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Highly Transparent *p*-Type ZnO Thin Films Prepared by Non-Toxic Sol-Gel Process

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In-N co-doped *p*-type ZnO thin films were demonstrated using a non-toxic sol-gel spin coating process. The resistivity of the *p*-type ZnO films is 4.43 Ω cm with the carrier concentration of 1.36×10^{18} cm^{-3} at room temperature. The X-ray photoelectron spectra of N 1s core level measured with an Al *K*α photon line identify the existence of nitrogen in the *p*-type ZnO. The secondary ion mass spectrometry depth profile also confirms the nitrogen contents in the In-N co-doped films. In addition, the In-N co-doped film with a thickness of 200 nm has a high transparency about 90% in the visible region.

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ZnO is a promising material for short-wavelength optoelectronics and thin film transistors because of its wide bandgap (3.37 eV), large exciton binding energy (60 meV), high carrier mobility, and high optical gain (320 cm^{-1}) at room temperature.[1,2] To realize ZnO-based CMOS-type circuits, it is essential to fabricate both high quality *n*-type and *p*-type films with a low cost process. Nevertheless, fabrication of *p*-type ZnO remains a major challenge due to the self-compensation by native donor-like defects such as oxygen vacancies and zinc interstitials, deep acceptor levels, low solubility of the dopants, and unintentional hydrogen doping which tends to bond to oxygen and behaves like fluorine.[3,4] In terms of the shallowness of the acceptor levels, group-I elements are the better choices than group-V elements theoretically, but the efficiency of doping is generally limited by the formation of compensating interstitials.[5] Among the group-V elements, N gives rise to the shallowest acceptor level, and the ionic radius of either N^{2-} (0.129 nm) or N^{3-} (0.132 nm) is close to that of O^{2-} (0.126 nm). As a result, N is considered as a relatively better candidate as *p*-type dopants for ZnO.[5,6] The co-doping method utilizing the group-III donors Al, Ga, or In, has been proposed to enhance the incorporation of N by decreasing the repulsive interactions between N acceptors and also bring about a shallower N acceptor level in *p*-type co-doped ZnO.[7] Although a considerable number of studies have been made on Al-N,[8–10] Ga-N,[11] and In-N [12] co-doping methods, little is prepared by sol-gel techniques. Compared with the conventional thin film deposition techniques, such as sputtering, pulsed laser deposition, and chemical vapor deposition, the sol–gel technique has advantages of easy control of the chemical composition and lower process costs. These characteristics make the sol-gel technique a very attractive approach, especially for the co-doping of ZnO thin films.

In the last few years, several researches have been devoted to the study of sol-gel derived III-N co-doped *p*-type ZnO.[13–16] Cao et al. reported the growth of In-N co-doped ZnO films by a sol-gel spin coating method and analyzed the chemical composition by X-ray photoelectron spectroscopy.[16] Unfortunately, the signals of LMM Auger electrons from Zn overlap the N 1s peak when Mg *K*α is used as the X-ray source, which means that the composition or even existence of N determined in this way is doubtful. In addition, the reported electrical properties were also debatable and had been commented by other research group.[17] Therefore, the fabrication of In-N co-doped *p*-type ZnO by sol-gel processes is still a challenge. On the other hand, it must be noticed that 2-methoxyethanol and diethanolamine, as the widely employed solvent and stabilizer, respectively, in the preparations for ZnO thin films by sol-gel processes, are both toxic to the human body. Accordingly, a great deal of effort has been made on the *n*-type ZnO films prepared by non-toxic sol-gel processes.[18–20] However, the *p*-type ZnO films prepared by non-toxic sol-gel processes have not been reported to date.

In this paper, we report that In-N co-doped *p*-type ZnO thin films were achieved through a sol-gel spin coating method with both non-toxic solvent and stabilizer. The chemical composition of In-N co-doped ZnO films is revealed by X-ray photoemission spectroscopy. The comparisons of electrical and optical properties between the co-doped and undoped ZnO films are also discussed.

In-N co-doped and undoped ZnO films were prepared by a sol-gel spin coating method using zinc acetate dihydrate ($Zn(CH3COO)2 \cdot 2H2O$) as a starting material and isopropyl alcohol and monoethanolamine (MEA) as the non-toxic solvent and stabilizer. To prepare In-N co-doped ZnO films, Indium nitrate pentahydrate ($In(NO3)3 \cdot 5H2O$) and ammonium acetate ($CH3COONH4$) were used as the In and N sources, respectively, with atomic ratio of 1:3:0.1 (Zn/N/In). The doped and undoped solutions, with a concentration of 0.5 M zinc acetate and 1:1 molar ratio of MEA/zinc acetate, were stirred at 75°C for 3 hrs and then served as the coating solutions after standing for 24 hrs. The respective solutions were spin-coated on cleaned glass substrates at 3000 rpm for 30 sec and preheated at 280°C for 10 min in air to remove residual organic materials. The process of coating and preheating was repeated five times to obtain a desired film thickness of 200 nm. After coating processes, both undoped and co-doped films were annealed at 550°C for 1.5 hrs in oxygen ambient.

The chemical states of the undoped and In-N co-doped ZnO films were characterized by X-ray photoelectron spectroscopy (XPS) (ESCA PHI 560, Al *K*α source). The ZnO samples were sputter-cleaned by argon ion at about 2.0×10^{-7} Torr with an ion gun energy of 3.8 kV and an emission current of 25 mA to remove surface contaminants. Secondary ion mass spectrometry (SIMS) (CAMECA IMS4F) was used to identify the existence of nitrogen in the films. The electrical properties at room temperature were carried out by a Hall measurement system (ECOPIA HMS-3000) in the van der Pauw configuration. Furthermore, the optical properties of both films were measured by a UV–vis spectrometer (JASCO V-670).

Fig. 1 illustrates the XPS full spectrum of the In-N co-doped ZnO sample. The binding energy of Zn $2p_{3/2}$ core level is located at 1022.0 eV, which indicates Zn components in the film are at Zn^{2+} states.[21] The O 1s peak at 530.6 eV confirms the bonding of oxygen with zinc in wurtzite structure of ZnO.[22] The inset of Fig. 1 shows the peaks of In 3d core levels obtained from the In-N co-doped ZnO thin films. The binding energies of In $3d_{5/2}$ (444.7 eV) and In $3d_{3/2}$ (452.2 eV), in contrast to 445.1 eV and 452.7 eV for In-O bonds, are in good agreement to the energy shifts of indium core levels in the In-N bond,[23,24] which indicates that indium atoms tend to bond to nitrogen atoms in In-N co-doped ZnO films. Thus, the repulsive interactions between N acceptors can be effectively reduced, leading to the enhancement of N incorporation as *p*-type dopants in ZnO.

The N 1s core level were measured via XPS with Al *K*α photon lines from the undoped and In-N co-doped ZnO films to identify the nitrogen contents in the In-N co-doped ZnO films. As shown in Fig. 2a, no obvious peak related to nitrogen is observed from the

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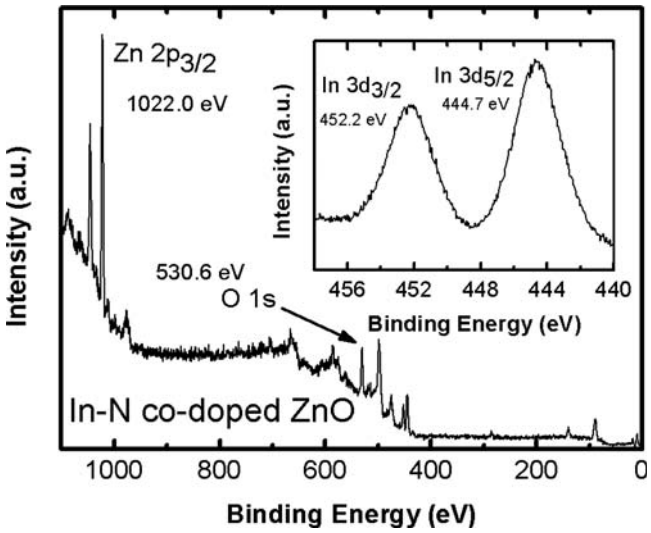


Figure 1. XPS spectra of In-N co-doped ZnO films. The inset shows In 3d core level spectrum of In-N co-doped ZnO films. XPS spectra were measured with Al *K*α photon lines.

undoped ZnO films. That is, the signal of N 1s core level is not interfered by the Auger electrons of Zn atoms when Al *K*α (1486.6 eV) is selected as the X-ray source, which cannot be achieved with Mg *K*α photon lines. For the In-N co-doped ZnO samples, as shown in Fig. 2b, an apparent peak corresponding to N 1s core level is detected at around 399 eV, which is close to the Zn-N bond.[9,25] It is believed that N and In existed in ZnO are mostly in the states of In-N and Zn-N bonds. The presence of N 1s peak demonstrates the successful doping of nitrogen into ZnO using this sol-gel solution-based process.

In order to further confirm the existence of nitrogen in the In-N co-doped ZnO films, SIMS measurement was performed. Fig. 3 exhibits the SIMS depth profile of the main elements in the In-N co-doped ZnO thin films prepared by the sol-gel spin coating method in this study. It is obvious that nitrogen has been well detected with a flat signal throughout the whole film, which indicates the uniform doping of nitrogen into the ZnO films. The incorporation of N in ZnO leads to the good *p*-type conduction of the In-N co-doped ZnO films.

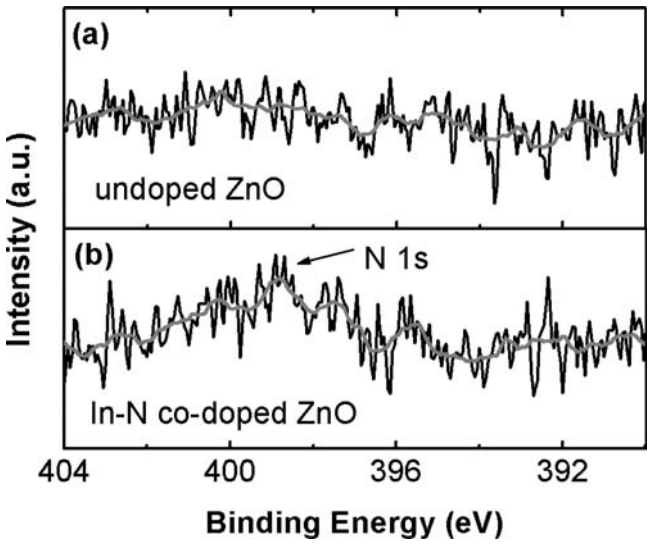


Figure 2. XPS spectra of N 1s core level of (a) undoped ZnO films and (b) In-N co-doped ZnO films. XPS spectra were measured with Al *K*α photon lines.

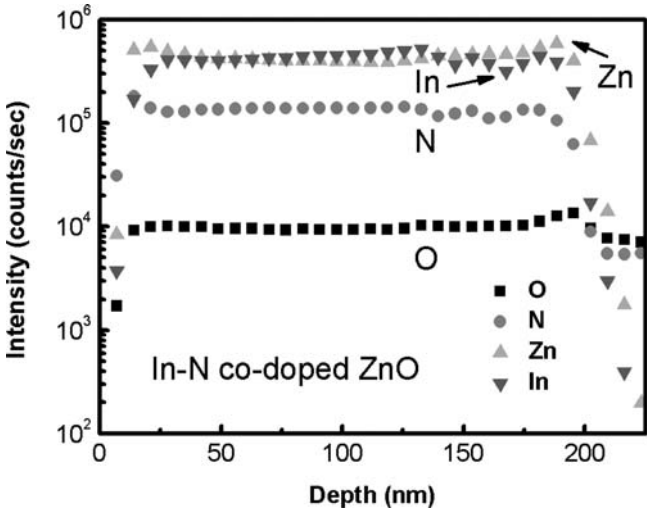


Figure 3. SIMS depth profile of In-N co-doped ZnO films prepared on glass substrates.

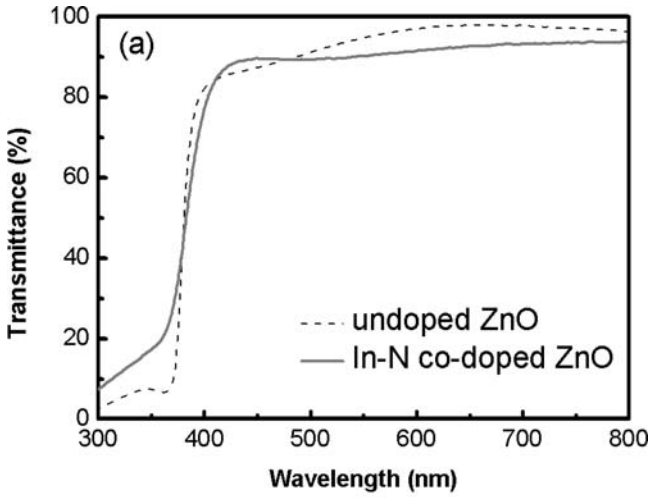
In addition, the thickness of the sample can be estimated from the SIMS depth profile to be about 200 nm, which is consistent with the measurement from depth profiler.

Table I summarizes the electrical properties of the undoped and In-N co-doped ZnO thin films annealed at 550°C under an ambient O_2. The *p*-type conductivity with a hole concentration of 1.36×10^{18} cm^{-3}, Hall mobility of 1.04 cm^2 V^{-1} s^{-1}, and resistivity of 4.43 Ω cm can be achieved on the In-N co-doped ZnO films using non-toxic processes in this study. The undoped ZnO films behave as an *n*-type semiconductor, which is attributed to not only native donor defects, such as oxygen vacancies and zinc interstitials, but also the unintentional incorporation of donor-like hydrogen from ammonium acetate or the growth environment. For In-N co-doped ZnO films, nitrogen occupies oxygen lattice site and tends to draw one more electron than oxygen does to fill its 2p electron orbitals (generally denoted as N_O^-). However, H^+ charged defects are easily to bond with N_O^- and therefore form the neutral nitrogen-hydrogen complexes (denoted as N_O-H), thereby compensating the N acceptors.[26] The annealing at an appropriate temperature can dissociate N_O-H complexes while Zn-N bonds are still present in ZnO.[27] The dissociation of N_O-H complexes and retained N acceptors in ZnO are considered as the main reasons for *p*-type conductivity in these films.

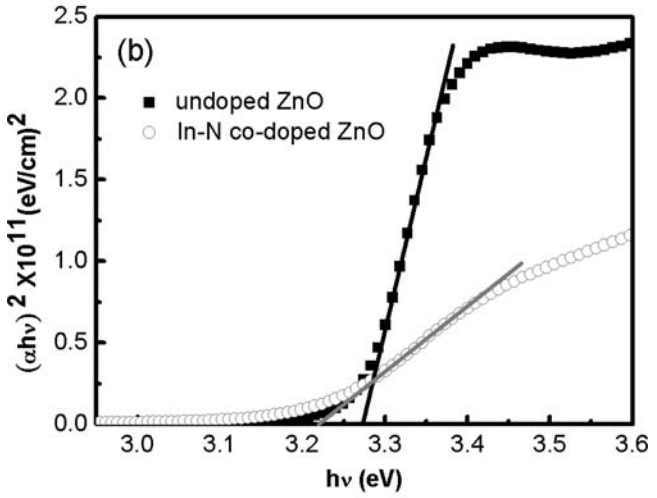
Fig. 4a shows the transmittance spectra of the undoped and In-N co-doped ZnO films in the wavelength range of 300 nm to 800 nm. The co-doped films with a thickness of 200 nm are highly transparent (90%) in the visible region and have a sharp fundamental absorption edge at about 380 nm. The high transmittance of the In-N co-doped ZnO films is comparable to that reported for the *p*-type ZnO films using RF magnetron sputtering.[8,10] The calculated optical bandgap of the undoped and In-N co-doped ZnO films are illustrated in Fig. 4b. A clear red-shift of the bandgap from 3.27 eV for the undoped ZnO films to 3.22 eV for the In-N co-doped ZnO films is observed. The narrowing of the bandgap after doping of impurities is presumably

Table I. Electrical properties of undoped and In-N co-doped ZnO films determined by Hall measurements.

Sample	Resistivity (Ω cm)	Hall mobility (cm^2 /V s)	Carrier concentration (cm^{-3})	Type
Undoped ZnO	31.1	0.578	-7.19×10^{17}	*n*
In-N co-doped ZnO	4.43	1.04	$+1.36 \times 10^{18}$	*p*



(a)



(b)

Figure 4. (a) Transmittance spectra and (b) the dependence of $(\alpha h\nu)^2$ on photon energy ($h\nu$) of undoped and In-N co-doped ZnO films.

due to near-band-edge defects. On the other hand, it is generally agreed that the co-doping with nitrogen and indium into ZnO induces the formation of In-N and Zn-N bonds. Since the bandgap of InN (0.7 eV) and $(ZnN)^-$ (0.8 eV) are much narrower than that of ZnO,[28] The In-N and Zn-N bonds may be also responsible for the reduction of the bandgap.

In summary, In-N co-doped *p*-type ZnO thin films have been realized through a sol-gel spin coating process with non-toxic solvent and stabilizer. The fabricated *p*-type ZnO films exhibit a low resistivity of 4.43 Ω cm, a high carrier concentration of 1.36×10^{18} cm^{-3}, and the Hall mobility of 1.04 cm^2 / V s. The binding energies of In $3d_{5/2}$ and In $3d_{3/2}$ imply that indium atoms are bonded to nitrogen atoms and reduce the repulsive interactions between N acceptors. The XPS and SIMS measurements both demonstrated the incorporation of N in the In-N co-doped ZnO films. The transmittance of the In-N co-doped film is about 90% in the visible region. In addition, the near-band-edge defects and the narrow bandgap of InN and $(ZnN)^-$ result in the narrowing of the optical bandgap of the In-N co-doped ZnO films.

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