Crystallographic and electrical properties of wide gap Ag(In$_{1-x}$Ga$_x$)Se$_2$ thin films and solar cells

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Abstract

Ag(In$_{1-x}$Ga$_x$)Se$_2$ (AIGS) thin films have been deposited on Corning 1737 and Mo-coated soda lime glass substrates by three-stage process using a molecular beam epitaxy (MBE) system. The crystallographic properties of AIGS thin film have been investigated using X-ray diffraction and scanning electron microscope (SEM). Near-stoichiometric AIGS thin films possessed a tetragonal Ag(In,Ga)Se$_2$ phase with a small amount of tetragonal Ag(In,Ga)$_5$Se$_8$ phase. A tetragonal Ag(In,Ga)Se$_2$ phase became predominant as Ga/(In+Ga) atomic ratio increased. Hall measurements and thermo probe analysis revealed that AgInSe$_2$ films showed n-type conduction with high electron mobility. A wide gap Ag(In$_{0.2}$Ga$_{0.8}$)Se$_2$ thin film solar cell with a band gap energy of 1.7 eV showed a total-area efficiency of 7.3% (8.0% active area efficiency) with open-circuit voltage $V_{oc}$ = 866 mV, short-circuit current $J_{sc}$ = 14.5 mA/cm$^2$, fill factor $FF$ = 0.584, and total area = 0.42 cm$^2$.

Keywords: Ag(In,Ga)Se$_2$; Thin films; Solar cells; Wide gap; Electrical properties

1. Introduction

Wide gap chalcopyrite materials are required for tandem solar cells and high-voltage devices. However, it is well known that the efficiency of Cu(In$_{1-x}$Ga$_x$)Se$_2$ (CIGS) thin film solar cells decreases as the band gap energy ($E_g$) increases above 1.3 eV [1]. Furthermore, the efficiency of CuGaSe$_2$ devices with $E_g$ = 1.68 eV at present remains below 10%. We thus have investigated an Ag(In$_{1-x}$Ga$_x$)Se$_2$ (hereafter AIGS) thin film as one of the absorber materials for a top cell of tandem solar cells. AIGS has several advantages over CIGS as follows: (1) the band gap energy is wider than that of CIGS by 0.2 eV [2], and (2) the melting point is lower than that of CIGS by 200 °C. The Al(G)S thin film solar cells including p-AGS/n-CdS [3], p-AIS/n-CdS [4], and p-AIGS/n-ZnCdS [5] heterojunctions have been reported so far. However, the cell performance was poor as compared to other chalcopyrite-based thin film solar cells. In addition, the AIS or AIGS thin films were prepared by conventional vacuum evaporation techniques and they were described as a p-type material. We thus have investigated the growth and properties of AIGS thin films deposited by three-stage process using molecular beam epitaxy (MBE) system in order to know the possibility of this material as a top cell for tandem devices. In this paper the growth and properties of AIGS thin films and devices fabricated with various film compositions are presented.

2. Experimental

AIGS thin films were deposited by three-stage process using an MBE system. In the first step, In, Ga, and Se were coevaporated at 250 °C followed by evaporation of Ag and Se at 550 °C. Finally, In, Ga, and Se were coevaporated at 550 °C to convert the film composition into an (In+Ga) excess. The substrate temperature was measured by using thermocouple mounted to the back side of the substrates. The composition monitoring method by measuring the substrate temperature could be used to decide the final composition of AIGS thin films. Similar change in the substrate temperature was observed in each stage during AIGS deposition. The details are presented in elsewhere. Corning 1737 glass and Mo-coated soda lime glass (SLG) were used as substrates. A CBD-CdS buffer layer was deposited onto the AIGS layers using a CdI$_2$ (0.0014 M)-ammonia (1.0 M)-thiourea (1.4 M) aqueous solution. Non-doped ZnO and transparent conducting ZnO:Al thin films were then subsequently deposited using rf magnetron sputtering at room temperature. The solar cells were completed by the vacuum deposition of Al for front electrode. Current–voltage...
characteristics of the devices were measured under AM1.5, 100 mW/cm² illumination.

3. Results and discussion

3.1. Crystallographic and electrical properties of Ag(In₁₋ₓGaₓ)Se₂ thin films

Fig. 1 shows SEM micrographs of AgInSe₂ thin films with different Ag/In atomic ratios ranging from 0.32 to 1.5. The maximum substrate temperature was maintained at 550 °C. The triangle-shape grains due to the (112) plane of tetragonal structure are clearly observed in all AIS thin films showing a good crystal quality. X-ray diffraction analysis revealed that a stoichiometric thin film showed a tetragonal AgInSe₂ phase (ASTM38-952), whereas In-rich thin films with Ag/In ≤0.9 included a tetragonal AgIn₅Se₈ phase (ASTM36-1397).

The electrical properties of AIS thin films deposited on Corning 1737 glass substrates were measured by Van der Pauw method at room temperature. Fig. 2 shows the carrier concentration (n), Hall mobility (μ), and resistivity (ρ) of the AIS thin films as a function of Ag/In atomic ratio. As seen in Fig. 2, the carrier concentration increased from the order of 10¹¹ to 10¹⁵ cm⁻³ and the Hall mobility (μ) increased from 75 to 283 cm² V⁻¹ s⁻¹ as the Ag/In atomic ratio increased from 0.32 to 1.5. The AIS thin film with the Ag/In = 0.75 showed a carrier concentration of 6.4×10¹² cm⁻³, electron mobility of 270 cm² V⁻¹ s⁻¹, and resistivity of 1.0×10⁵ Ω cm.

The mobility increased with increasing the carrier concentration. The tendency is opposite to the typical semiconductor materials. This behavior is presumably related to the coexistence of the secondary phases such as a tetragonal AgIn₅Se₈ phase and low resistivity AgₓSe, which increased with increasing the Ag/In atomic ratio in AIS thin films.

X-ray diffraction analysis revealed that In-rich thin films (Ag/In = 0.32) showed a tetragonal AgIn₅Se₈ phase. However, the AgInSe₂ phase became dominant as the Ag/In ratios increased from 0.4 to 0.9. Hall measurements and thermoprobe analysis revealed that all films showed an n-type conductivity. It should be noted that AIS films showed fairly high mobility. Unfortunately, the electrical properties of AIGS and most of AGS thin films could not be measured since the resistivity was too high to be measured by Hall measurement. However,
the n-type conduction could be found for slightly Ag excess AIGS films.

Fig. 3 shows SEM photographs of Ag(In$_{1-x}$Ga$_x$)Se$_2$ films with different Ga/(In + Ga) ratios ranging from 0 to 1.0. As the Ga content in Ag(In$_{1-x}$Ga$_x$)Se$_2$ thin film increased, the crystal grains of surface region became small. This phenomenon is well known in Cu(In,Ga)Se$_2$ thin films. X-ray diffraction analysis revealed that the AIGS thin films possessed the tetragonal Ag(In,Ga)Se$_2$ phase with a small amount of tetragonal Ag(In,Ga)$_5$Se$_8$ phase. The Ag(In,Ga)Se$_2$ phase became predominant as the Ga/(In + Ga) atomic ratio increased.

3.2. Cell performance of Ag(In$_{1-x}$Ga$_x$)Se$_2$ devices

Fig. 4 shows the structure of AIGS thin film solar cells. The cell structure is similar to that of CIGS thin film solar cells. However, it should be noted that the conduction type of AIGS absorber is n-type as mentioned above. In the previous paper, we have found Cd diffusion into CIGS thin films during CBD process of CdS buffer layers. This behavior can be interpreted as the substitution of Cd for Cu atoms or Cu vacancies in the CIGS thin film resulting in the increased electron concentration. If similar substitution of Cd for Ag atoms occurs at the surface of AIGS during CBD process, a junction model of n-AIGS/Cd/n$^-$-AIGS could be proposed. However, further experiments are needed to confirm this model.

Fig. 5 shows J–V characteristics of a ZnO:Al/ZnO/CBD-CdS/AIGS/Mo/SLG solar cells. As can be seen in this figure the $V_{oc}$ increased as increasing the Ga content, whereas the $J_{sc}$ decreased. This trend is similar to that observed in CIGS-based thin film solar cells. The spectral response curves of the same devices are shown in Fig. 6. For AIS ($x=0$) thin film, the fall-off at long wavelengths of the spectral response curve is 1020 nm, which corresponds to the band-gap energy of 1.21 eV. This value is higher than that of CuInSe$_2$ by 0.2 eV, which is one of the merits of this material for fabricating wide gap devices.

Fig. 6. The spectral response curve of Ag(In$_{1-x}$Ga$_x$)Se$_2$ thin film solar cells fabricated with different $x = \text{Ga/(In + Ga)}$ atomic ratios.

Fig. 7. Cell performance of Ag(In$_{1-x}$Ga$_x$)Se$_2$ thin film solar cells fabricated with different $x = \text{Ga/(In + Ga)}$ atomic ratios.
Fig. 7 shows the cell performance of Ag(In$_{1-x}$Ga$_x$)$_2$Se$_2$ thin film solar cells fabricated with different Ga/(In+Ga) atomic ratios, where Ag/(In+Ga) atomic ratio was 0.75. As can be in Fig. 7, the $V_{oc}$ increased and the $J_{sc}$ lineally decreased as the $E_g$ increased. On the other hand the $FF$ was almost constant value. As a result, the maximum efficiency was achieved for the Ga/(In+Ga) atomic ratio of 0.8 which corresponds to $E_g = 1.7$ eV.

Table 1 summarizes the cell performance of AIGS thin film solar cells. A total-area efficiency of 7.3% (8.0% active area efficiency) with $V_{oc} = 866$ mV, $J_{sc} = 14.5$ mA/cm$^2$, $FF = 0.584$, and total area $= 0.42$ cm$^2$ was achieved for a Ag(In,Ga)Se$_2$ thin film solar cell with a band-gap energy of 1.7 eV.

4. Conclusions

We have investigated Ag(In,Ga)Se$_2$ thin films and solar cells as one of the candidates for top cell of future tandem devices. A total-area efficiency of 7.3% (8.0% active area efficiency) was achieved for a Ag(In,Ga)Se$_2$ thin film solar cell with a band-gap energy of 1.7 eV. The AgInSe$_2$ thin films showed an n-type conduction with high electron mobility. Further experiments are needed for understanding this material and junction model.

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