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Effect of Deposition and Annealing Temperature on Structural, Electrical and Optical Properties of Ag Doped ZnO Thin Films

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Abstract The effects of the deposition and annealing temperature on the structural, electrical and optical properties of Ag doped ZnO (ZnO : Ag) thin films were investigated. All of the films were deposited with a 2wt% Ag_2O-doped ZnO target using an e-beam evaporator. The substrate temperature varied from room temperature (RT) to 250°C. An undoped ZnO thin film was also fabricated at 150°C as a reference. The as-grown films were annealed in temperatures ranging from 350 to 650°C for 5 h in air. The Ag content in the film decreased as the deposition and the post-annealing temperature increased due to the evaporation of the Ag in the film. During the annealing process, grain growth occurred, as confirmed from XRD and SEM results. The as-grown film deposited at RT showed n-type conduction; however, the films deposited at higher temperatures showed p-type conduction. The films fabricated at 150°C revealed the highest hole concentration of 3.98×1019 cm^{-3} and a resistivity of 0.347 Ω·cm. The RT PL spectra of the as-grown ZnO : Ag films exhibited very weak emission intensity compared to undoped ZnO; moreover, the emission intensities became stronger as the annealing temperature increased with two main emission bands of near band-edge UV and defect-related green luminescence exhibited. The film deposited at 150°C and annealed at 350°C exhibited the lowest value of I_{vis}/I_{uv} of 0.05.

Key words p-type ZnO, e-beam evaporation, photoluminescence, Ag doping.

1. Introduction

ZnO is a II-VI compound semiconductor material which has a direct wide band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature. The exciton binding energy of ZnO is higher than that of GaN (25 meV) and ZnSe (20 meV).[1] The large exciton binding energy would allow for stable high-yield luminescence even at room temperature. Currently, *p*-type doping of ZnO has attracted great attention because it is essential for realizing ZnO based devices such as UV and blue light emitting diodes and lasers which have great potential in the reduction of energy consumption. However, it is difficult to achieve sufficiently high-quality *p*-type ZnO with low resistivity and high mobility because undoped ZnO is usually *n*-type, which is associated with native donor defects such as oxygen vacancy V_O or interstitial zinc Zn_i and/or hydrogen residual hydrogen impurities.[2-6] To compensate and suppress the native donor defects, it is needed to find proper *p*-type dopant material. Many research groups have reported group I (Li, Na and K),[7-9] group V (N, P, Sb and As),[10-15] and group IB (Cu and Ag)[16-19] elements as *p*-type dopants. It was found that lithium tends to occupy the interstitial sites due to its small atomic radii, and therefore acts as a donor or deep trap. It was also reported that the bonding lengths of Na and K are much longer than the ideal Zn-O bonding length (1.93Å), which yields lattice strain resulting in native defects that will compensate for any acceptor states that may form. To avoid this problem, doping with group IB elements was theoretically suggested[20] and a very few reports are available on *p*-type ZnO with Ag doping deposited by sputtering method and PLD.[17-19)]

In this work, realization of *p*-type ZnO thin films by e-beam evaporation of ZnO:Ag_2O target are reported. The e-beam evaporation method has several advantages. It is suitable for large area deposition and source target can easily be replaced and the deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute. The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films. Systematic

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study of electrical, structural and optical properties of the ZnO:Ag thin films was investigated as a function of deposition and annealing temperatures.

2. Experiments Procedure

Target was prepared from powder mixture of ZnO (99.9%, Cerac, U.S.A.) and 2wt% of Ag_2O (99%, Kojima Chemicals, Japan). The powder mixtures were ground for 24 h with zirconia balls in ethanol, and then dried at 110°C. Dry powder mixtures were uniaxially cold-pressed into disks at a pressure of 2000 psi. Heat treatment at 1400°C was then performed for 4 h in a box furnace for densification. The ZnO:Ag thin films were deposited by e-beam evaporator (SNTek, Korea). Before deposition, the chamber was evacuated down to 5×10^{-6} Torr. High voltage and current of electron gun were kept at 5.10 kV and 20-27 mA, respectively. Substrate temperature was measured using a bending thermocouple attached to the slide glass, and was varied from RT to 250°C. The substrate was rotated at a rate of 20 rpm for uniform deposition. As-deposited thin films underwent a post-annealing process in a temperature range from 350 to 650°C for 5 h in air. Heating rate was kept constant at 10°C/min. All annealed films were vacuum-packed to avoid further contamination.

The compositions of the films were investigated using electron probe x-ray micro analysis (EPMA, JXA-8900R, Jeol, Japan). The crystal orientation was investigated with X-ray diffractometer (XRD, Rigaku Japan, D/max-II) with Cu Kα radiation. Images of the microstructure were obtained using field emission scanning electron microscope (FE-SEM, S4200, Hitach, Japan) with ×60,000 magnification. Electrical properties were measured using Hall effect measurement system (HMS-3000, ECOPIA, Korea) using Van der Pauw method. The magnetic field was 0.53 T and indium electrode was made on the film. The photoluminescence was measured at room temperature with a He-Cd laser of 325 nm in wavelength and a power of 50 mW as the excitation source (PL, SPEX1403, USA).

3. Result and discussion

Figure 1 shows Ag content in accordance with the deposition and annealing temperature. The Ag contents of the films were calculated using the equation, Ag/(Ag + Zn). As shown in Figure 1 (a), Ag content of the film

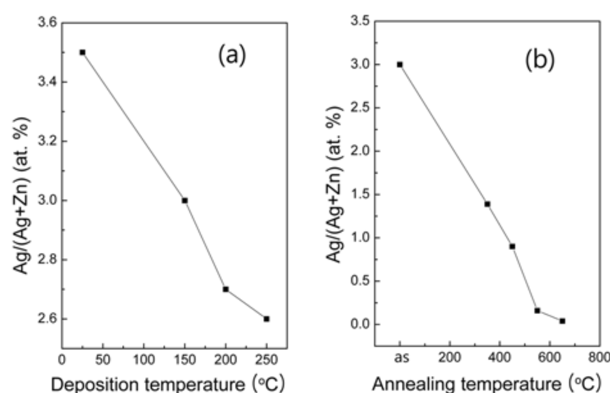


Fig. 1. Variation of Ag content according to (a) deposition temperature, and (b) annealing temperature.

deposited at RT was 3.5at% however, the Ag content continuously decreased to 2.6 at% as the deposition temperature increased. It is considered that re-evaporation of thermally activated Ag atoms from the substrate occurred. The binding energy of Ag-O, 220.1±20.9 kJ/mol, and Ag-Ag, 160.3±3.4 kJ/mol are higher than 159±4 kJ/mol of Zn-O and 29 kJ/mol of Zn-Zn. The melting points of Ag and Zn are 961°C and 419°C, respectively. Thus, it is expected that Zn atoms will evaporate more during the post-annealing process, and as a result, Ag content ratio would increase. However, the results were totally opposite from what we expected. Ag content ratio decreased instead of Zn with increasing annealing temperature. In the literature,[21] it was reported that Ag_2O molecules begin to decompose at about 200°C, and at 250-300°C, decomposition takes place rapidly and it also breaks up into its constituents in sunlight. Additionally, the melting point of ZnO is 1975°C, which is much higher than the decomposition temperature of Ag_2O. Thus, we concluded that Ag decomposed from Ag_2O is easier to evaporate than Zn bonded to oxygen.

Figure 2 shows the XRD spectra with the variation of deposition temperature. According to the previous reports,[22] ZnO thin film tends to grow with c-axis preferred orientation. The (002) plane is the close-packed plane of hexagonal structure, so thin films grow along the c-axis that is perpendicular to the substrate to reduce the surface free energy.[18,23-24] However, the thin films deposited at different temperatures show different diffraction peak intensities. Additionally, as the annealing temperature increased, the intensity of (101) became stronger instead of (002). Figure 3 shows the SEM images of 550°C annealed films and the films have some voids on their

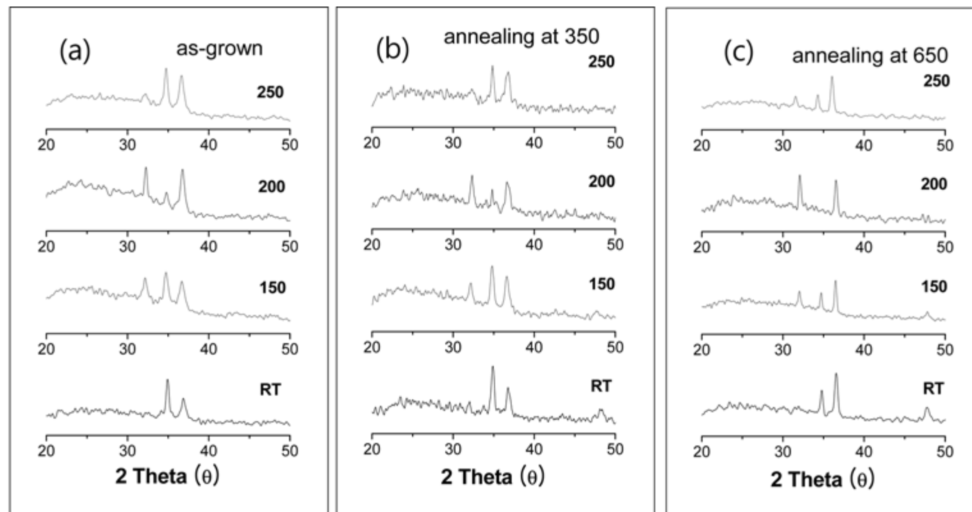


Fig. 2. XRD spectra of the films deposited at temperatures between RT and 250°C in accordance with different annealing temperatures; (a) as-grown films (b) 350°C annealed films, and (c) 650°C annealed films.

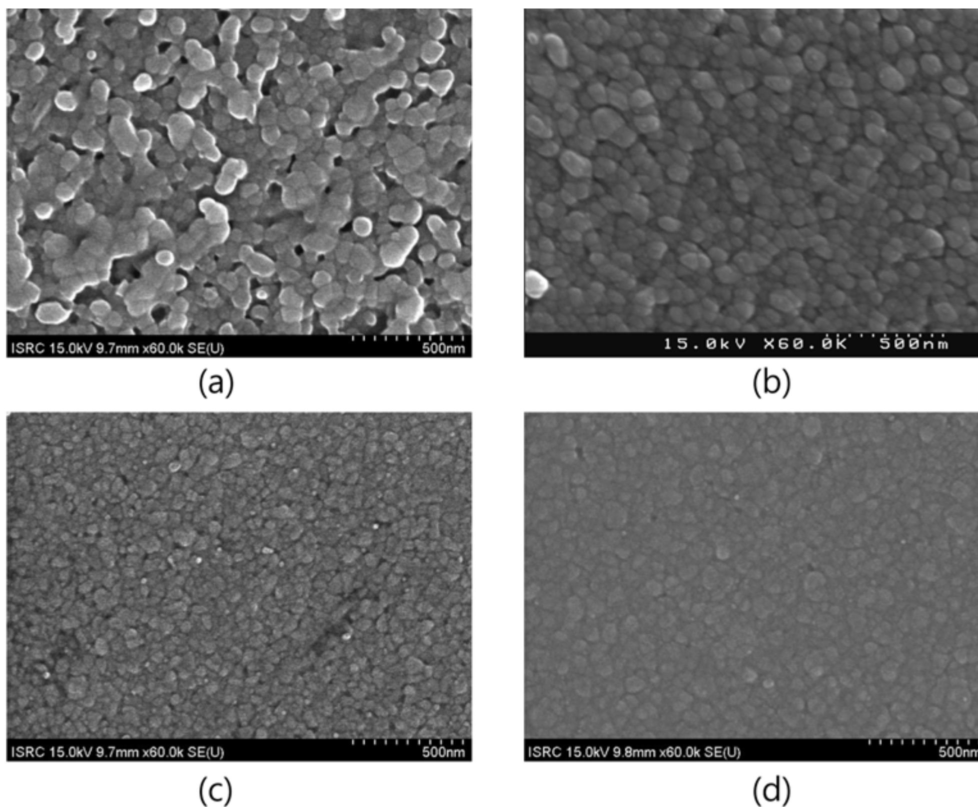


Fig. 3. Surface microstructures of the films annealed at 550°C; films deposited at (a) RT, (b) 150°C, (c) 200°C, and (d) 250°C.

surface. Of these annealed samples, especially, RT deposited thin film has very large voids, making the surface look very porous. It is believed that RT deposited thin film had more Ag content compared with the others deposited at higher temperatures.

Figure 4 shows the XRD spectra of 150°C deposited films according to annealing temperature. The full width at half maximum (FWHM) values of the ZnO:Ag films were found to be 0.46°, 0.36°, 0.37°, 0.36°, and 0.29° for as deposited and annealed at 350°C, 450°C, 550°C and 650°C films, respectively. The FWHM value of undoped ZnO film was 0.34°. From FWHM of the diffraction peaks,

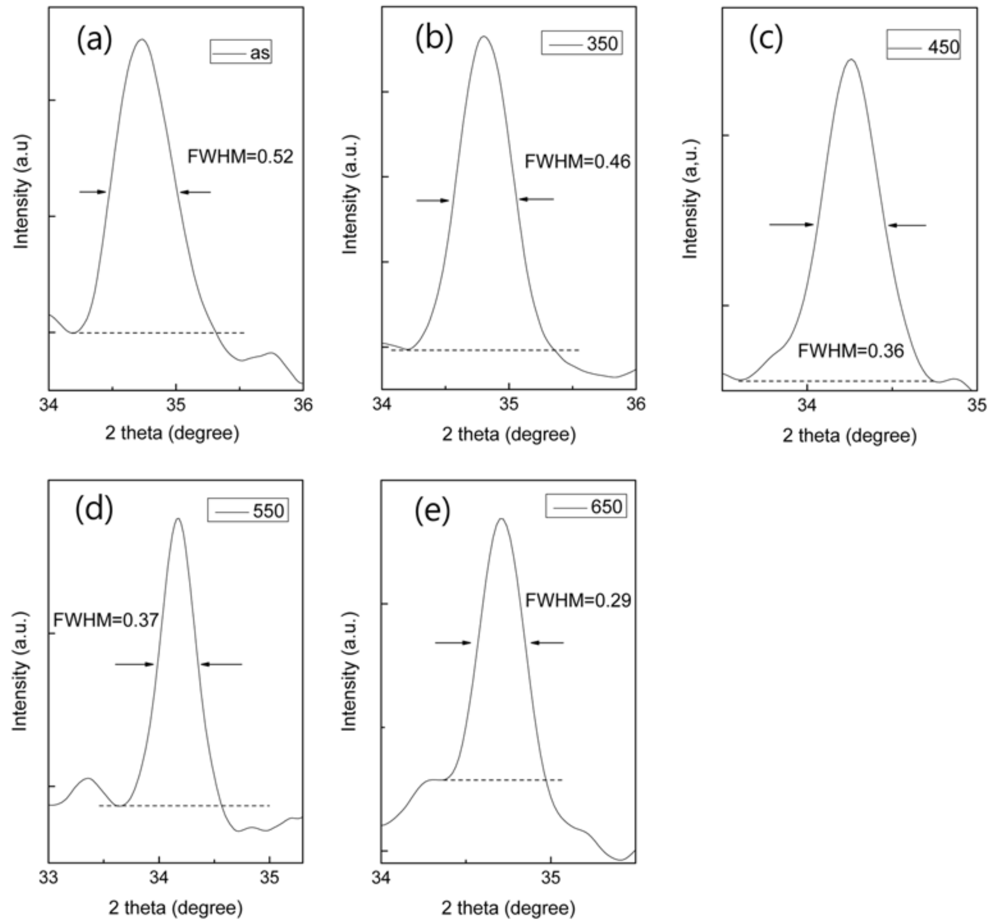


Fig. 4. X-ray diffraction patterns of (002) plane obtained from ZnO:Ag films grown at 150°C; (a) as-grown, (b) annealed at 350°C, (c) annealed at 450°C, (d) annealed at 550°C, and (e) annealed at 650°C.

one can calculate the average diameters of the crystals using the Scherrer formula.[25)] The decrease in FWHM value means an increase in grain size. Although Ag evaporated, recrystallization occurred during post-annealing process, and this was confirmed from micro-structure images. Figure 5 shows the surface micro-structure of 150°C deposited films with annealing temperature. The grain size increased gradually as the annealing temperature increased.

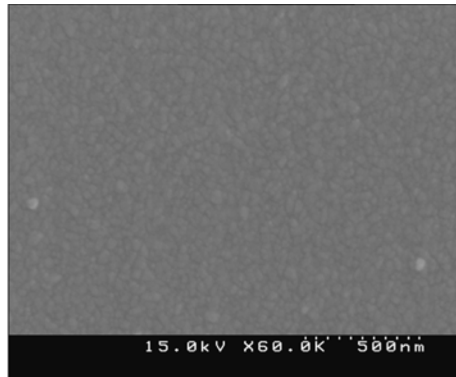
Table 1 shows the electrical properties of ZnO:Ag thin

Table 1. Electrical properties of undoped and Ag doped ZnO films measured by Hall effect measurement system

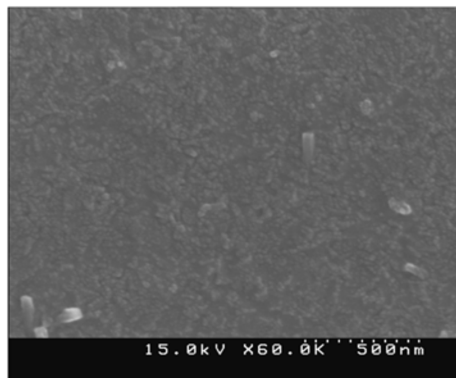
Deposition temp (°C)	Annealing temp.(°C)	Carrier Conc. (#/cm^3)	Mobility (cm^2/V-s)	Resistivity (Ω-cm)	Carrier Type
pure ZnO deposited at 150°C	as	-2.96×10^{19}		8.29×10^{-3}	n
Room temp.	as	-2.22×10^{12}		1.58×10^{5}	n
	350	-3.63×10^{13}		4.68×10^{5}	n
	450	-5.78×10^{14}		1.18×10^{3}	n
150	as	3.98×10^{19}		3.47×10^{-1}	p
	350	5.01×10^{20}		7.35×10^{-3}	p
200	as	1.86×10^{13}		7.75×10^{4}	p
	350	-6.45×10^{11}		6.54×10^{5}	n
250	as	1.50×10^{12}		1.26×10^{5}	p
	350	1.71×10^{10}		3.06×10^{7}	p

films. Since glass was used as the substrate, it is definite that the electrical properties measured were totally from the films. Among Ag doped thin films, only RT deposited thin films showed *n*-type conduction, and the others showed *p*-type conduction. Although RT deposited thin film had *n*-type conduction, electron concentration was several orders lower than $2.96\times10^{19}/cm^3$ of undoped ZnO. It is concluded that Ag acceptors compensated electrons from native donors but RT was such a low temperature to activate Ag acceptors, thus the thin films still remained as *n*-type. Additionally, Ag is known as amphoteric dopant, which means that Ag can act not only as an acceptor occupying Zn site but also as a donor occupying interstitial site.[26] Substitution of a large cation Ag on the smaller zinc site and/or incorporation into interstitial site should cause an increased in lattice spacing. However, the observed decrease in lattice spacing, as shown in Figure 6, is inconsistent with what we have expected. H. S. Kim et al. [12] also reported the inconsistency between substitution of large phosphorus (P) anion on the smaller oxygen site and decrease in lattice *d*-spacing. They suggested that an alternative location for the P, possibly as an antisite P_{Zn} defect, brought the inconsistency. In this point of view, inconsistency observed in Figure 6 can be explained by adopting antisite Ag_O defect. Because Ag^+ has the smaller ion size of 1.00Å than 1.38Å of O^{2-}, if Ag is incorpo- rated in interstitial site, the film will show the reduced lattice *d*-spacing.

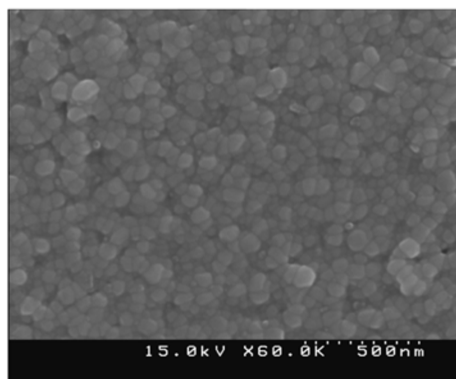
Electron concentration of RT deposited thin film increased with increasing annealing temperature of up to 450°C. As mentioned above, Ag acceptor atoms evaporated during the post-annealing process, leading to an increase in the electron concentration. However, above 450°C, it was not possible to make ohmic contact between electrode and film due to the high resistance of the film. It is considered that very rough surface caused by Ag evaporation acted as scattering center of electrical flow. The thin film deposited at 150°C showed the highest hole



(a)



(b)



(c)

Fig. 5. Surface microstructures of the films grown at 150°C; (a) as-grown, (b) annealed at 350°C, and (c) annealed at 650°C.

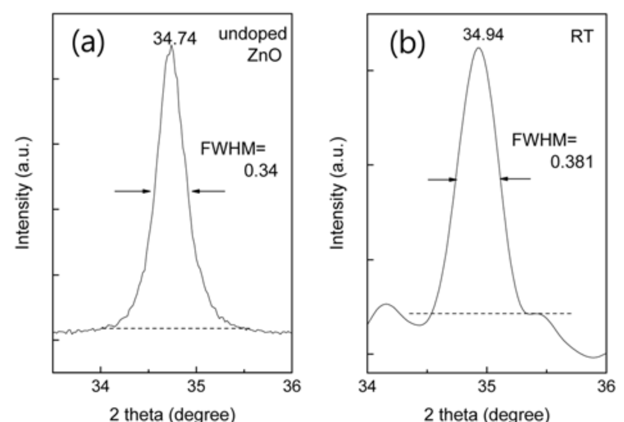


Fig. 6. X-ray diffraction patterns of (002) plane; (a) undoped ZnO film grown at 150°C, (b) ZnO:Ag film deposited at RT.

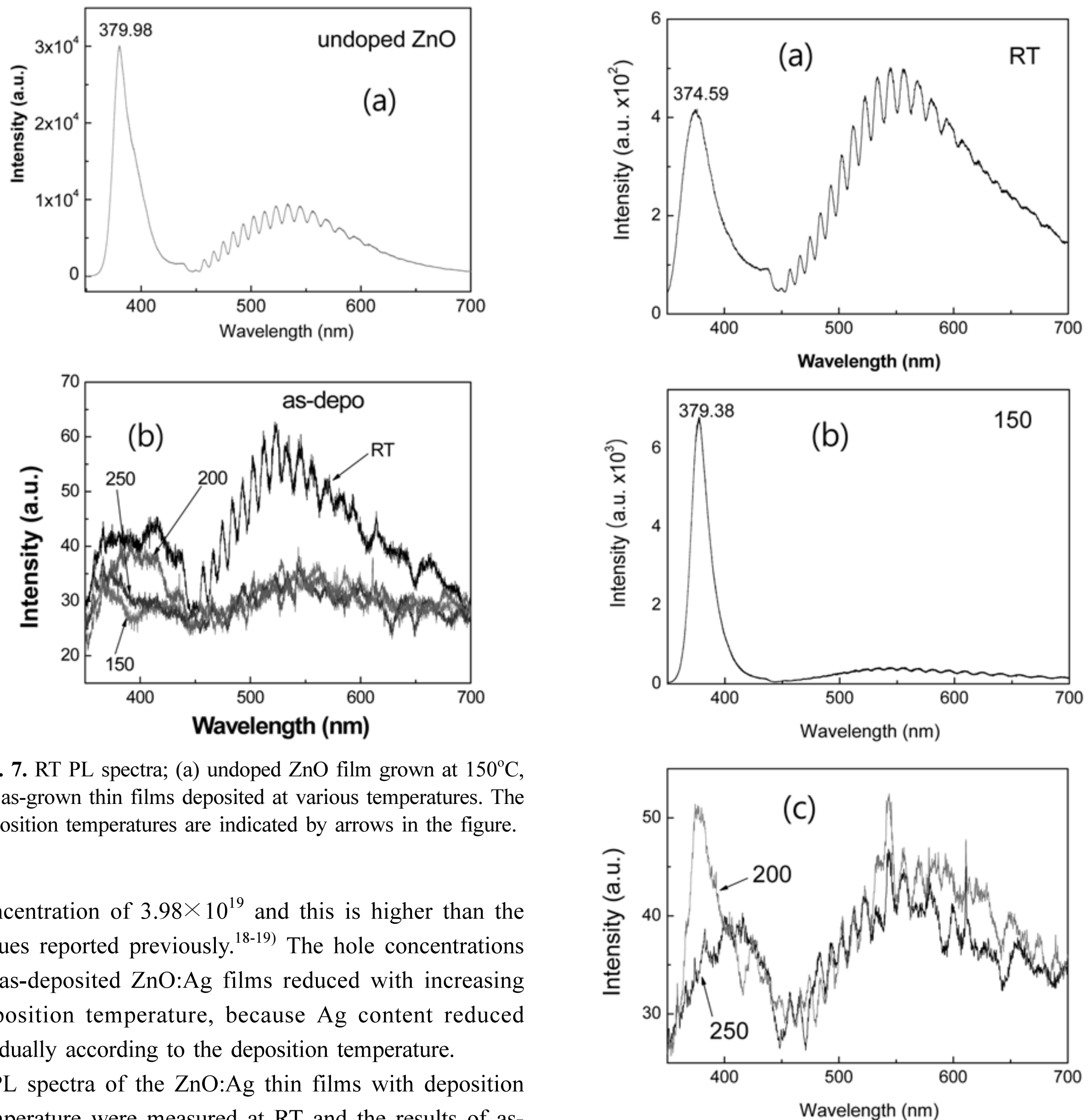


Fig. 7. RT PL spectra; (a) undoped ZnO film grown at 150°C, (b) as-grown thin films deposited at various temperatures. The deposition temperatures are indicated by arrows in the figure.

Fig. 8. RT PL spectra of the films annealed at 350°C; (a) grown at RT, (b) grown at 150°C, and (c) grown at 200 and 250°C.

concentration of 3.98×10^{19} and this is higher than the values reported previously.[18-19] The hole concentrations of as-deposited ZnO:Ag films reduced with increasing deposition temperature, because Ag content reduced gradually according to the deposition temperature.

PL spectra of the ZnO:Ag thin films with deposition temperature were measured at RT and the results of as-grown films are illustrated in Figure 7 and 8. Due to the intrinsic defects, which are always present in ZnO, PL spectrum of undoped ZnO in Figure 7 (a) exhibits deep-level visible emission in addition to the near band-edge UV emission. However, Ag doped ZnO PL spectra of as-grown films did not show clear emission bands as shown in Figure 7 (b). They only exhibit very weak emission bands including near band-edge UV band and broad visible emission band.

Figure 8 shows PL spectra of films annealed at 350°C. All films exhibit quite different PL intensities. The PL spectrum of RT deposited films shows a relatively stronger defect-related broad green emission as shown in Figure 8 (a). The PL of film deposited at 150°C and annealed at 350°C shows very strong near band-edge UV emission positioned at 379.38 nm and the ratio of I_{VIS}/I_{UV} was as low as 0.05, while that of as-grown undoped ZnO deposited at 150°C was 0.31. Li Duan et al.[17] reported the enhancement of UV emission from ZnO films by Ag doping. They suggested the holes existing in the interface between Ag_2O nanoclusters and ZnO grains as reasons for enhancement of UV emission. They insisted that the electrons in ZnO arrive at the interface easily because of their short mean free path and the Coulomb force based

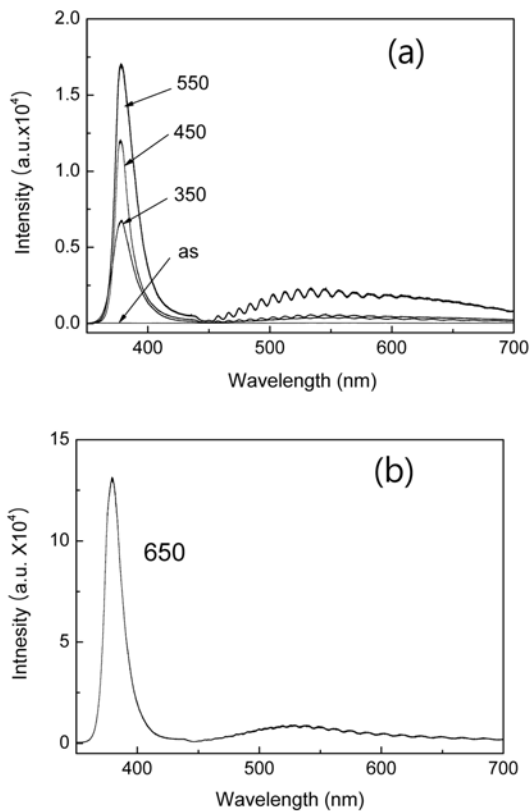


Fig. 9. RT PL spectra of the films grown at 150°C according to the annealing temperature; (a) as-grown and annealed at 350-550°C, and (b) annealed at 650°C. The annealing temperatures are indicated in the figures.

on quantum confinement effect, therefore the UV emission was enhanced. The PL spectrum of films deposited at 200°C also showed slightly increased emission intensity, but that of 250°C deposited film did not increase as much as the others did, despite annealing at 350°C.

Figure 9 shows the changes in PL spectra of films deposited at 150°C according to annealing temperature. Both emission intensity of near band-edge UV and defect related green emission increased with increasing annealing temperature. Especially, the PL intensity of films annealed at 650°C increased enormously.

4. Conclusion

The effect of the deposition and annealing temperature on structural, electrical and optical properties of Ag doped ZnO thin films by e-beam evaporation method were studied. It is noticed that the deposition temperature affects the content of Ag in the film and Ag atoms can easily be evaporated during thermal annealing. The as-grown thin films deposited at 150-250°C showed *p*-type conduction, although the films deposited at RT exhibited *n*-type conduction. The PL spectra of as-grown ZnO did not show clear emission bands, while the emission intensity increased as the post-annealing temperature increased. The film deposited at 150°C and annealed at 350°C exhibited the lowest value of I_{vis}/I_{uv} of 0.05.

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