Annealing effects of In-doped ZnO films grown by spray pyrolysis method

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Abstract. In-doped (2 mol%) ZnO films on glass substrate were grown by spray pyrolysis method at 500 °C. Samples were annealed under N2 atmosphere between 100 and 600 °C for 5 min. The X-ray diffraction spectra indicated that the c-axis intensity ratio for a-axis was slightly increased with increasing annealing temperature. This meant that a degree of crystalinity increased with increasing annealing temperature. However, photoluminescence intensity decreased with annealing temperature, indicating that the increased the number of nonradiative recombination centers in the In-doped ZnO films.

1. Introduction
Wide bandgap oxide-semiconductors have attracted much attention for optical devices, liquid crystal displays and solar cells. In particular, ZnO material has been a promising material for many different applications such as gas sensors [1], transport electrodes [2], piezoelectric devices [3], varistors [4] and surface acoustic wave devices [5]. Its direct optical bandgap of 3.4 eV at room temperature is wide enough to transmit most of the useful solar radiation in ZnO/CuInSe2 based solar cells [6]. Furthermore, ZnO is a good candidate to substitute for ITO (In-doped In2O3) and FTO (F-doped SnO2) in transparent conductive electrodes. Optically pumped UV emission of ZnO at RT has been reported previously [7].

Many techniques have been employed to produce the ZnO thin film including molecular beam epitaxy [8], metal organic chemical vapor deposition [9], radio frequency magnetron sputtering [6], spray pyrolysis [10] and sol-gel [11] methods. The spray pyrolysis method is effective for thin film ZnO growth because damage to the surface due to plasma is avoided, high vacuum is not required, and equipments costs are low.

In our previous work [12], The undoped and In-doped ZnO poly crystalline films were successfully grown by spray pyrolysis at temperature of 300 ~ 500 °C. Indium concentrations varied between 1 and 5 mol% in ZnO. The resistivities decreased with increasing indium concentration. The intensity of bound exciton emissions from the acceptor (A0, X) decreased and bound exciton emission from the...
donor (D0, X) increased in the PL spectrum with increasing indium concentration. This indicated that indium atoms acted as substitutional donor impurities sitting on Zinc sites.

In this work, In-doped ZnO films samples were annealed under N2 atmosphere. There are few reports on annealing under N2 atmosphere [13, 14]. The samples were examined by X-ray diffraction (XRD), SEM, Hall and photoluminescence (PL) measurements for structural, electrical and optical characterization.

2. Experimental procedures

In-doped (2 mol%) ZnO films on glass substrate were grown by the spray pyrolysis method at 500 °C. The thickness of the samples is approximately 0.6 μm. Samples were annealed under N2 atmosphere at from 100 °C to 450 °C for 5 min. Samples were examined by XRD and SEM for structural characterization. Hall measurement was carried out at room temperature using the Van der Pauw method for electrical characterization. Indium was used as ohmic contact. The PL measurements were also measured at liquid helium temperature. The sample was excited by a He-Cd laser (325 nm). The PL spectra were taken by using a grating monochromator (JOVIN YVON HR-1000) and a photomultiplier (Hamamatsu Photonics R2368) for optical characterization.

3. Results and discussion

Figure 1 shows the XRD spectra of In-doped ZnO films as-deposited and annealed at 100 ~ 600 °C under N2 atmosphere. A JCPDS file is also included as a reference [15]. A peak of (0002) which is c-axis is dominant in the as-deposition sample. The c-axis intensity ratio to a-axis ((10-10)) slightly increases with increasing annealing temperature. This means that a degree of crystallinity increases with increasing annealing temperature. This is good agreement with other reports [14]. Values of full width at half maximum (FWHM) of the (0002) peak in the XRD spectra is not almost changed with increasing annealing temperature. This indicates that grain size becomes constant with increasing annealing temperature.

Figures 2 shows SEM images of as-deposition and annealed at 450 °C in the In-doped ZnO films. The average surface roughness is almost constant with
increasing annealing temperature. Average grain size is also constant with increasing annealing temperature. This corresponds to the results of the XRD. The same size of grain is due to low annealing temperature [14]. However, each grain size becomes uniform with increasing annealing temperature.

Figure 3 shows resistivity and carrier concentration of In-doped ZnO films as a function of annealing temperature obtained by Hall measurements at room temperature. A resistivity decreases below 450 °C and increases above 450 °C. The figure shows clearly that this behaviour is due to the electron mobility. A carrier concentration slightly increases with increasing annealing temperature. This behaviour corresponds to air annealing in other reports [13]. A low resistivity of $4.0 \times 10^{-2} \Omega \cdot \text{cm}$ with electron mobility of $3.0 \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$ and carrier concentration of $7.0 \times 10^{19} \ \text{cm}^{-3}$ obtained at annealing temperature of 450 °C.

Figure 4 shows PL spectra of undoped and In-doped (2 mol%) ZnO films at liquid helium temperature. Five distinct peaks can be observed at 3.357, 3.324, 3.250, 3.176 and 3.115 eV in the undoped ZnO films. The peaks at 3.357 and 3.324 eV are due to bound exciton emission of donor ($D^0$, X) and acceptor ($A^0$, X), respectively [17]. The three peaks at 3.250, 3.176 and 3.115 eV are due to phonon replicas of the ($A^0$, X) peak. On the other hand, one broad peak is dominant at 3.378 eV in the In-doped ZnO film. This peak is related to In impurity because the peak is not observed in the undoped sample. Therefore, it is assumed that this peak is due to donor bound exciton of In interstitial (In$_i$) or In atom in Zn site (In$_{Zn}$) defects because of sample is n-type conductivity. No deep emission bands attract attention in the all undoped and In-doped ZnO films. This means that oxygen vacancy (V$_O$) and/or Zn interstitial (Zn$_i$) defects are few in the ZnO films [16]. The peak energy of the PL spectra is not changed with increasing annealing temperature (Fig. 5). However, the PL intensity varies by annealing temperature. The PL intensity decreases with annealing temperature. This behaviour corresponds to the results of Al-doped ZnO film annealed under air atmosphere [17]. Therefore, this is due to increase the number of nonradiative recombination centers in the ZnO films.
4. Conclusion
In-doped (2 mol%) ZnO films on glass substrate were grown by the spray pyrolysis method at 500 °C. Samples were annealed under N₂ atmosphere between 100 and 600 °C for 5 min. The XRD spectra indicate that the c-axis intensity to a-axis is slightly increased with increasing annealing temperature. This meant that a degree of crystalinity increases with increasing annealing temperature. The average surface roughness and average grain size were almost constant with increasing annealing temperature. However, each grain size became uniform with increasing annealing temperature. A low resistivity of $4.0 \times 10^{-2}$ Ω cm with electron mobility of 3.0 cm² V⁻¹ s⁻¹ and carrier concentration of $7.0 \times 10^{19}$ cm⁻³ were obtained at annealing temperature of 450 °C. The PL indicated that five distinct peaks, donor and acceptor bound exciton and its phonon replicas, could be observed in the undoped ZnO film. On the other hand, one broad peak was dominant in the In-doped ZnO film. This peak was due to donor bound exciton of the In₀ or In Za defects because of the sample was n-type conductivity and the peak was not observed in the undoped sample. No deep emission bands were observed in the all undoped and In-doped ZnO films. This meant that the V₀ and/or Zn defects were few in the ZnO films. The peak energy of the PL spectra was not changed with increasing annealing temperature. However, the PL intensity decreased with annealing temperature. This was due to increase the number of nonradiative recombination centers in the ZnO films.

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