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Research Article

$Cu(In,Ga)Se_2$ Thin Films Codoped with Sodium and Bismuth Ions for the Use in the Solar Cells

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The codoping effects of sodium and bismuth ions on the characteristics of $Cu(In,Ga)Se_2$ films prepared via the solution process were investigated in this study. When sodium and bismuth ions were incorporated into $Cu(In,Ga)Se_2$, the ratio of the intensity of (112) diffraction peak to that of (220/204) diffraction peak was greatly increased. The codoping process not only enlarged the sizes of the grains in the films but also resulted in densification of the films. The carrier concentration of $Cu(In,Ga)Se_2$ was found to be effectively increased to cause a reduction in the resistivity of the films. The above phenomena were attributed to the densified microstructures of the films and a decrease in the amount of the donor-type defects. The leakage current of the solar cells was found to be also decreased via the codoping process. Owing to the improved electrical properties of $Cu(In,Ga)Se_2$ films, the conversion efficiency of the fabricated solar cells was significantly enhanced.

1. Introduction

Solar energy has played an important role in energy production due to the increasing demand for renewable energy. $Cu(In,Ga)Se_2$ solar cells have reportedly reached the highest efficiency with the value of 20.3% among all thin-film solar cells [1]. Traditionally, $Cu(In,Ga)Se_2$ films are prepared via the vacuum processes including a multistage coevaporation route [2, 3] and the sputtering route [4, 5]. These methods have several shortcomings such as high cost and sophisticated processes; therefore, these problems cause the difficulty of large-scale manufacturing [6]. For overcoming the drawbacks of the vacuum processes, several kinds of nonvacuum processes such as the printing method [7], the electrodeposition process [8], and the spray pyrolysis method [9] have been developed to synthesize $Cu(In,Ga)Se_2$ films.

Although $Cu(In,Ga)Se_2$ films have been successfully obtained via these nonvacuum methods, further controlling the grain sizes of the films as well as the morphologies is required for improving the electrical properties of the solar cells. Doping sodium ions [10] and antimony ions into [11] $Cu(In,Ga)Se_2$ has been demonstrated to be effective way for enhancing the conversion efficiency of the fabricated solar cells. The incorporation of sodium ions is reported to increase the open-circuit voltage and the fill factor of the solar cells [12]. The growth of the (112)-oriented $Cu(In,Ga)Se_2$ films can be also enhanced [13]. Sodium ions are considered to substitute on a copper site in the form of Na_{Cu} and result in the annihilation of the amount of the donor-type defects in the form of In_{Cu} [14]. On the other hand, the authors have examined the doping effects of bismuth ions into $Cu(In,Ga)Se_2$ on the characteristics of the fabricated solar cells [15]. Doping bismuth ions has been found to result in densification of films and the enlargement of the grain sizes. The open-circuit voltage of the bismuth-doped $Cu(In,Ga)Se_2$ solar cells has been significantly enhanced. Although the doping effects of sodium ions and bismuth ions have been confirmed, the codoping effects of sodium and bismuth ions for $Cu(In,Ga)Se_2$ films have not been investigated in detail.

For exploring the codoping influence of sodium and bismuth ions, $Cu(In,Ga)Se_2$ films doped with the above two ions were prepared via the solution process on the sodium-free substrates. The doping effects of sodium and bismuth ions on the properties of the films were investigated. The relation between the electrical properties of the prepared films and the dopants was investigated. The electrical properties of the films doped with a single kind of ions were compared with those of the codoped films.

Table 1: Sample names for Cu(In,Ga)Se_2 films doped with varied ions.

Sample	Na	Bi
A	W/o	W/o
B	With	W/o
C	W/o	With
D	With	With

2. Experimental

Analytical $Cu(NO_3)_2$ (99.99%), $In(NO_3)_3$ (99.99%), and $Ga(NO_3)_3$ (99.99%) were used as the starting materials and dissolved in ethanol. The molar ratios of copper ions to indium ions to gallium ions were set to be 0.9 : 0.7 : 0.3. Bismuth nitrate and sodium nitrate were added to the above solutions as the bismuth source and the sodium source, respectively. The molar ratio of sodium ions to IIIA ions (indium and gallium ions) and that of bismuth ions to IIIA ions were set at 1.0 mol%, respectively. The solutions were mixed and stirred, followed by adding ethylcellulose that was used as a binder. Subsequently, the solution was spin-coated on the sodium-free glass and dried to 200°C on a hot plate for 0.5 h. The precursor films were placed in a tubular reactor. Selenium powders (99.99%) were used as the selenium source. The mixed gas (5% H_2/95% N_2) was used as the carrier gas to supply the heated selenium source. The Se partial pressure was about 2 Torr in the reactor. The precursor films were selenized at around 500°C for 30 min. The temperature was controlled via a PID controller. The prepared film without adding dopants was named as sample A, and the films doped with sodium ions, bismuth ions, and sodium ions as well as bismuth ions are named as samples B, C, and D, respectively. The kinds of the dopants added and the corresponding sample names are as listed in Table 1.

Cu(In,Ga)Se_2 films formed on the sodium-free glass were identified via X-ray diffraction diffractometer (XRD, Philips X'Pert) operated at 40 kV and 40 mA with Cu Kα radiation. The microstructures of the selenized specimens were observed using a scanning electronic microscope (SEM, Hitachi S800). The effects of the added ions on the electrical properties of Cu(In,Ga)Se_2 films were investigated via a Hall effect measurement (HMS-3000) at room temperature. The low-temperature photoluminescence (PL) spectra of the prepared films were recorded under the excitation of a laser diode (808 nm, 50 W) using an InGaAs array spectrometer (512 elements, 900–1650 nm). In order to examine the electrical properties of the prepared films, the solar cells with a structure of sodium-free glass/Mo/CIGS/CdS/i-ZnO/ITO were fabricated. The current-voltage (I-V) measurement under AM1.5G conditions at 25°C was used to investigate the fabricated Cu(In,Ga)Se_2 solar cells.

3. Results and Discussion

The X-ray diffraction patterns of 500°C selenized Cu(In,Ga)Se_2 films without adding dopants (sample A) are shown in Figure 1(a), and that of the films doped with sodium

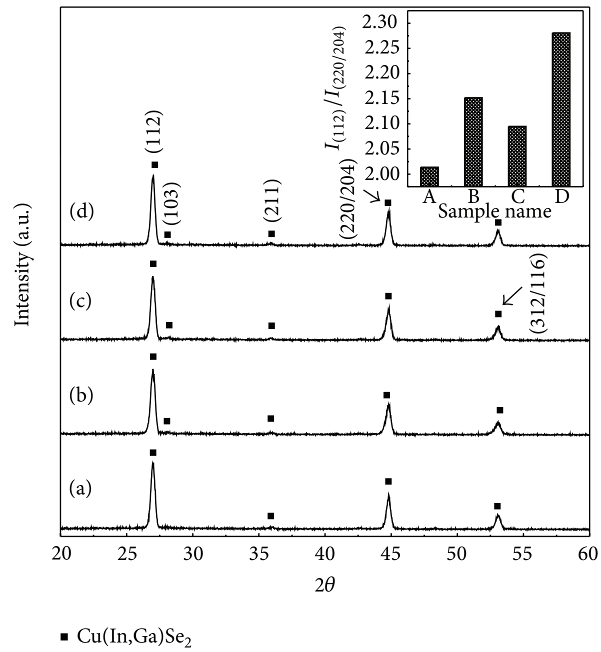

Figure 1: X-ray diffraction patterns of Cu(In,Ga)Se_2 films doped with (a) absence of dopants, (b) sodium ions, (c) bismuth ions, and (d) sodium ions and bismuth ions upon heating at 500°C for 30 min. Inset refers to relation between the ratio of $I_{(112)}/I_{(220/204)}$ and the sample name.

ions (sample B), bismuth ions (sample C), and sodium ions as well as bismuth ions (sample D) are illustrated in Figures 1(b), 1(c), and 1(d), respectively. The obtained results reveal that well-crystallized Cu(In,Ga)Se_2 films were successfully synthesized. The obtained films were confirmed to exhibit a chalcopyrite structure and the diffraction patterns matched well with the data reported in ICDD card number 35-1101. The insets in Figure 1 show the ratios of the intensity of the (112) peak to that of the (220/204) peak ($I_{(112)}/I_{(220/204)}$) for four different samples. The ratio of $I_{(112)}/I_{(220/204)}$ of sample A was 2.01. When sodium ions and bismuth ions were separately added to Cu(In,Ga)Se_2 (samples B and C), the ratios of $I_{(112)}/I_{(220/204)}$ were found to be increased. When sodium and bismuth ions were codoped (sample D), the ratio of $I_{(112)}/I_{(220/204)}$ was greatly increased to 2.28. The above results indicated that the doping of sodium and bismuth ions might vary the preferred orientation of the prepared films. Moreover, Cu(In,Ga)Se_2 films with the preferred (112) orientation are reportedly suitable for lattice matching with the window layers of solar cells [16, 17].

Figure 2 illustrates the microstructural evolution of the obtained Cu(In,Ga)Se_2 films doped with various kinds of ions. The size of the grains of Cu(In,Ga)Se_2 without dopants (sample A) was around 0.3 μm (Figure 2(a)). When sodium ions were incorporated (sample B), the particle size of the prepared films was significantly enlarged to 1 μm (Figure 2(b)). On the other hand, the size of the grains in the bismuth-doped films (sample C) was around 0.5 μm (see Figure 2(c)). Upon codoping sodium ions and bismuth ions (sample D), the microstructures became effectively densified, and

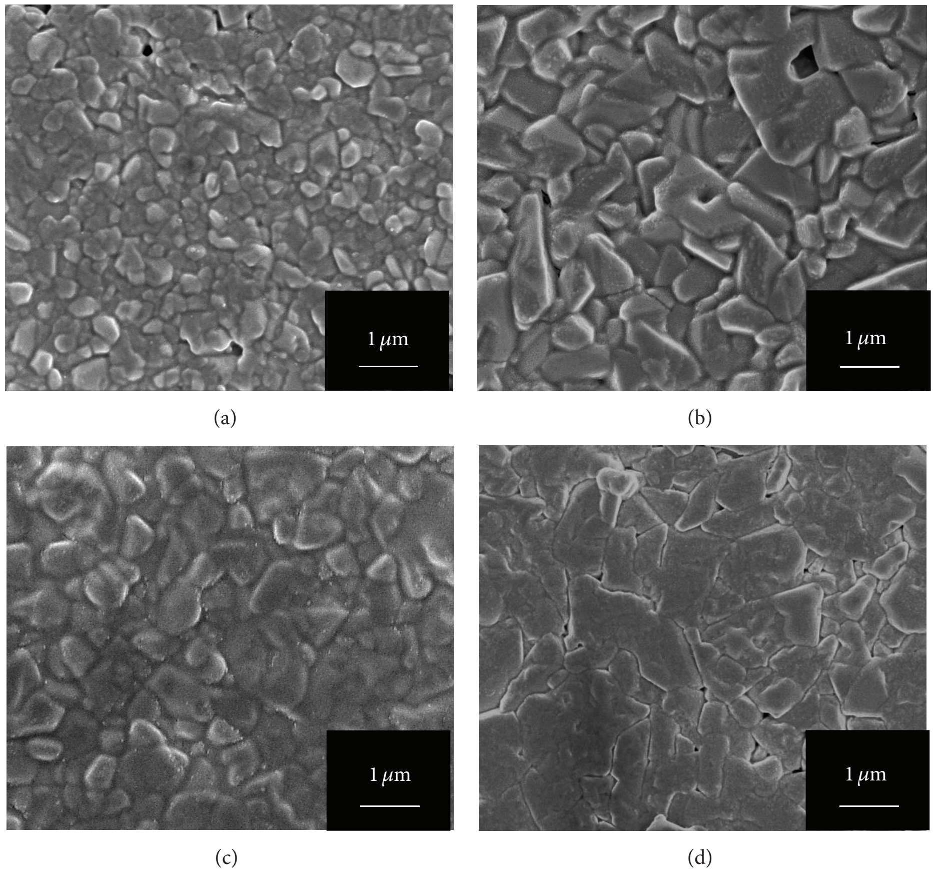

FIGURE 2: Scanning electron micrographs of $Cu(In,Ga)Se_2$ films doped with (a) absence of dopants, (b) sodium ions, (c) bismuth ions, and (d) sodium ions and bismuth ions upon heating at 500°C for 30 min.

the particle size was enlarged to around 2 μm as seen in Figure 2(d). Figure 3 shows the surface morphology of the corresponding films via the atomic force micrographs (AFM). The values of root-mean-square (RMS) roughness for samples A, B, C, and D were 86 nm, 68 nm, 60 nm, and 56 nm, respectively. It implies that the roughness of the films was greatly reduced as sodium and bismuth ions were codoped. When sodium ions are added to $Cu(In,Ga)Se_2$ films, sodium selenides are reported to be formed and act as a flux agent to facilitate the grain growth during the selenization process [18]. As bismuth ions are incorporated into $Cu(In,Ga)Se_2$ films, copper bismuth selenide compound is considered to be formed and plays a fluxing role according to our previous study [15]. Hence, the codoping of sodium and bismuth ions into $Cu(In,Ga)Se_2$ can effectively facilitate the densification process of the films and enlarge the grain sizes.

The J-V characteristics of the fabricated $Cu(In,Ga)Se_2$ solar cells are depicted in Figure 4, while the corresponding parameters of the devices are summarized in Table 2. The value of short-circuit current density (J_{sc}) was around 32–34 mA/cm^2 for four different samples. The values of open-circuit voltage (V_{oc}) and the values of fill factor (FF) were found to increase when sodium and bismuth ions were codoped. The conversion efficiency of the solar cells without any kinds of dopants was merely 4.8%. The values of the efficiency increased to 6.5% and 6.3% for samples separately doped with sodium ions and bismuth ions, respectively. Codoping both ions greatly increased the conversion efficiency to 6.9%. Based on the data shown in Table 2, codoping both ions also effectively increased V_{oc} and the FF of the solar cells. The current for solar cells under illumination can be expressed as

$$J = J_0 \left\{ \exp\left[\frac{q\left(V - JR_s\right)}{AkT} - 1 \right] \right\} + G\left(V - JR_s\right) - J_L, \quad (1)$$

where J is the diode current density, V is voltage, J_0 is the saturation current density, q is the electron charge, A is the diode ideality factor, k is the Boltzmann constant, T is the temperature in Kelvin, R_s is the series resistance, G is the shunt conductance, and J_L denotes the photocurrent density. Diode parameters determined from the J-V curve in Figure 4 are depicted in Figures 5 and 6, and the obtained data are summarized in Table 2. The value of the shunt conductance (G) can be extracted from Figure 5 (dJ/dV versus V). When the value of G is small, the internal leakage of the current through the cell will be decreased. The values of G of samples A, B, C, and D were calculated to be 21.0 mS/cm^2, 9.6 mS/cm^2, 14.8 mS/cm^2, and 9.8 mS/cm^2, respectively. The value of G was significantly reduced after the incorporation of sodium and

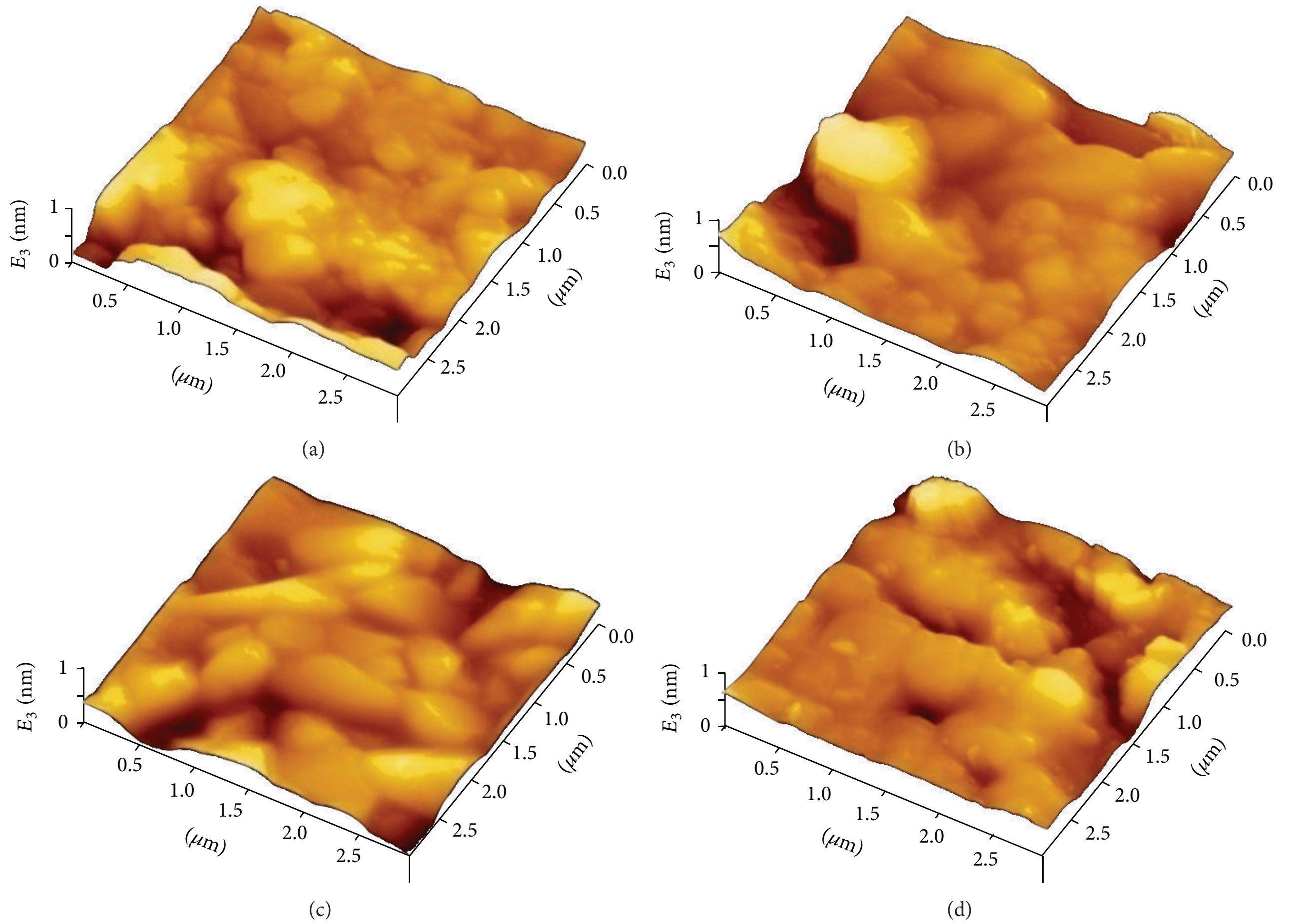

FIGURE 3: Atomic force micrographs of Cu(In,Ga)Se_2 films doped with (a) absence of dopants, (b) sodium ions, (c) bismuth ions, and (d) sodium ions and bismuth ions upon heating at 500°C for 30 min.

TABLE 2: Solar cell parameters of Cu(In,Ga)Se_2 films.

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	G (mS/cm^2)	R_s (Ω cm^2)	η (%)
A	0.34	32.98	43.66	21.0	1.46	4.8
B	0.41	33.42	46.70	9.6	0.94	6.5
C	0.40	33.67	47.20	14.8	0.83	6.3
D	0.43	32.58	48.70	9.8	0.76	6.9

bismuth ions, indicating that the amount of leakage current through the cells was decreased. A formula for the relation between the V_{oc} and G is expressed as [19]

$$V_{oc} = \frac{AkT}{q}\left(\frac{J_L}{J_0} + 1 - \frac{V_{oc}G}{J_0}\right). \tag{2}$$

As shown in (2), a reduction in G results in an increase in V_{oc}. Hence, codoping sodium and bismuth ions caused a decrease in G and an increase in V_{oc}. From the figure shown in Figure 6, the value of R_s can be obtained from dV/dJ versus $(J + J_{sc})^{-1}$. It can be seen that sample D has the lowest value of R_s compared with other devices as shown in Table 2.

The carrier concentration and the resistivity of Cu(In,Ga)Se_2 films were also examined via the Hall effect measurement and the results were listed in Table 3.

TABLE 3: Electrical properties of Cu(In,Ga)Se_2 films.

Sample	Carrier concentration (N_p) (cm^{-3})	Resistivity (ρ) (Ω-cm)
A	$2.47E + 16$	$6.11E - 02$
B	$6.50E + 16$	$5.83E - 02$
C	$5.99E + 16$	$5.40E - 02$
D	$8.56E + 16$	$5.04E - 02$

The carrier concentration was $2.47 * 10^{16}$ cm^{-3} for sample A and increased for films incorporated with dopants. The films codoped with both ions (sample D) had a maximum value of the carrier concentration ($8.56 * 10^{16}$ cm^{-3}). On the other hand, the resistivity of the codoped samples was

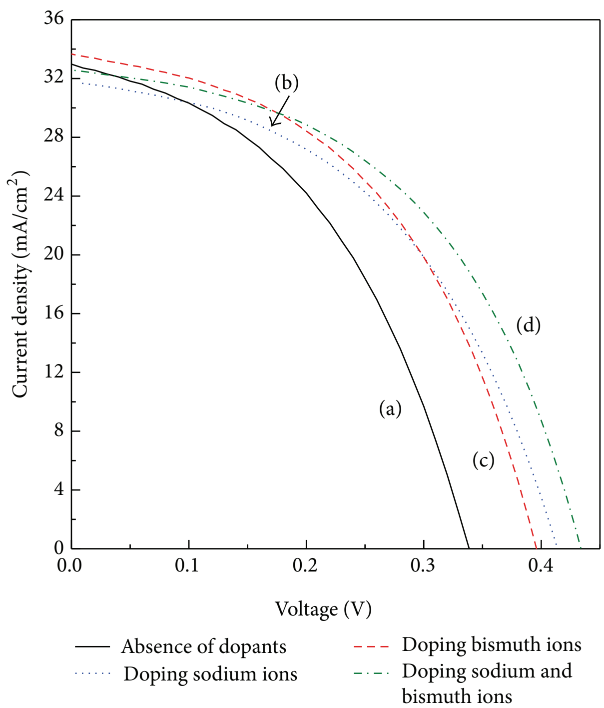

FIGURE 4: Current-voltage characteristics of $Cu(In,Ga)Se_2$ films doped with (a) absence of dopants, (b) sodium ions, (c) bismuth ions, and (d) sodium ions and bismuth ions upon heating at 500°C for 30 min.

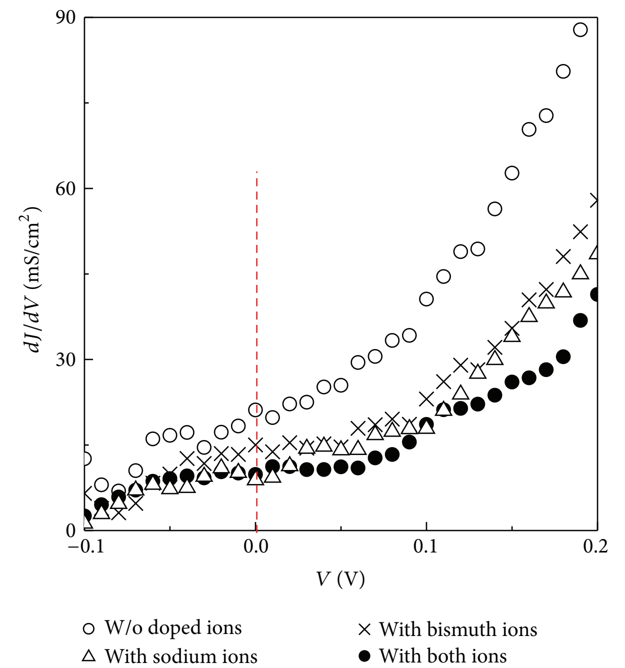

FIGURE 5: dJ/dV versus V for the determination of the shunt conductance (G).

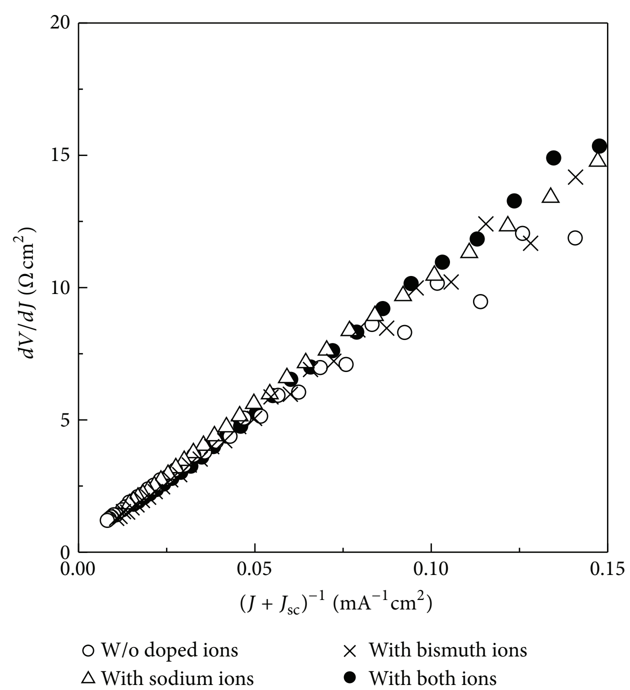

FIGURE 6: dV/dJ versus $(J + J_{sc})^{-1}$ for the determination of the series resistance (R_s).

greatly decreased to $5.04 * 10^{-2}\ \Omega$ cm due to the densified microstructures. Hence, the value of R_s of the films which codoped both ions was effectively reduced (Table 2).

The incorporation of sodium ions into $Cu(In,Ga)Se_2$ is verified to result in a decrease in the amount of the donor-type defects in the form of $In_{Cu}^{\bullet\bullet}$ [14]. The formation of defects can be expressed as

$$Na^{\bullet} + In_{Cu}^{\bullet\bullet} + 2e' \longrightarrow Na_{Cu}^{\times} + In_{In}. \tag{3}$$

When sodium ions are doped into $Cu(In,Ga)Se_2$, sodium ions could substitute the site of $In_{Cu}^{\bullet\bullet}$. Hence, the amount of donor-type defects in the form of $In_{Cu}^{\bullet\bullet}$ is decreased. Besides, the amount of the donor-type defects in the form of $V_{Se}^{\bullet\bullet}$ is also found to be reduced for bismuth-doped films [15]. Therefore, the codoping of sodium as well as bismuth ions can significantly decrease the amount of the donor-type defects ($In_{Cu}^{\bullet\bullet}$ and $V_{Se}^{\bullet\bullet}$), thereby causing an increase in the relative amount of holes that acted as the major carriers in $Cu(In,Ga)Se_2$. Hence, the carrier concentration of holes was considerably raised as sodium and bismuth ions were codoped. If the influence of the tunneling mechanism and the surface recombination can be ignored, the variation of the V_{oc} and the carrier concentration (N_P) is expressed as [20]

$$\Delta V_{oc} = \left(\frac{2kT}{q}\right) \ln\left(\frac{N_{P2}}{N_{P1}}\right), \tag{4}$$

where k is the Boltzmann constant, T denotes the temperature in Kelvin, q is the charge of an electron, and N_{P1} and N_{P2} represent the carrier concentration of the films with absence and presence of dopants, respectively. From (4), an increase in N_{P2}/N_{P1} results in a positive value of ΔV_{oc}. The carrier concentration in $Cu(In,Ga)Se_2$ films was substantially increased via the codoping process, thereby leading to a significant improvement of the V_{oc}.

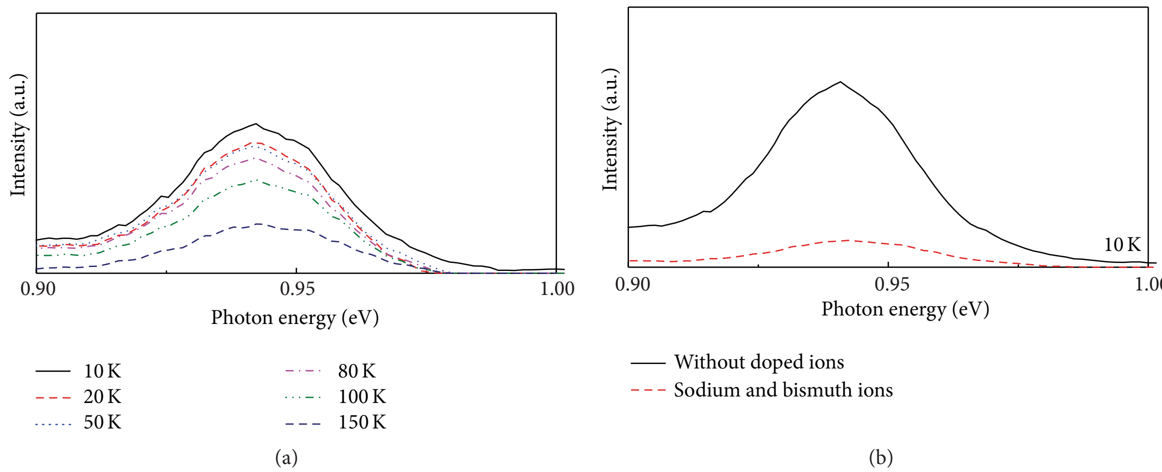

Figure 7: (a) Temperature dependence of PL spectra for $Cu(In,Ga)Se_2$ films doped with sodium and bismuth ions, and (b) low-temperature PL spectra for $Cu(In,Ga)Se_2$ films at 10 K.

For investigating the codoping effects on $Cu(In,Ga)Se_2$ films, the low-temperature photoluminescence (PL) spectra were measured. Figure 7(a) shows temperature dependence of the PL spectra for $Cu(In,Ga)Se_2$ films codoped with sodium and bismuth ions. A peak at 0.94 eV was observed, which is attributed to the donor-acceptor pair (DAP) recombination [21, 22]. As the temperature was increased, the intensity of the DAP PL peak became reduced. It is due to the thermal quenching behavior. The thermal quenching equation in PL spectra can be described as [23]

$$I(T) = \frac{I_0}{\left(1 + \varphi_1 T^{3/2} + \varphi_2 T^{3/2} \exp\left(-E_T/kT\right)\right)}, \quad (5)$$

where I_0, φ_1, and φ_2 are the three fitting parameters and E_T is the thermal quenching energy. It is clearly demonstrated that the intensity of the PL peak decreases as the temperature elevates. In Figure 7(b), the low-temperature PL spectra measured at 10 K showed that the intensity of the DAP peak for $Cu(In,Ga)Se_2$ codoped with sodium and bismuth ions was lower than that of the films without doped ions, indicating that the amount of donor-type defects was decreased via the codoping process. Hence, it is verified that the carrier concentration of holes was increased as shown in Table 3. The above results confirmed that codoping sodium and bismuth ions effectively improved the microstructures and enhanced the electrical properties of $Cu(In,Ga)Se_2$, therefore increasing the conversion efficiency of the fabricated solar cells.

4. Conclusions

The influences of codoping sodium and bismuth ions in the electrical properties of $Cu(In,Ga)Se_2$ films prepared via a solution route were examined. An increase in the ratio of the intensity of (112) diffraction peak to that of (220/204) diffraction peak was found in the films codoped with sodium and bismuth ions. Codoping these ions led to the densification of the films and the enlargement of the particle sizes. The Hall effect characteristics indicated that the incorporation of sodium and bismuth dopants effectively increased the carrier concentration of $Cu(In,Ga)Se_2$ films and enhanced the open-circuit voltage of the fabricated solar cells. The resistivity of the prepared films was substantially decreased; therefore, the series resistance of the fabricated solar cells was effectively reduced. The codoping of sodium and bismuth ions was also found to reduce the amount of leakage current through the solar cells and substantially increased the conversion efficiency of $Cu(In,Ga)Se_2$ solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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