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Effects of Codoping with Fluorine on the Properties of ZnO Thin Films

Young-Woo Heo† and D. P. Norton*

Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Korea
**Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA*
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ABSTRACT

We report on the effects of co-doping with fluorine on properties of ZnO thin films grown by pulsed-laser deposition. The transport characteristics of Ag-F and Li-F codoped ZnO films were determined by Hall-effect measurements at room temperature. Ag-F codoped ZnO films showed n-type semiconducting behaviors. An ambiguous carrier type was observed in Li-F codoped ZnO films grown at a temperature of 500°C with the oxygen pressures of 20 and 200 mTorr. The qualities of the codoped ZnO films were studied by X-ray diffraction, atomic force microscopy, X-ray photoemission spectroscopy, and photoluminescence.

Key words : ZnO, p-type, Codoping

1. Introduction

Zinc oxide (ZnO) exhibits many interesting properties, including anisotropy in crystal structure, nonstoichiometric defect structures, wide bandgap, optical transparency in the visible region, high refractive indices, large piezoelectric constants, and nonlinear optical coefficients.[1)] It has been used for acoustic wave devices, varistors, gas sensors, and piezoelectric transducers.[2-6)] In recent years, a significant amount of attention has been paid to ZnO as a wide bandgap semiconductor and transparent conducting oxide for LEDs, LDs, transparent electrodes, window material for solar cells, and transparent thin film transistors.[7-9)]

Semiconductor devices using a p-n junction structure are required to use ambipolar (n- and p-type) doping. The limited dopability for both p-type and n-type behaviors in one material hinders its application for electronic and optoelectronic devices. For example, ZnTe can be p-doped to extremely high levels with most column V dopants,[10)] but it is difficult for ZnTe to be n-doped. In contrast, ZnS and ZnSe are easily n-doped with Al. There are two possible explanations for this unipolarity of doping in compound semiconductors, namely the pinning of the Fermi level or unstable dopant configurations due to the thermodynamic energy.

Several theoretical and experimental investigations have addressed this asymmetry in n-type versus p-type doping in ZnO.[11-13)] Recent research has focused on the doping of group V ions, such as N, P, As, Sb, for the realization of p-type ZnO.[14-24)] Much of this has been reviewed by Look and Claflin.[20)] Theoretical approaches have attempted to address the doping problem of the wide-bandgap semiconductor ZnO.[25,26)] It was suggested that the codoping method using acceptors (A) and donors (D) as reactive codopants contributes to the enhancement of acceptor incorporation, with a decrease in the lattice energy and the lowering of the energy levels of the acceptors in the band gap due to the strong attractive interactions between the acceptor and donor. A non-random configuration, such as A-D-A trimers which occupy the nearest-neighbor sites or trimer-like complexes, is postulated to produce the required reduction ionization energy of the acceptor impurities for p-type ZnO.[26)]

In this study, we investigated the effects of co-doping with fluorine on the properties of ZnO thin films grown by pulsed-laser deposition. Ag with F and Li with F were used as the codopants into ZnO thin films.

2. Experimental Procedure

Pulsed laser deposition was used for film growth. (Ag, F) and (Li, F) codoped ZnO targets were fabricated using high-purity ZnO (99.999%), Ag_2O (99.99%), Li_2CO_3 (99.99%), and ZnF_2 (99.995%). Ag of 5 at% with F of 2.5 at% and Li of 5 at% with F of 2.5 at% were codoped into ZnO, respectively. The targets were pressed and sintered at 1000°C for 12 h in air. A KrF excimer laser was used as the ablation source. A laser repetition rate of 1 Hz was used with a target to substrate distance of 6.3 cm and a laser pulse energy density of 1-3 J/cm^2. The ZnO growth chamber exhibits a base pressure of 10^{-6} Torr. Single crystal (0001) Al_2O_3 (sapphire) was used as the substrate material in this study. The substrates were attached to the heater platen using Ag paint. Film thickness ranged from 200 to 500 nm. Film growth was performed over a temperature range of 300-600°C. The oxygen pressure varied from 2 to 200 mTorr. After growth, the sam-

†Corresponding author : Young-Woo Heo
E-mail : ywheo@knu.ac.kr
Tel : +82-53-950-7587 Fax : +82-53-950-5645

ples were cooled to room temperature while maintaining the growth pressure.

The film properties are determined using Atomic Force Microscopy (AFM), X-Ray Diffraction (XRD), and photoluminescence. Four-point van der Pauw Hall measurements were performed to determine transport properties. X-ray Photoemission Spectroscopy (XPS) was performed using the PHI-5100 surface analysis system (RIBER, France). XPS measurements were carried out using Mg-K_α X-rays (1253.6 eV), and the pressure in the XPS analysis chamber was $\sim 10^9$ Torr. Samples were etched by Ar^+ bombardment to examine the chemical state of each element in the film body.

3. Results and Discussion

Fig. 1(a) shows the X-ray diffraction patterns of Ag-F codoped ZnO thin films as a function of the growth temperature at an oxygen pressure of 20 mTorr. Only the (000l) peaks are observed. The highest (0002) peak intensity of the c-axis oriented Ag-F codoped ZnO film was observed at a growth temperature of 500°C. A growth temperature of 500°C was applied to the growth of Li-F codoped ZnO films

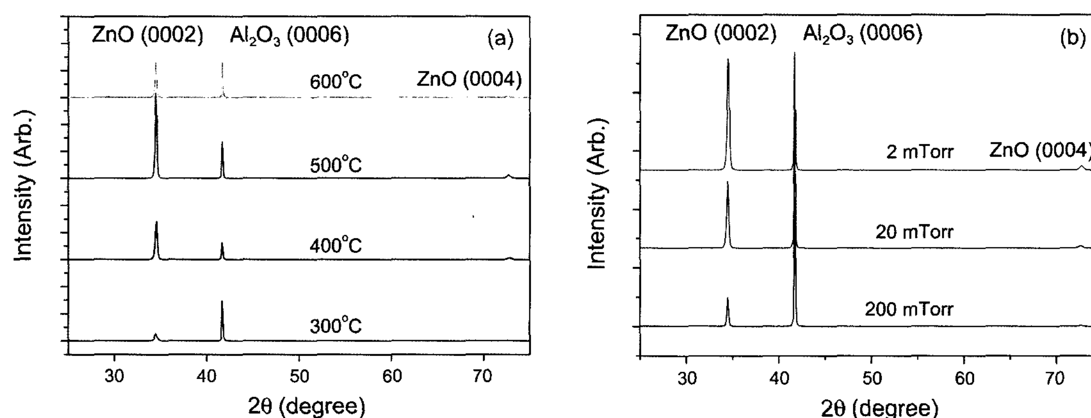

Fig. 1. X-ray diffraction patterns of (a) Ag-F codoped ZnO thin films as a function of growth temperature at the oxygen pressure of 20 mTorr and (b) Li-F codoped ZnO thin films as a function of the oxygen pressure at a growth temperature of 500°C.

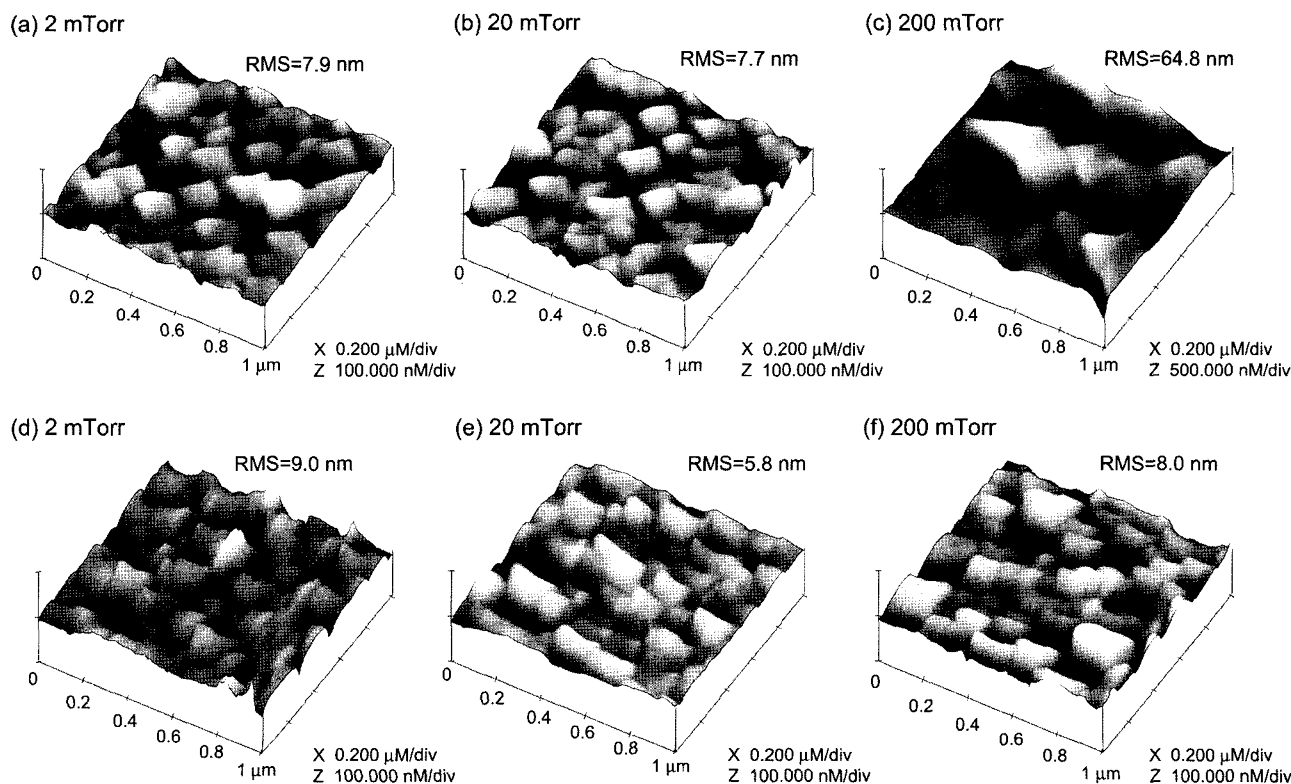

Fig. 2. Atomic force microscopy images of Ag-F codoped ZnO films ((a), (b), and (c)) and Li-F codoped ZnO films ((d), (e), and (f)) grown on sapphire with different oxygen pressures at a growth temperature of 500°C.

according to the growth condition of Ag-F codoped ZnO. Fig. 1(b) shows the X-ray diffraction patterns of Li-F codoped ZnO thin films as a function of the oxygen pressure at a growth temperature of 500°C. The oxygen pressure varied from 2 and 200 mTorr. The observed intensity of (002) peak decreased as the oxygen pressure increased. However, it was observed that ZnO films were highly c-axis oriented on c-plane Al_2O_3 regardless of the oxygen pressures.

The surface morphology of the ZnO films was measured using Atomic Force Microscopy (AFM) measurements. AFM measurement was performed in air using a Nanoscope III. All samples were scanned over a 1×1 μm^2 area. Fig. 2 shows the AFM images for codoped ZnO films grown on sapphire with different oxygen pressures at the growth temperature of 500°C. The surface roughness of Li-F codoped ZnO films did not vary much with the oxygen pressure. However, the roughness of Ag-F codoped ZnO films grown with 200 mTorr of oxygen pressure was considerably higher than that of the films grown with the lower oxygen pressure.

Fig. 3 shows the X-ray Photoelectron Spectroscopy (XPS) spectrum of Ag-F and Li-F co-doped ZnO thin films grown at the growth temperature of 500°C with the oxygen pressure of 20 mTorr. Fig. 3(a) shows the $3d_{3/2}$ and $3d_{5/2}$ peaks of Ag in Ag-F codoped ZnO thin films that were observed at 374 and 368 eV, respectively. The Li 1s peak at 56 eV was not observed in Li-F codoped ZnO thin films as shown in Fig. 3(b). This is likely to result from the fact that the atomic sensitivity factor of Li 1s line for X-ray source at 54.7° is as low as 0.025 and the amount of Li in ZnO is 5 at%. The F 1s peak was located at 686.5 eV. Due to the small amount of dopants, the local chemical bonding environment and oxidation state of individual dopants could not be resolved in this work, except for the existence of Ag and N in the films.

The transport properties of Ag-F and Li-F codoped ZnO films were characterized using Hall measurements. Table 1 summarize the carrier concentration, hall mobility, and resistivity of Ag-F codoped ZnO grown at a growth temperatures of 500°C with the various oxygen pressures. The carrier concentration increased and the hall mobility decreased as the oxygen pressure increased. The higher carrier concentration of Ag-F codoped ZnO than ZnO films grown at the same oxygen pressure of 20 mTorr is probably due to the donor doping of fluorine. All of Ag-F codoped ZnO films show n-type semiconducting behaviors. The codoping of Ag with fluorine did not contribute to the change of the carrier type.

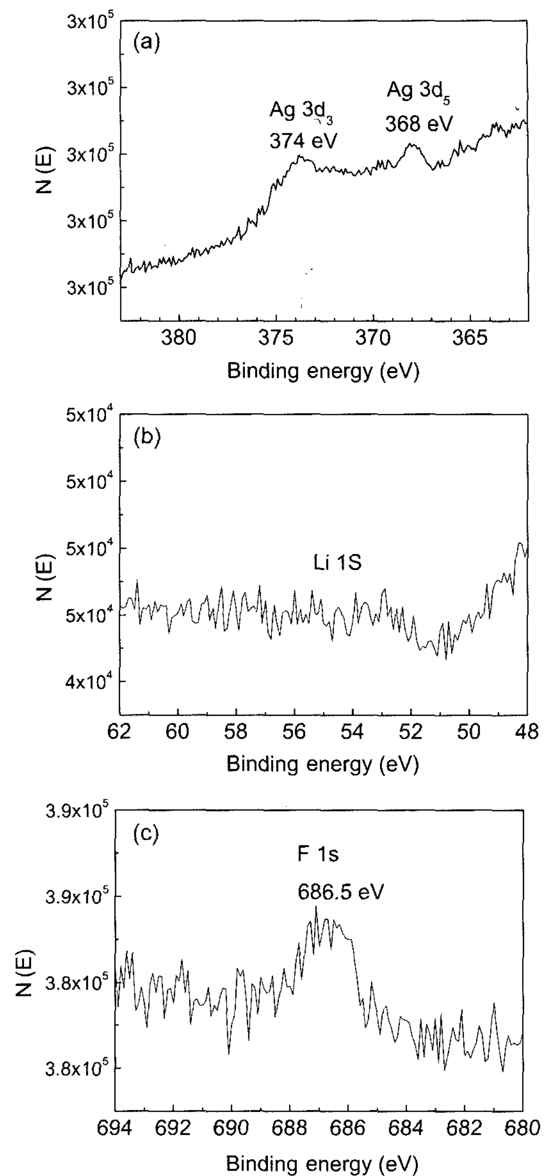

Fig. 3. X-ray Photoelectron Spectroscopy (XPS) spectrum of (a) Ag $3d_3$ and $3d_5$ in the Ag-F co-doped ZnO thin film and (b) Li 1s and (c) F 1s in the Li-F co-doped ZnO thin film grown at a growth temperature of 500°C with the oxygen pressure of 20 mTorr.

Fig. 4 presents the hall coefficient and carrier concentration of Li-F codoped ZnO grown at the growth tem-

Table 1. The Carrier Concentration, Hall Mobility, and Resistivity of ZnO and Ag-F Codoped ZnO Grown at a Growth Temperatures of 500°C with the Various Oxygen Pressures

Sample	Growth temperature (°C)	P_{O2} (mTorr)	Carrier concentration (cm^{-3})	Mobility ($cm^2/V{\cdot}s$)	Resistivity (Ω-cm)	Carrier type
ZnO	500	20	2.4×10^{18}	16	0.154	n
ZnO:Ag, F	500	2	1.2×10^{21}	29	1.7×10^{-4}	n
ZnO:Ag, F	500	20	9×10^{19}	19	3.1×10^{-3}	n
ZnO:Ag, F	500	200	5×10^{18}	7	1.7×10^{-1}	n

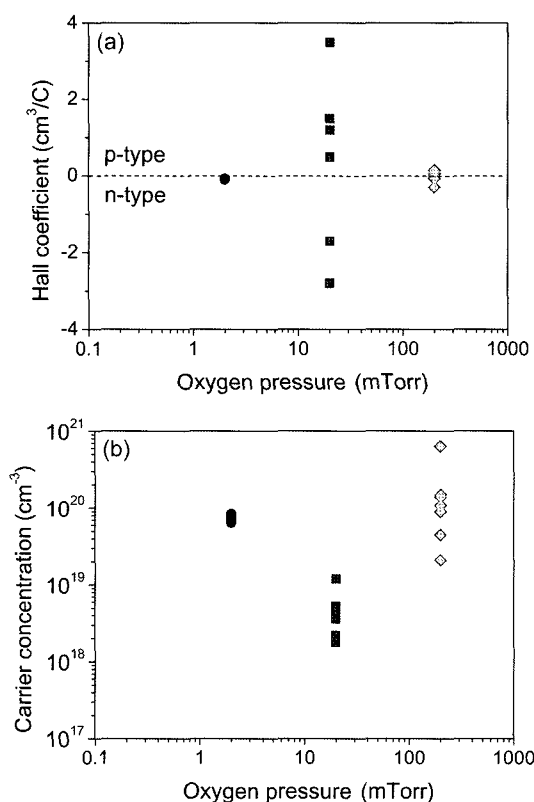

Fig. 4. (a) Hall coefficient and (b) carrier concentration of Li-F codoped ZnO grown at a growth temperature of 500°C with the various oxygen pressures.

perature of 500°C with the various oxygen pressures. Li-F codoped ZnO grown with 2 mTorr of oxygen pressure showed an n-type behavior with the carrier concentration of $\sim 7\times 10^{19}$ cm^{-3} and hall mobility of ~ 30 $cm^2/V\cdot s$. With the further increase of the oxygen pressure, an ambiguous carrier type was observed at the oxygen pressures of 20 and 200 mTorr. The carrier concentration of the samples grown with 200 mTorr of oxygen pressure was as high as $10^{19}\sim 10^{20}$ cm^{-3}, and this could not be explained only by the presence of n-type carrier because the increase of the oxygen pressure decreases the density of the intrinsic n-type donor dopants such as zinc interstitial and oxygen vacancy.

The doping of Li^+ can possibly change the carrier type of ZnO to p-type by the substitution of Li^+ in the Zn^{2+} site in terms of the consideration of the cation oxidation states. However, no p-type behavior in Li-doped ZnO has been observed. Li dopants make ZnO insulative by the formation of deep level acceptors. According to theoretical predictions,[27] the codoping of acceptors and donors contributes to the enhanced incorporation of the acceptors and the lowering of the acceptor energy level due to the strong attractive interactions between the acceptor and donor dopants. The evidence of the codoping effect was reported in the Al-N codoped ZnO films.[27] In this work, the observation of the intermediate carrier type in Li-F codoped ZnO films grown with the oxygen pressures of 20 and 200 mTorr may be explained by the lowering of the deep acceptor level due to the codoping with fluorine.

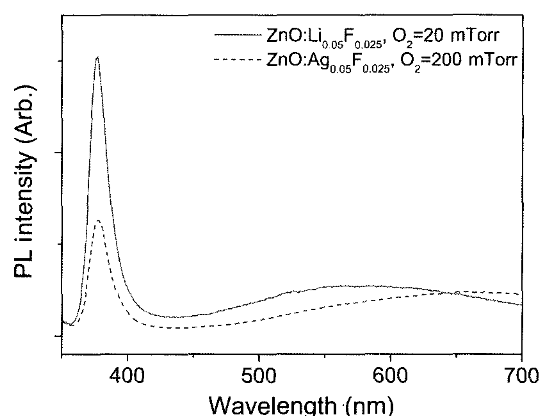

Fig. 5. Photoluminescence spectra for Li-F and Ag-F codoped ZnO films grown at a growth temperature of 500°C.

Optical properties of these MBE-grown ZnO films using ozone were characterized using photoluminescence at room temperature. Photoluminescence spectra for Li-F and Ag-F codoped ZnO films grown at a growth temperature of 500°C were measured using a He-Cd laser (325 nm). The power density was 1 W/cm^2. A 0.3 m scanning grating monochromator with a Peltier-cooled GaAs photomultiplier was utilized. The spectra shown in Fig. 5 present strong near band-edge UV photoluminescence peaks at ~ 3.2 eV and weak orange-red emissions indicating low deep level densities of the films. The acceptor and deep level states in the energy bandgap of the Li-F codoped ZnO films should be addressed in order to clearly explain the electrical and optical properties.

4. Conclusions

The properties of ZnO films codoped with Ag-F and Li-F grown by pulsed-laser deposition were examined. Ag-F codoped ZnO films showed n-type semiconducting behaviors. For Li-F codoped ZnO grown with the oxygen pressures of 20 and 200 mTorr, the unambiguous carrier type was not observed. Future work will focus on the study of the acceptor energy levels in the bandgap and the activation processes for the realization of p-type ZnO.

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