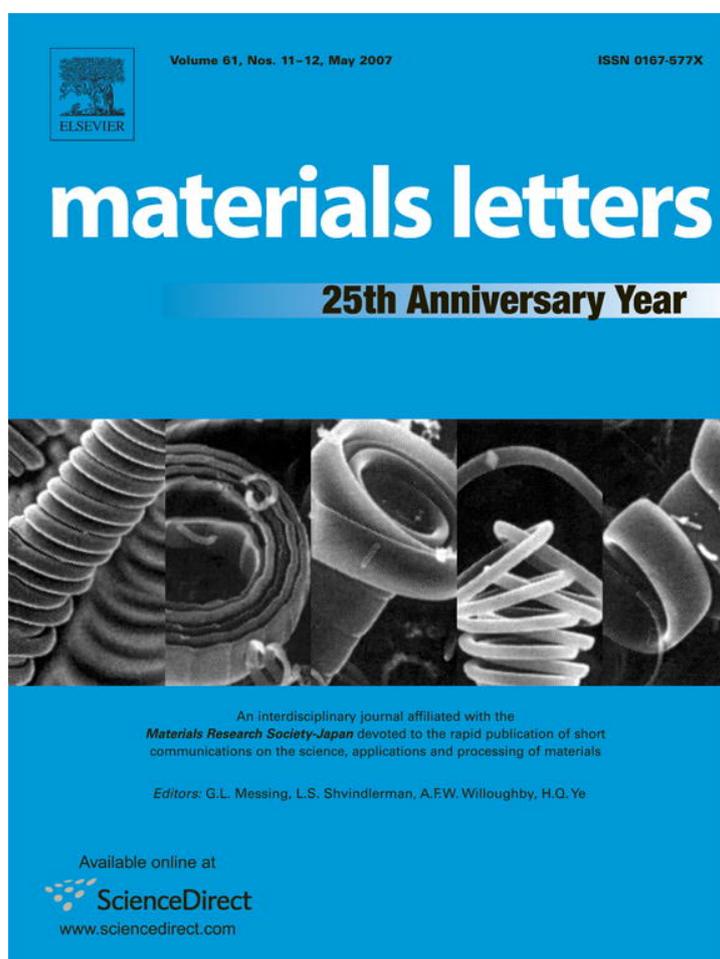


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Growth of p-type ZnO thin films by using an atomic layer epitaxy technique and NH₃ as a doping source

Chongmu Lee ^{*}, Su Young Park, Jongmin Lim, Hyoun Woo Kim

Department of Materials Science and Engineering, Inha University, 253 Yonghyeon-dong, Incheon 402-751, Korea

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Abstract

Nitrogen-doped, p-type ZnO thin films have been grown successfully on sapphire (0001) substrates by atomic layer epitaxy (ALE) using Zn (C₂H₅)₂ [Diethylzinc, DEZn], H₂O and NH₃ as a zinc precursor, an oxidant and a doping source gas, respectively. The lowest electrical resistivity of the p-type ZnO films grown by ALE was 210 Ω cm with a hole concentration of 3.41 × 10¹⁶ cm⁻³. Low temperature-photoluminescence analysis results support that the nitrogen ZnO after annealing is a p-type semiconductor. Also a model for change from n-type ZnO to p-type ZnO by annealing is proposed.

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1. Introduction

ZnO is a promising, direct, wide band gap (3.37 eV) semiconductor with a wurtzite structure. It is one of a few materials which can be utilized to make optical devices emitting light in the short wavelength region [1]. ZnO has many advantages over GaN which is currently used for fabricating optoelectronic devices in the industry. They include a large exciton binding energy (~60 meV), the availability of ZnO substrates, amenability to chemical wet etching, the possibility of low temperature epitaxial growth, and excellent radiation-resistance [2]. One of the obstacles in realizing optoelectric devices based on ZnO is the difficulty in fabrication of p-type ZnO thin film because almost all the as-grown unintentionally doped ZnO films exhibit n-type characteristics [3]. Recently, many techniques have been used to grow nitrogen-doped, p-type epitaxial ZnO films, including molecular beam epitaxy (MBE) [4], pulsed laser deposition (PLD) [5–8], chemical vapor deposition (CVD) [9], metal-organic CVD (MOCVD) [10–12], MOMBE [13], DC magnetron sputtering [14,15], and RF magnetron sputtering [16].

On the other hand, ALE is an important technique for epitaxial growth of ZnO thin films. ALE is a self-limiting, thin film growth process producing several practical advantages including accurate and simple thickness control, large area and large batch capability, good conformality and reproducibility, straight forward doping and scale-up, the ability to produce sharp and tailored interfaces as well as the capability to prepare multilayer structures in a continuous process which is required for fabrication of optoelectronic devices [17]. However, there have been almost no reports on epitaxial growth of ZnO by ALE, although growth of boron-doped, ZnO thin films on glass substrates for solar cell applications by atomic layer deposition has been reported before [18,19]. We have previously reported on the growth of undoped-ZnO epitaxial films using ALE [20], but successful growth of a p-type ZnO film by ALE has not been reported before.

High level p-type doping to overcome the background self-compensation effect of the intrinsic n-type defects, such as oxygen vacancies and zinc interstitials, is needed to realize a p-type ZnO thin film [3], but the problem is that the solubility limits of most elements in ZnO for p-type doping are not high enough. Postannealing is also generally necessary to remove hydrogen atoms which passivate acceptors. It is well known that nitrogen is the most promising candidate for a p-type dopant for

^{*} Corresponding author. Tel.: +82 32 860 7536; fax: +82 32 862 5546.
E-mail address: cmlee@inha.ac.kr (C. Lee).

ZnO, although P and As also have been successfully used to make p-type ZnO. Nevertheless, N has a much smaller ionic size than P and As and the energy level of substitutional N_O is lower than that of substitutional P_O and As_O [21]. Therefore, N is more favorable as a p-type dopant than the other two candidates. Nitrogen doping into ZnO has been tried by employing various doping sources such as NH₃, N₂O, NO, N₂, Zn₃N₂, and MMHy. In this study we report on the growth of p-type ZnO films by ALE using NH₃ as a doping source for nitrogen. Effects of NH₃ gas flow rate and annealing on the carrier concentration and carrier mobility of a ZnO thin film will be discussed. We also tried N₂O as a doping source for nitrogen, but failed to make p-type ZnO with N₂O doping.

2. Experimental

Nitrogen-doped ZnO films were grown on sapphire (0001) substrates by using an ALE technique. Diethylzinc (DEZn) and H₂O (99.99%), which are a precursor for zinc and an oxidant, respectively, were kept at 10 °C, before they, along with NH₃ gas (99.99%), were fed into the reaction chamber through separate inlet lines and nozzles and purged in an ALE cycle. This cycle was performed repeatedly. The opening and closing sequences of the valves were controlled by a computer. Typical pulse times for DEZn, H₂O, and NH₃ feeds were 0.15 s, 0.2 s, and 0.05 s, respectively, and the purge time between the reactants was 2 s. The substrate temperature was fixed at 150 °C. The NH₃ gas flow rate was 3 sccm and the NH₃ feed step was between the DEZn and H₂O feed steps in each cycle. Three samples of the same kind were prepared in this way and they were annealed at 1000 °C in an oxygen (99.99%) atmosphere of 1 atm for 1 h using an annealing furnace after growth of ZnO films by ALE. The carrier concentrations, carrier mobilities and resistivities of the ZnO films were investigated by using a Hall effect measurement system (HMS-2000, Ecopia, Korea). The crystallinity of the ZnO film was characterized using an X-ray diffractometer in a θ - 2θ configuration with CuK α radiation. A photoluminescence (PL) spectrum was obtained

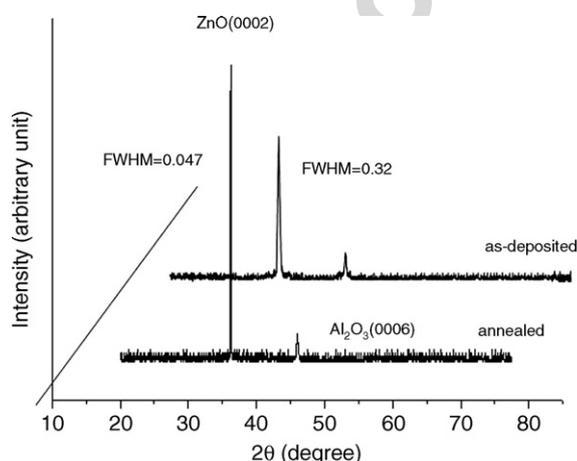


Fig. 1. The X-ray diffraction spectra of nitrogen-doped ZnO thin films (a) as-deposited and (b) annealed at 1000 °C.

Table 1

The carrier concentrations, mobilities and resistivities of ZnO thin films doped with nitrogen before and after annealing

Sample no.		Carrier conc. ($\times 10^{16}/\text{cm}^3$)	Mobility (cm^2/Vs)	Resistivity ($\Omega \text{ cm}$)
G1	As-grown	1.87	3.64	86
G2	As-grown	2.52	3.25	71
G3	As-grown	3.71	3.21	49
G	Average	2.70	3.37	69
A1	Annealed	2.43	1.01	235
A2	Annealed	2.84	0.90	227
A3	Annealed	3.41	0.81	210
A	Average	2.89	0.91	224

at 10 K with a 325 nm line of a He–Xe laser with a maximum power of 200 mW as an excitation source.

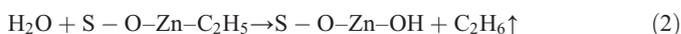
3. Results and discussion

The XRD spectra of the ZnO thin films as-deposited and annealed at 1000 °C are shown in Fig. 1(a) and (b), respectively. They show that the film has a high *c*-axis orientation with good crystallinity. No other peaks such as zinc and nitride peaks are found in the spectra maybe because of easy dissociation of NH₃ gas. A comparison of the full width at half maximum (FWHM) values of the (0002) peak of the as-deposited (0.32) and annealed (0.047) ZnO films confirms us that the crystallinity has been substantially enhanced by annealing as was expected.

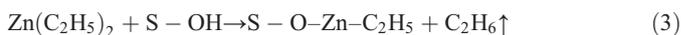
The electrical properties of the ZnO thin film samples doped with nitrogen before and after annealing are listed in Table 1. All these samples showed n-type characteristics in an as-grown state, but the electrical properties of all of them were changed from n-type to p-type by annealing at 1000 °C in an oxygen atmosphere. The electron mobility in the as-grown samples seems to be quite low. This may be attributed to the surface effects or the substrate/film interface effects because the ZnO thin films are as thin as 300 nm. Change of carrier concentration and carrier mobility with annealing can be explained by using the model shown in Fig. 2. If NH₃ doping is conducted, NH₃ will be adsorbed and react with C₂H₅ as in the equation:



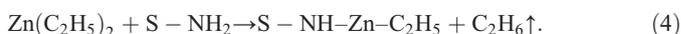
where S denotes a surface site. At the next step of H₂O pulse, C₂H₅ is substituted by OH through the reaction:



The oxygen vacancy in the top figure of Fig. 2 indicates the one which exists commonly in as-grown ZnO thin films. This vacancy may be either charged or neutral, but it is more probable that it is charged since most as-grown ZnO films exhibit n-type characteristics. At the next step of DEZn pulse, OH is substituted by Zn–O through the reaction:



and NH₂ changes to NH by the reaction:



We can see that NH occupies an oxygen site of the ZnO wurtzite lattice after a cycle. The NH impurity which has a bond with a Zn atom generally does not generate a hole because the hydrogen atom passivates the nitrogen atom.

If an annealing process is conducted at this stage, the hydrogen atom in NH will be removed and NH will be reduced to a single nitrogen atom which will generate a hole to be an ionized acceptor. Therefore, the n-type ZnO film will change to the p-type ZnO film only if the concentration of nitrogen in the ZnO film is high enough. The NH impurity at an oxygen site in the as-grown ZnO thin film is electrically neutral, whereas the nitrogen impurity at an oxygen site in the annealed ZnO thin film is an ionized acceptor. In general, carrier mobility is reduced more significantly by an ionized impurity than by a neutral impurity. Therefore, the carrier mobility of the ZnO thin film grown by ALE is decreased by annealing.

Low temperature PL analyses were carried out for an annealed sample (A2) and the result is shown in Fig. 3. In the low temperature PL spectrum in Fig. 3 the peak located around 3.36 eV is attributed to the near band-edge (NBE) emission of excitons bound to donors ($D^{\circ}X$). The peak around 3.31 eV is due to the NBE emission of excitons bound to acceptors ($A^{\circ}X$) associated with N_{O} . This result agrees well with other's findings concerning the low temperature PL of nitrogen-doped ZnO [22].

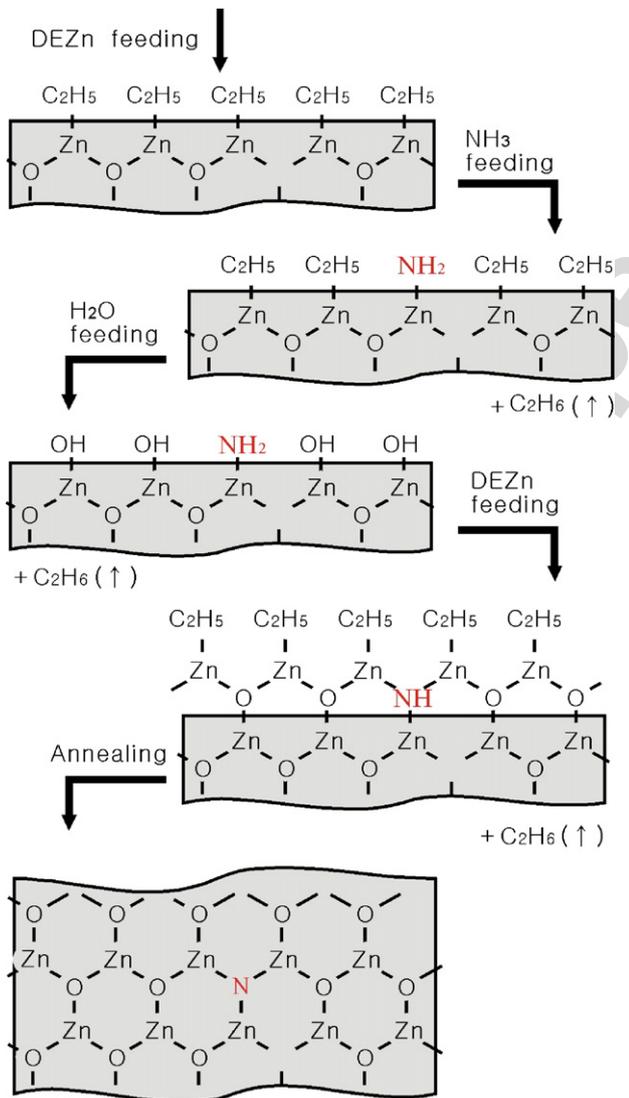


Fig. 2. A model for the arrangement of atoms in the ZnO lattice doped with NH₃ to describe the annealing effect.

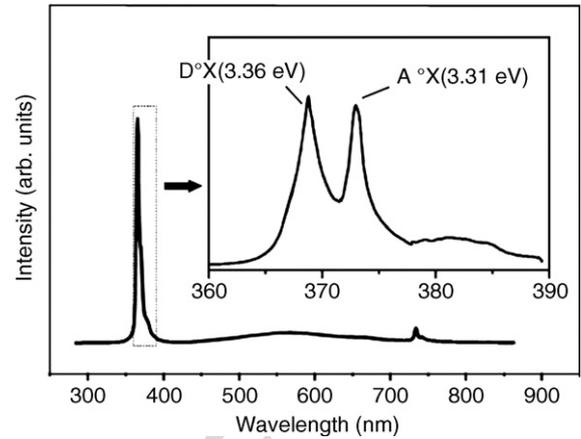


Fig. 3. PL spectra at 10 K for nitrogen-doped ZnO films grown by ALE.

The annealing temperature of 1000 °C which was used for annealing ZnO thin films in this work was not the optimal condition as determined by systematic experiments. This temperature of 1000 °C was chosen as that just high enough to obtain a sufficient annealing effect, but the same annealing effect can probably be obtained using a lower annealing temperature. We are presently conducting research to determine the optimum annealing temperature.

4. Conclusions

We have successfully grown nitrogen-doped, p-type ZnO thin films on sapphire (0001) substrates by ALE using DFZn, H₂O, and NH₃ as a zinc precursor, an oxidant and a doping source gas, respectively. Hall-effect measurement on the film gives a resistivity of 210 Ω cm and a hole concentration of $3.14 \times 10^{16}/\text{cm}^{-3}$. Also a model for change from n-type ZnO to p-type ZnO by annealing is proposed.

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