PHOTOVOLTAIC PROPERTIES OF $Cu(In,Ga)Se_2$ THIN FILM SOLAR CELL FABRICATED BY COEVAPORATION PROCESS

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ABSTRACT

Thin film solar cells based on $Cu(In,Ga)Se_2$ films were fabricated, and their junction and photovoltaic properties were investigated. Ga in $CuInSe_2$ thin films formed by so-called "bilayer process" was incorporated homogeneously. The fabricated cell structure was glass/Mo/$Cu(In,Ga)Se_2$/CdS/ZnO /ITO(/MgF_2). The incorporations of Ga into $CuInSe_2$ films up to about 20 mol% improved the photovoltaic performance. From the study of photoluminescence, capacitance-voltage and current-voltage characteristics, it was clarified that the incorporation of Ga not only widened the bandgap energy, but also played an important role in the effect which yield hole concentration. The best cell with an AR-coating(MgF_2) exhibited an efficiency of 15.2% ; Jsc=33.9mA/cm^2, Voc=0.616V, FF=0.730. The device performance can be improved by the development of the film with higher hole concentration, keeping the crystalline quality.

INTRODUCTION

$CuInSe_2$ is one of the most promising materials for photovoltaic devices with low cost and high efficiency. Thin film solar cells based on this material and the related compounds have been previously reported to show an efficiency of more than 15% [1-3].

Primarily, the incorporation of Ga into $CuInSe_2$ was tried in order to widen the bandgap energy more matched to the solar spectrum.[4,5] Other roles of Ga in $CuInSe_2$ were also reported ; Jensen et al.[6] reported about the improvement of the adhesion to the Mo back electrode, and Walter et al.[7] showed Ga was necessary to avoid a significant drop of the hole concentration in $CuIn(S,Se)_2$ alloys. For the development of higher performance cell, it is important to study such electrical and mechanical effect of Ga. Especially, it is very difficult, but significant works to research a correlation of optical and electrical film properties and device characteristics through the defect chemistry of $CuInSe_2$ and the related compounds which is mainly dominated by intrinsic defects.

So far, we have been continuing to investigate the feasibility of the efficiency on thin film solar cells based on $Cu(In,Ga)Se_2$ films, using a coevaporation process from its controllability. In this paper, we report the progress of our development for $Cu(In,Ga)Se_2$ thin film solar cells with the results of the analyses from photoluminescence and electrical measurements.

EXPERIMENTAL

The $Cu(In,Ga)Se_2$ films used in this experiment were prepared on a Mo-coated soda-lime glass by either multi-source coevaporation of Cu, In, Ga and Se. The films were prepared by the so-called "bilayer process" [8] based on our coevaporation process described elsewhere in detail [9]. The substrate temperature was about 500°C, a Ga flux was kept constant during the deposition. The total thickness of the film was in the range of 2.5-3.0μm. The heterojunctions were completed by the deposition of a thin CdS (CBD,40-60nm thickness), an undoped ZnO film (RF magnetron sputtering, 0.3μm thickness) and an ITO film (RF magnetron sputtering, 0.5μm thickness). Furthermore, a MgF_2 AR-coating (electron-beam evaporation) was deposited onto the best devices.

Photoluminescence (PL) measurements of the $Cu(In,Ga)Se_2$ films were carried out at 4.2K and 77K with Ar^+ laser on the various excitation intensity. For the estimation of hole concentration, capacitance-voltage (CV) measurements of the fabricated $Cu(In,Ga)Se_2$ cells were performed at a frequency of 1 MHz. For the observation of the junction properties, an electron beam induced current (EBIC) method was used at the accelerating voltage of 10keV under the low injection condition. Current-voltage measurements were also performed in the dark and under AM1.5, 100mW/cm^2 condition in the temperature range of 288-328K. Quantum efficiency of the fabricated cell was measured in the wavelength range of 300-1400nm.

RESULTS and DISCUSSION

Figure 1 shows PL spectra of $CuIn_{1-X}Ga_XSe_2$ (X=0.0,0.13,0.21,0.60) films measured at 4.2K. The PL peak was shifted to higher energy with increasing Ga content, mainly due to widening the bandgap energy. The dependence of PL spectra on excitation intensity (10-100mW), observed in $Cu(In,Ga)Se_2$ films, shows that every PL emission intensity have a tendency to saturate besides the emission peak energy doesn't a shift. However, in the PL spectra measured at 77K, we observed the blue shift of the PL emission peak with the increase of the excitation intensity even in the range of 10-100mW. It suggests that the observed emissions may be due to the donor-acceptor(DA) pair emissions. Each PL emission intensity at 77K was almost same level except the emission intensity from the $CuIn_{0.4}Ga_{0.6}Se_2$ film, which was approximately one order weaker. We suppose that the $CuIn_{0.4}Ga_{0.6}Se_2$

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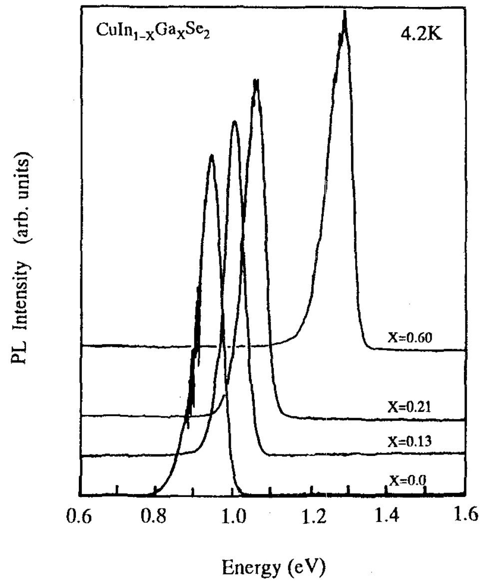

Fig.1 Photoluminescence spectra of $CuIn_{1-X}Ga_XSe_2$ films measured at 4.2K.

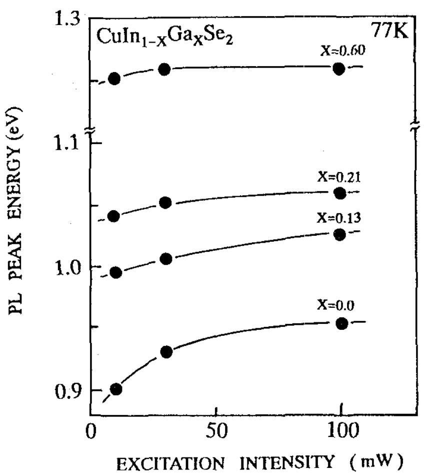

Fig.2 The photoluminescence peak energy of $CuIn_{1-X}Ga_XSe_2$ films measured at 77K as a function of the excitation intensity.

film was inferior to the other films in quality, and that the PL emission was weakened due to non–radiative recombination rather than having the lower concentration of the DA pair. Figure 2 shows the PL peak energy of $CuIn_{1-X}Ga_XSe_2$ (X=0.0,0.13,0.21,0.60) films measured at 77K as a function of the excitation intensity. We can find in Fig.2 that the peak energy was less dependent on the excited intensity with the increase of the Ga content. Those dependence suggests that Ga in $CuInSe_2$ not only widened the bandgap, but also played an important role in the native defect formation such as a decrease of donor concentration.

Figure 3 shows the values of hole concentration, or Na(acceptor density)–Nd(donor density), obtained from CV measurements of the CdS/Cu(In,Ga)Se_2 heterojunction as a function of Ga content. For the estimation of the hole concentration (P), an abrupt n^+p junction with constant doping levels was assumed. The values obtained should be regarded as relative ones to each other rather than absolute ones.[7] From the results, the $CuInSe_2$ films were considered to be significantly compensated and the addition of Ga seemed to yield the increasing of hole concentration. However, the larger amount of Ga such as $CuIn_{0.4}Ga_{0.6}Se_2$ film saturated the effect. These results coincided the result obtained from PL measurements. Therefore, as for our preparation process of Cu(In,Ga)Se_2 films, the film with high hole concentration and high quality can be produced in the region around Ga content of 20 mol%.

The characterized results obtained from PL and CV measurements were well reflected in the junction properties of Cu(In,Ga)Se_2 solar cell devices. Figure 4 shows junction EBIC profile observed in the $CuIn_{1-X}Ga_XSe_2$ (X=0.0,0.13,0.21,0.60) cells. According to Evehart et al.[10], the diameter of the generation volume (Rg) in $CuInSe_2$ at the accelerating voltage of 10kV is about 0.6μm. In addition, Shea et al.[11] suggest the necessary condition, Rg/4<L(the minority carrier diffusion length), for the validity of the point source approximation. In other words, the Rg at 10kV in $CuInSe_2$ is approximated by a point source as long as the L in $CuInSe_2$ is longer than about 0.15μm. However the profile of EBIC linescans are affected by surface recombination.[12] Ordinarily, the collective region of the generated carrier in the p–n junction consists of the space charged region and the diffusion region. The observed EBIC profile seemed to vary from the dominant profile of the space charged region to that of the diffusion region with the increase of Ga content. The variation of the profile corresponds to the variation of the hole concentration on Cu(In,Ga)Se_2 films shown in Fig.4, since the space charged region is proportional to the square root of 1/P on the assumption of the abrupt junction with the constant doping level. Furthermore, the minority carrier diffusion length of the $CuIn_{1-X}Ga_XSe_2$ (X=0.21,0.60) film was estimated from the EBIC profile by using the point source approximation, and the values of 1.5μm and 0.7μm were obtained in the films of

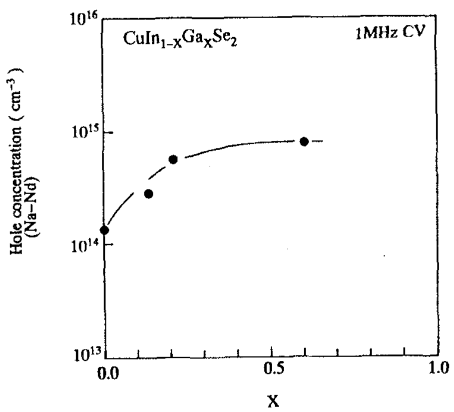

Fig.3 The hole concentration of $CuIn_{1-X}Ga_XSe_2$ films as a function of Ga content, obtained from capacitance–voltage measurements of the CdS/Cu(In,Ga)Se_2 heterojunction.

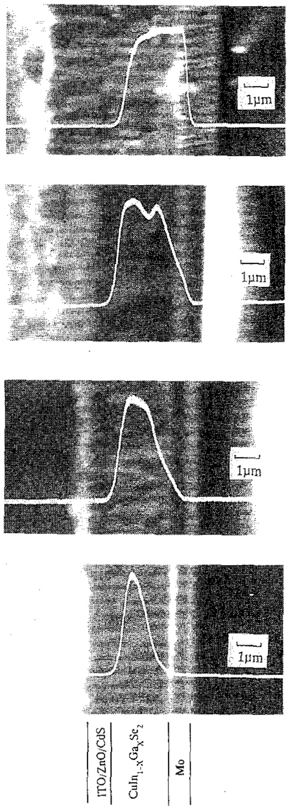

Fig.4 Electron beam induced current profiles of $CuIn_{1-X}Ga_XSe_2$ solar cell devices.

X=0.21 and X=0.6, respectively. Those values satisfied the criterion for the point source approximation (Rg/4<L), self-consistently. The difference of the diffusion length between the films of X=0.21 and X=0.60 would be reflected that of the quality of the two films, which is qualitatively understood from the PL measurements as already mentioned.

Current-voltage measurements of the $CuIn_{1-X}Ga_XSe_2$ (X=0.0,0.13,0.21,0.60) cells in the dark at the temperature range of 288-328K showed a thermally activated behavior. The diode quality factors (n) were approximately independent of temperature and came up to two with the increase of Ga content. The values of the activation energy of the saturated current (I_0) estimated by a Arrhenius plot of I_0 were almost independent of Ga content. Each value of the activation energy times the diode quality factor was close to the bandgap of $Cu(In,Ga)Se_2$. This implies that the fabricated junctions in this work was primarily determined by Shockley-Read-Hall (SRH) recombination in the space charged region.[7] Current-voltage measurements of the $CuIn_{1-X}Ga_XSe_2$ (X=0.0,0.13,0.21,0.60) cells under AM1.5, 100mW/cm^2 at the temperature range of 288-328K showed the decrease of Voc due to thermally activated recombination process, however Jsc was independent of temperature. The dark and illuminated properties of the $Cu(In,Ga)Se_2$ cell were summarized in Table 1. According to these results, the device performance can be improved by the development of the film with higher hole concentration, keeping the crystalline equality.[7]

Table 1 Dark and illuminated current-voltage characteristics of the $CuIn_{1-X}Ga_XSe_2$ cells.

X	Jsc (mA/cm²)	Voc (V)	FF	Eff. (%)	J_0 (A/cm²)	n	Ea (eV)
0.00	35.6	0.426	0.691	10.5	7.96×10^{-7}	1.63	0.602
0.13	34.2	0.494	0.705	11.9	4.29×10^{-7}	1.76	0.614
0.21	33.2	0.581	0.708	13.7	3.82×10^{-8}	1.84	0.643
0.60	23.1	0.691	0.676	10.8	6.89×10^{-9}	1.93	0.657

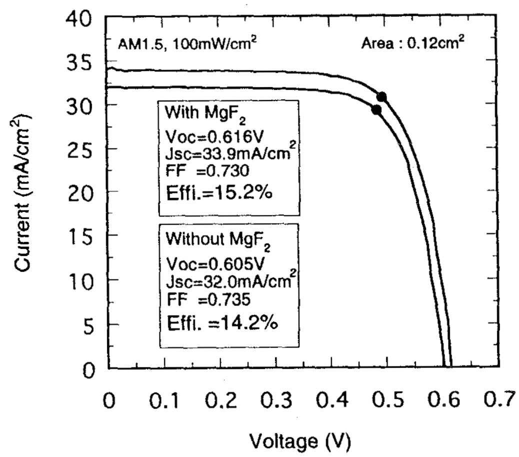

Fig.5 Current-voltage characteristics of the best $Cu(In,Ga)Se_2$ cell with and without an AR-coating under AM1.5, 100mW/cm^2.

As an anti-reflection (AR) coating, a MgF_2 film was deposited onto the device and Si substrate by electron beam evaporation. The value of the refractive index of the MgF_2 film was 1.39, obtained by ellipsometric measurement using He-Ne laser. From the calculation of the reflectivity on the structure of MgF_2/ITO, the optimized thickness of MgF_2 film was about 0.1μm. Figure 5 shows photovoltaic characteristics of the best device obtained so far, which was fabricated by using the $Cu(In,Ga)Se_2$ film with Ga content of about 20 mol%, with and without the AR coating. An active area efficiency of 15.2% (Jsc=33.9mA/cm^2, Voc=0.616V, FF=0.730, active area=0.12cm^2) was obtained in the device structure of glass/Mo/$Cu(In,Ga)Se_2$/CdS/ZnO/ITO/MgF_2. Figure 6 shows the external quantum efficiency of the cell measured in the wavelength range of 300-1400nm. A few percent recovering was observed in the range of 500-900nm by using the 0.1μm thickness of MgF_2 film as an AR-coating.

CONCLUSION

From the analyses of PL and CV measurement, the incorporation of Ga into $CuInSe_2$ not only widened the bandgap, but also played an important role in the defect chemistry such

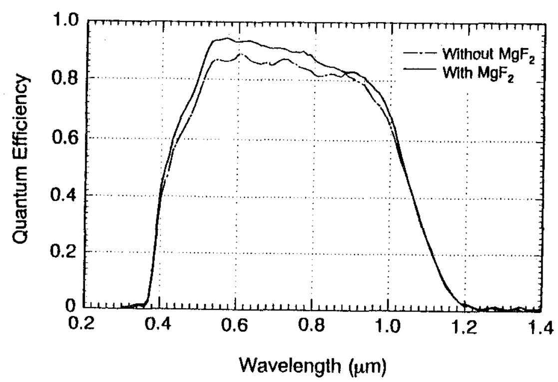

Fig.6 External quantum efficiency of the best $Cu(In,Ga)Se_2$ cell with and without an AR–coating

as a decrease of donor concentration which yield hole concentration as a result. These characteristics were well reflected in the EBIC profiles of $Cu(In,Ga)Se_2$ solar cell devices. As for our preparation process of $Cu(In,Ga)Se_2$ films, the film with high hole concentration and quality would be produced in the region around Ga content of 20 mol%.

Current–voltage characteristics show that the fabricated junctions in this work was primarily determined by Shockley–Read–Hall (SRH) recombination in the space charged region. Therefore, the device performance can be improved by the development of the film with higher hole concentration, keeping the crystalline equality.

The best cell fabricated so far with an AR–coating has an active area efficiency of 15.2% (Jsc=33.9mA/cm^2, Voc=0.616V, FF=0.730, active area=0.12cm^2).

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