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Structural and Optical Properties of Cu-In-Se and MgₓZn₁₋ₓO Thin Films Prepared by Chemical Spray Pyrolysis*

Tomoaki TERASAKO**, Yuji UNO**, Akira MIYATA**, Tomomi KATAOKA***, Masakazu YAGI****, Tetsuya KARIYA***** and Sho SHIRAKATA**

Structural and optical properties of polycrystalline In-rich Cu-In-Se (0.55<In/(Cu+In)<0.85) and MgₓZn₁₋ₓO (x<0.20) films prepared by chemical spray pyrolysis (CSP) were investigated. Raman spectra of In-rich Cu-In-Se films exhibited a characteristic Raman peak shifting to the lower frequency side as the In/(Cu+In) ratio increased, which can be utilized for the study of structural disordering. For the ZnO films, the optical gap energy (E_{g,opt}) and the photoluminescence (PL) peak energy of the near-band-edge (NBE) emission shifted to the high energy side with increasing substrate temperature (Tₛ), suggesting the shift is due to the Burstein-Moss effect. The successful growth of the MgₓZn₁₋ₓO films (x<0.20) has been achieved. A dominant NBE emission and E_{g,opt} exhibited the blue shift with increasing alloy composition x.

Keywords: Chemical Spray pyrolysis, CuInSe₂, Ordered Vacancy Compound, ZnO, MgₓZn₁₋ₓO, Photoluminescence, Photoacoustic Spectroscopy, Raman Scattering

1. Introduction

Copper indium diselenide (CuInSe₂) has a direct band gap of 1.04 eV [1],[2] and high absorption coefficient up to 6×10⁵ cm⁻¹ [3]. Therefore, this compound is one of the promising materials for photovoltaic applications, as a form of polycrystalline thin film solar cell. Recently, thin film solar cells with the quaternary compound Cu(In,Ga)Se₂ (CIGS) absorber layers formed by physical vapor deposition (PVD) attained a very high conversion efficiency of over 19 % [4]. Ordered vacancy compounds (OVC), such as CulnₓSe₃ and Cu-In₄Se₅, formed on the surface of the polycrystalline CuInSe₂ layer, play an important role for achieving high-efficiency solar cells [5]-[8].

The zinc oxide (ZnO) transport conductive oxide (TCO) film is commonly used as the window layers of CIGS-based thin-film solar cells. The major requirement of the n-type ZnO TCO is high transmittance as a window to incident light and low resistivity as an electrode to reduce the series resistance and enhance the fill factor (FF). Recently, Minemoto et al. pointed out that the application of MgₓZn₁₋ₓO to the window layer of solar cells can improve the overall conversion efficiency by decreasing the absorption loss [9],[10] and the interface recombination. A variety of growth techniques, such as laser molecular beam epitaxy (L-MBE) [11], pulse laser deposition (PLD) [12] and RF magnetron sputtering [9], has been employed to prepare MgₓZn₁₋ₓO films.


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Chemical spray pyrolysis (CSP) is an attractive method, because large-area films with good uniformity can be grown at low cost. The authors have been studying preparation of CuInSe$_2$, Cu(In,Ga)Se$_2$ and CuIn(SSe)$_2$ by the CSP method and their characterization \[^{[13]-[16]}\].

In this study, structural and optical properties of Cu-In-Se and Mg$_x$Zn$_{1-x}$O polycrystalline films prepared by CSP have been investigated in terms of substrate temperature and composition.

2. Experimental

2.1 Preparation of Cu-In-Se films

Fig. 1 shows the schematic representation of the CSP apparatus used in this study. It consists of a bell jar made of acrylic resin (190 mm in diameter and 250 mm in height), a spray nozzle of the two-fluid type (IKEUCHI, AK-104) and a stainless steel substrate heater block (60 $\times$ 90 $\times$ 28 mm$^3$). The distance between the spray nozzle and the substrate is 215 mm. Nitrogen was used as a carrier gas.

As a spray solution, the 20 volume percent ethanol aqueous solution of the chemical compounds including CuCl$_2$, InCl$_3$ and NH$_2$(CH$_3$)$_2$NCSe (dimechylselenourea, DMSeU) was used for preparing Cu-In-Se films. The In/(Cu+In) ratio in the solution was varied in the range from 0.50 to 0.83. The pH value in the spray solution was adjusted to the value of 3.5 by adding NH$_4$OH. Growth time was 50 min. The conventional slide glass for the optical microscope was used as the substrate. Substrate temperature ($T_S$) was 360 or 400 $^\circ$C. Thickness of the films were in the range from 0.5 to 1.5 $\mu$m.

2.2 Preparation of Mg$_x$Zn$_{1-x}$O films

The CSP system is the same as used for preparing the Cu-In-Se films. An ethanol solution of Zn(CH$_3$COO)$_2$ $\cdot$ 2H$_2$O and Mg(CH$_3$COO)$_2$ $\cdot$ 4 H$_2$O (0.01M) was used as spray solution. The $T_S$ was changed in the range from 200 to 500 $^\circ$C. Films were grown on glass substrate, Si(100) wafer with a thermally formed SiO$_2$ layer and sapphire substrate (a- and c-plane). The growth time was an hour. Thickness of the films changed from 0.1 to 0.5 $\mu$m depending on growth conditions and alloy composition $x$.

2.3 Characterization

The In/(Cu+In) ratios in the Cu-In-Se films and the alloy composition $x$ in the Mg$_x$Zn$_{1-x}$O films were determined by the electron probe microanalyzer (EPMA: JEOL, JXA-8600MX) using an acceleration voltage of 7 kV and a beam diameter was 10 $\mu$m. Crystal structures of the films were characterized by the X-ray diffraction (XRD) method using the Cu-K$\alpha$ radiation. Two types of goniometers used in this study are as follows: (i) A conventional $\theta$ -2$\theta$ goniometer and (ii) a goniometer with a fixed small-angle X-ray incidence.
(2° incidence) and 2θ scanning mechanism with sample rotation within the plane. Surface morphologies were observed by a scanning electron microscope (SEM: Hitachi, S-3100H).

Raman scattering measurements were performed at room temperature (RT) using the microscopic Raman system with a multichannel detector (Renishaw, System 1000). The excitation light was the 514.5 nm line from an Ar+-laser. Transmittance spectra of the Cu-In-Se films were measured using a monochromator (Ritsu Oyo Kogaku, MC-20) combined with a lock-in amplifier (NF Circuit Design Block, LI-572B). A photomultiplier and a PbS photoconductive detector were used for the light detection. For the Mg,Zn1-xO films, transmittance spectra were measured by UV-Vis-NIR spectrometer (Hitachi, U-4000) at room temperature (RT). Photoacoustic (PA) measurements were performed at RT. A Xe lamp (Wacom, KXL500F) in conjunction with a monochromator (Ritsu Oyo Kogaku, MC-20L) was used as the excitation light source. The PA cell was composed of a closed vessel with a small channel in which a microphone was attached. The output signal from the microphone was amplified by a lock-in amplifier (NF Circuit Design Block, 5610B). The modulation frequency was 10 Hz. The PA spectra were normalized using the PA signals for carbon black deposited on a thin aluminum seat. Photoluminescence (PL) measurements of Mg,Zn1-xO films were carried out under the excitation of the 325 nm line of a He-Cd laser (10mW). PL was dispersed by a monochromator (50 cm focal length) and detected by a photomultiplier (Hamamatsu R-636) and processed by a photon counting system.

3. Results and Discussion

3.1 In-rich Cu-In-Se films

Fig. 2 shows the molar ratio (In/(Cu+In)) in the film (y) plotted as a function of ion ratio (In/(Cu+In)) in the spray solution (Y). Although the y values are slightly smaller than the Y value for 0.5 < Y < 0.65 and scattered for 0.65 < Y < 0.8, the y value tends to increase linearly with increasing Y. This result suggests that the In/(Cu+In) ratio in the film can be well controlled by the In/(Cu+In) ratio in the spray solution.

Fig. 3 shows XRD patterns of the Cu-In-Se films with y=0.50, 0.70 and 0.75 grown at T_S=360 °C. All the films are dominated by the (112) diffraction peak. The film with y=0.50, i.e. CuInSe_2, shows weak diffraction peaks unique to the chalcopyrite structure, such as (101), (211), (105)/(213), (301), (417)/(217) and (501).

Fig. 4 shows SEM micrographs of the Cu-In-Se films with y=0.55, 0.60 and 0.72 grown at T_S=360 °C. Surface of both the films with y=0.55 and 0.60 consist of round grains. Diameters of the round grains on the films with y=0.55 and 0.60 are 0.1-0.3 and 0.3-0.4 μm, respectively. The surface of the film with y=0.72 is filled with platelet grains and differs from those of the films with y=0.55 and 0.60. Similar surface morphology
(y=0.72) was observed in the evaporated OVC films anodized in the iodide electrolyte\cite{17}.

Fig. 5 shows Raman spectra of the Cu-In-Se films with y=0.50, 0.64 and 0.77 grown at $T_s=360$ °C. A Raman spectrum of the chalcopyrite CuInSe$_2$ (y=0.5) film is dominated by the $A_1$ mode at 174 cm$^{-1}$, which is totally symmetric vibration of Se atoms in the c-plane. A Raman spectrum of the film with y=0.64 exhibits an intense peak at 183 cm$^{-1}$ and a shoulder at 163 cm$^{-1}$. The former Raman peak is the same peak referred to as the S peak, which has been assigned to be the characteristic Raman mode for CuInSe$_2$ with the sphalerite structure\cite{14}. The latter Raman peak is denoted hereafter by ‘O’ peak. When the y value increases from 0.64 to 0.77, the O peak shifts continuously to the lower frequency side and its intensity relative to that of the S peak becomes larger. Similar tendency to the films grown at $T_s=360$ °C was also observed for the films grown at $T_s=400$ °C. In the inset of Fig. 5, Raman frequencies are plotted as a function of y for $A_1$, S and O modes in the films grown at $T_s=360$ and 400 °C. The Raman frequencies of the S peak are slightly scattered around 182 cm$^{-1}$. Although the Raman frequency of the O peak is almost constant in the range from y=0.57 to 0.64, the O peak shifts from 163 to 153 cm$^{-1}$ as the y value increases from 0.64 to 0.78. Frequency of the O peak observed on the film with y=0.78 agrees well with that of the dominant Raman mode reported for CuIn$_3$Se$_5$ epitaxial layers. Therefore, the O peak is probably attributed to the Raman modes related to the OVC phase. The co-existence of the A and O peaks suggests that the films are composed of the sphalerite CuInSe$_2$ and the OVC phases. This is consistent with the microstructural model for the In-rich films fabricated by the physical vapor deposition (PVD) by Tuttle et al.\cite{18}. We expect that the ratio of the intensity of the O peak to that of the S peak is considered to be a measure of the degree of mixture of the two phases. These Raman results are utilized for the characterization and the achievement of high efficiency of the solar cell.
The optical gap energy estimated by the linear extrapolation for slope of $\hbar \nu - (\alpha \hbar \nu)^2$ curve is denoted by 'E$_{g,opt}$'. Fig. 6 shows values of E$_{g,opt}$ for the films as a function of y. According to Wei and Zunger [19], bandgap energy is indicated by the solid line in the figure. For the films with y>0.67, the E$_{g,opt}$ values are close to the solid line. For the films with y<0.67, however, the E$_{g,opt}$ values differ from the solid line and are approximately 1.22 eV, which agrees well with the band gap energy of Cu$_2$In$_4$Se$_7$ bulk crystal. Optical absorption spectra of many films exhibited a strong optical absorption band below E$_{g,opt}$. As the y value increased from 0.57 to 0.75, low energy edge of the absorption band shifted from $\sim$1.0 to $\sim$1.2 eV. The existence of the absorption band below E$_{g,opt}$ was also confirmed by PA measurements. Taking into account of the Raman results, the deviation from the theoretical value of E$_{g,opt}$ observed for the films with 0.54<y<0.75 and the appearance of the absorption band below E$_{g,opt}$ are probably related to spatial fluctuation of optical band gap energy caused by the coexistence of sphalerite CuInSe$_2$ and OVC Cu$_2$In$_4$Se$_7$ phases.

Fig. 5. Raman spectra of Cu-In-Se films with In/(Cu+In) ratios (y) of 0.50, 0.64 and 0.77. The inset shows frequencies of A$_1$, S and O Raman peaks plotted as a function of y. Closed circles and closed squares are results for the films grown at $T_S$=360 °C. Open circles and open squares are results for $T_S$=400 °C. A closed triangle is the A$_1$ mode frequency of CuInSe$_2$ film grown by CSP method.

Fig. 6. Optical gap energy (E$_{g,opt}$) as a function of y together with the reported E$_{g,opt}$ values for CuInSe$_2$, Cu$_2$In$_4$Se$_7$ and CuIn$_3$Se$_5$. Closed circles and open circles represent E$_{g,opt}$ values for the films grown at $T_S$=360 and 400 °C, respectively. The reported E$_{g,opt}$ values are indicated by open triangles with alphabets (a: Schmidt et al.[5], b: Negami et al.[7], c: Manhanty et al.[20], d: Marin et al.[21], e: Shirakata et al.[2]).
3.2 ZnO films

Fig. 7 shows XRD patterns of the ZnO films grown on glass, SiO₂/Si(100) and c- and a-plane sapphire substrates at $T_S=400\,°C$. All the films exhibit a dominant (002) diffraction peak, suggesting that highly c-axis oriented films are grown. It was confirmed by the XRD measurements that the films grown at higher substrate temperature than 400 °C exhibited c-axis growth independent of substrate materials.

Fig. 8 shows SEM images of the ZnO films grown on the glass substrate at $T_S=400$ and 500 °C. The film grown at $T_S=400\,°C$ exhibits rounded grains with diameters ranging from 0.2 to 0.3 μm. When the $T_S$ decreased from 400 to 320 °C, the diameter of the grains became small. The surface of the film grown at $T_S=500\,°C$ consists of flake-like grains with length of about 0.3 μm and round grains with diameter of about 0.05 μm.

Fig. 9 shows transmittance, PA and PL spectra of the films grown at $T_S=400$ and 500 °C. It can be easily noticed that the tail of the transmittance and PA spectra shifts to the higher energy side with increasing $T_S$. Intensity of the PA signal below 3.0 eV for the film grown at $T_S=500\,°C$ is larger than that for the film grown at $T_S=400\,°C$. This result suggests that non-radiative centers are introduced by the increase in $T_S$. The PL spectrum from the film grown at $T_S=400\,°C$ consists of a broad emission band with at 2.4 eV (denoted hereafter by ‘GB’ emission) and a near-band-edge (NBE) emission at 3.27 eV. When the $T_S$ increases from 400 to 500 °C, the NBE emission shifts from 3.27 to 3.31 eV and the ratio of intensity of the GB emission to that of the NBE emission becomes smaller. The peak energy of the NBE emission of the film grown at $T_S=500\,°C$ is higher than the photon energy of the free exciton emission (~3.30 eV). The carrier concentration increased from $1.7 \times 10^{20}$ to $2.8 \times 10^{21}$ cm$^{-3}$ as $T_S$ increased from 400 to 500 °C. The carrier concentrations were much higher than the Mott density ($10^{18}$-10$^{19}$cm$^{-3}$)\(^{[22]}\), suggesting that the films were degenerated semiconductors. Therefore, it is considered that the Burstein-Moss (BM) effect \(^{[23]}\) contributes to the blue shift of the band edge observed on the transmittance and PA spectra. However, the blue shift of ~160 meV is roughly one order of magnitude smaller than that calculated on the basis...
of the BM effect. This fact suggests the contribution of band gap narrowing effects such as electron-electron and electron-impurity interactions. These interactions may relax the momentum conservation rule in radiative transitions. Therefore, the NBE emission observed on the film grown at $T_S=500 \, ^\circ\text{C}$ is probably due to the non-k-conserving band-to-band transitions. The similar NBE emission was also observed on the films grown on Si(100) substrate at $T_S=500 \, ^\circ\text{C}$.

### 3.3 Mg$_x$Zn$_{1-x}$O films

Fig. 10 shows the alloy composition (x) in the Mg$_x$Zn$_{1-x}$O/glass film plotted as a function of that in the spray solution (X). Although the alloy compositions in the films are smaller than those in the solutions, the x value increases from 0.00 to 0.20 linearly when the X value increases from 0.00 to 0.25. Similar tendency was also observed on the films grown on Si(100) substrate. These results suggest that the alloy composition x can be well controlled by the composition X in the solution at least x<0.20.

Fig. 11 shows XRD patterns of the Mg$_x$Zn$_{1-x}$O films with x=0.00, x=0.04, x=0.12 and 0.15 grown on a-plane sapphire substrate at $T_S=400 \, ^\circ\text{C}$. All XRD patterns are dominated by (002) peak. It can be seen that the (002) peak slightly shifts to the high angle side as the composition x increases. The inset shows c-axis lattice constants for the films grown at $T_S=400$, 420 and 450 \, ^\circ\text{C}$ plotted as a function of alloy composition x. The c-axis lattice constants for the films grown at $T_S=400$ and 450 \, ^\circ\text{C}$ tend to decrease with increasing the alloy composition x. This tendency agrees with that for the L-MBE films reported by Matsumoto et al. \cite{27}. The films grown on Si(100) substrate did not exhibit any c-axis oriented XRD pattern.

Fig. 12 (a) shows $h \nu$ - $(\alpha h \nu)^2$ curves for the Mg$_x$Zn$_{1-x}$O/glass films with different alloy compositions grown at $T_S=400 \, ^\circ\text{C}$. It can be easily noticed that the absorption edge shifts to the high energy side with increasing alloy composition.
Fig. 12 (b) shows $E_{g,\text{opt}}$ values of the Mg$_x$Zn$_{1-x}$O/glass films plotted as a function of alloy composition $x$, together with reported values. $E_{g,\text{opt}}$ values for the CSP films grown at $T_S=400$ and 420 °C agree well with reported $E_{g,\text{opt}}$ values (solid line), but are lower than the free exciton energy (dashed line). On the other hand, $E_{g,\text{opt}}$ values for films grown at $T_S=450$ °C are higher than the reported values. Mg$_x$Zn$_{1-x}$O films grown at $T_S=450$ °C showed relatively low resistivities ranging from 1 to 10 Ω cm, approximately two orders of magnitude lower than those for the films grown at $T_S=400$ and 420 °C. This fact implies that the carrier concentrations in the films grown at $T_S=450$ °C are much higher than those in the films grown at $T_S=400$ and 420 °C. Therefore, the blue shift of $E_{g,\text{opt}}$ for the films grown at $T_S=450$ °C may be due to the contribution of the BM effect.

Fig. 13 shows PA spectra of Mg$_x$Zn$_{1-x}$O/glass films with $x=0.04$, 0.05 and 0.12 grown at $T_S=400$ °C. The absorption edge shifts to higher energy side with increasing alloy composition $x$. Similar tendency was also observed on the films grown at $T_S=420$ and 450 °C. In addition, all the films grown at $T_S=450$ °C exhibit strong absorption band extending to 1.55 eV. The appearance of the intraband absorption is probably due to the deviation from stoichiometric composition and/or the spatial fluctuation of the alloy composition $x$.

Fig. 14 (a) shows NBE emissions observed on Mg$_x$Zn$_{1-x}$O/a-plane sapphire films with different alloy compositions grown at $T_S=400$ °C. With increasing alloy composition $x$, the peak energy shifts towards higher energies and the FWHM becomes large. Fig. 14 (b) shows peak energy of the NBE emission plotted as a function of alloy composition $x$, together with the reported values for the L-MBE films.
L-MBE films, the PL peak energy increases sublinearly with increasing alloy composition $x$. However, the differences between the free exciton energy and the peak energy of the NBE emission for the CSP films are 50-100 meV larger than those for the L-MBE films. Moreover, the increase in FWHM between 0.0 and 0.12 was approximately three times larger than that of the calculated value on the basis of alloy broadening of excitonic emission [29]. Taking into account of these facts, the mechanism of the NBE emissions in the CSP film are considered to be the band-to-band transition associated with the tail state of the conduction band. The electron-electron and electron-impurity interactions play an important role in radiative transition processes in the

Fig. 12. (a) $h\nu - (\alpha h\nu)^2$ curves for the Mg$_{x}$Zn$_{1-x}$O films with $x$=0.04, 0.05 and 0.12 grown on the glass substrate at $T_S$=400 °C. (b) Optical gap energy as a function of alloy composition $x$. Optical gap energies of the L-MBE films[27], RF sputtering films[9] and PLD films[12] are also plotted for comparison. Solid and broken lines in the inset indicate free exciton energy and bandgap energy, respectively.

Fig. 13 Photoacoustic (PA) spectra of Mg$_{x}$Zn$_{1-x}$O films with $x$=0.04, 0.05 and 0.12 grown on the glass substrate at $T_S$=400 °C.
Mg$_x$Zn$_{1-x}$O films similar to the case of ZnO films as described above.

4. Conclusion

The main conclusions in this study are as follows:
(i) The In-rich Cu-In-Se films exhibited a characteristic Raman peak, in which the frequency changes continuously from 163 to 153 cm$^{-1}$ depending on In/(Cu+In) ratio.
(ii) The $E_{\text{g,opt}}$ value increased from 1.22 to 1.36 eV as the In/(Cu+In) ratio increased from 0.67 to 0.78, while for 0.54<In/(Cu+In)<0.67, it was approximately constant value of 1.22 eV. (iii) For the ZnO films, both $E_{\text{g,opt}}$ and the peak energy of the NBE emission shifted to the high energy side with increasing $T_S$, which are probable due to the Burstein-Moss effect. (iv) Mg$_x$Zn$_{1-x}$O ($x>0.20$) films without any secondary phases were successfully grown on the a-plane sapphire substrate by CSP. (v) Optical absorption and PA measurements showed that the absorption edge of the Mg$_x$Zn$_{1-x}$O film shifted to the high energy side with increasing alloy composition $x$. (vi) Mg$_x$Zn$_{1-x}$O films showed the NBE emission shifting to the high energy side with broadening as the alloy composition $x$ increased. The NBE emissions were ascribed to the band-to-band transition associated with the tail state of the conduction band.

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Fig. 14. (a) NBE emissions of the Mg$_x$Zn$_{1-x}$O films with $x=0.00, 0.05, 0.08$ and 0.16 grown on the a-plane sapphire substrate at $T_S=400$ °C. (b) Peak energies of the NBE emission plotted as a function of alloy composition $x$. Reported PL peak energies of the L-MBE films [28] are also plotted for comparison.

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