga)S_2$ film normalized to the (112) intensity as a function of degree of vacuum during deposition. $Cu(In,Ga)S_2$ films deposited over 0.07Pa have (204) orientation whether with hydrogen or without hydrogen. All films were prepared in Cu-rich condition, namely, it indicates that orientations depend on degree of vacuum during deposition, and are independent of Cu-rich or poor condition. It can be considered that increase of degree of vacuum may increase oxygen contamination [15]. We presume that an irradiation of hydrogen gas may decrease oxygen contamination by means of a reducing process. The mechanism of change of orientation with degree of vacuum during deposition is not yet well-established. However we believe that content of oxygen contamination of films may be independent on the orientation in this case, since orientations change with degree of vacuum during deposition in spite of presence or absence of hydrogen.

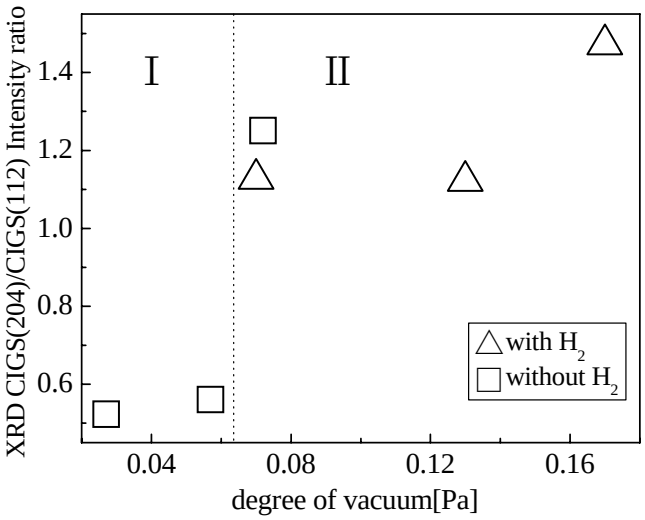

Fig.2 (204) XRD intensity of $Cu(In,Ga)S_2$ film normalized to the (112) intensity as a function of degree of vacuum during deposition

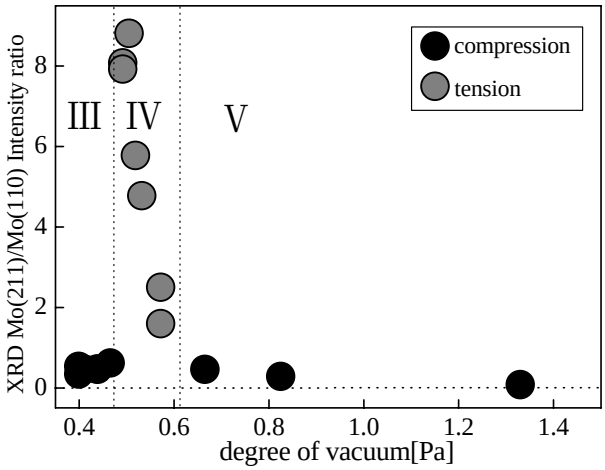

Fig.3 (211) XRD intensity of Mo film deposited on polyimide substrate normalized to the (110) intensity as a function of degree of vacuum during deposition

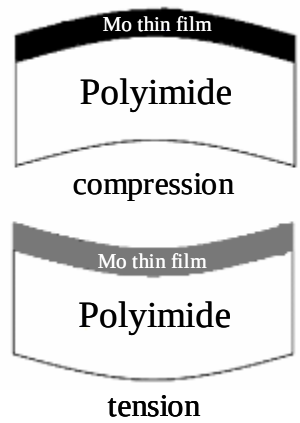

Fig.4 Schematic drawing of the Mo films on polyimide substrate of compression and tension condition.

Figure 3 show that (211) XRD intensity of Mo film deposited on polyimide substrate normalized to the (110) intensity as a function of degree of vacuum during deposition. Relative intensities of powder diffraction of (211) and (110) are 31 and 100, respectively (JCPDS 42-1120). Mo films which deposited at narrow region of degree of vacuum from 0.5Pa to 0.6Pa have (211) orientation on tension condition, and other Mo films have (110) orientation on compression condition as shown in Fig.4.

Hoffman *et al.* have investigated stress dependent of degree of vacuum pressure from 0.07Pa to 0.5Pa[14]. They reported stress of film due to compression under 0.3Pa, and tension between 0.3Pa and 0.5Pa. Their data has slight different from our data, however their tendency is similar to our data. Although they did not investigate degree of vacuum pressure-dependence of stress above 0.5Pa, we have found that stress of films prepared over 0.6 Pa change again to compression.

Table 1 The conditions of $Cu(In,Ga)S_2$ film prepared in Ⅰand Ⅱ region of degree of vacuum in Fig2 on Mo films prepared in Ⅲ, Ⅳ, and Ⅴ region of degree of vacuum in Fig3. ○ and × show surface conditions as shown in Fig.5(a) and (b), respectively.

$Cu(In,Ga)S_2$ \ Mo	**Ⅲ**[0.41Pa]	**Ⅳ**[0.51Pa]	**Ⅴ**[1.33Pa]
Ⅰ [0.036Pa]	○	×	○
Ⅱ [0.099Pa]	○	×	○

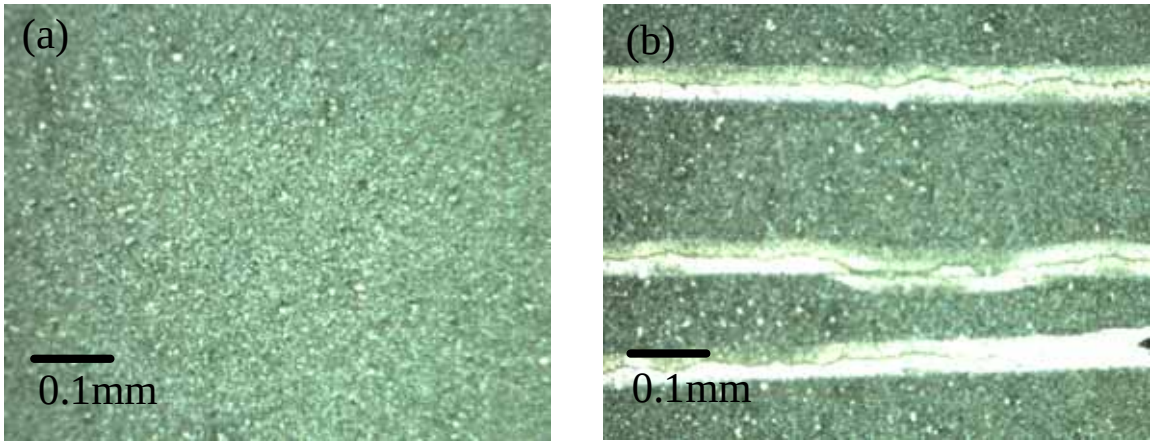

Fig.5 Photograph of typical surface of $Cu(In,Ga)S_2$ film in condition shown by ○(a) and ×(b) in table 1.

Table 1 shows that conditions of $Cu(In,Ga)S_2$ film prepared in Ⅰ(0.036Pa) and Ⅱ(0.099Pa) region in Fig2 on Mo films prepared in Ⅲ(0.41Pa), Ⅳ(0.51Pa), and Ⅴ(1.33Pa) region in Fig3. We have confirmed that $Cu(In,Ga)S_2$ film in Ⅰ on polyimide without Mo has compression condition, however that in Ⅱ doesn't have almost stress (polyimide substrates keep flat). Crack in $Cu(In,Ga)S_2$ film were not observed by optical microscope (Fig.5(a)) and SEM in condition shown by ○. However a large amount of cracks were observed on the film shown as × in Fig.5(b). In the bright parts in Fig.5(b), $Cu(In,Ga)S_2$ film are exfoliated, then Mo appeared on the surface. We have found that $Cu(In,Ga)S_2$ film prepared on Mo film under tension condition are easily exfoliated from Mo film.

Conclusions

We have investigated the relation between the orientation of $Cu(In,Ga)S_2$ and degree of vacuum during deposition. We have found that the orientation of $Cu(In,Ga)S_2$ film change to (204) orientation over 0.07Pa. Mo back contact films which are only deposited at narrow degree of vacuum region from 0.5Pa to 0.6Pa have (211) orientation with tension condition. We have found that $Cu(In,Ga)S_2$ film prepared on Mo film deposited from 0.5Pa to 0.6Pa are easily exfoliated from Mo film.

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