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Growth of nitrogen-doped p-type ZnO thin films prepared by atomic layer epitaxy

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Abstract: Nitrogen-doped, p-type ZnO thin films were grown successfully on sapphire (0001) substrates by using atomic layer epitaxy (ALE). $Zn(C_2H_5)_2$[Diethylzinc, DEZn], H_2O and NH_3 were used 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 and annealed at 1000 ℃ in an oxygen atmosphere for 1 h was 18.3 Ω·cm with a hole concentration of 3.71×10^{17} cm^{-3}. Low temperature-photoluminescence analysis and time-dependent Hall measurement results support that the nitrogen-doped ZnO after annealing is a p-type semiconductor.

Key words: p-type ZnO; atomic layer deposition; electrical resistivity; carrier concentration; photoluminescence

1. Introduction

ZnO is a very promising, direct, wide-band-gap (3.37 eV) semiconductor with a wurtzite structure. It is one of the few materials that 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. The advantages are 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[2-3]. One of the obstacles in realizing optoelectric devices based on ZnO is the difficulty in fabricating a p-type ZnO thin film because almost all the as-grown undoped ZnO films exhibit n-type characteristics [4]. Recently, many techniques, including molecular beam epitaxy (MBE), pulsed laser deposition (PLD), chemical vapor deposition (CVD), metal-organic CVD (MOCVD), MO-MBE, and magnetron sputtering, have been used to grow nitrogen-doped, p-type epitaxial ZnO films.

On the other hand, ALE is a very promising 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 and the capability to prepare multilayer structures in a continuous process which is required for fabricating optoelectronic devices [5]. However, there have been almost no reports on the growth of p-type ZnO by using ALE, although growth of boron-doped, n-type ZnO films on glass substrates for solar cell applications by using atomic layer deposition has been reported before[6-7]. We previously reported the growth of undoped-ZnO epitaxial films by using ALE[8-9], but successful growth of a p-type ZnO film by using ALE and the dependences of the carrier concentration and the carrier mobility on the doping sequence in an ALE cycle have not been reported before.

High-level p-type doping to overcome the background self-compensation effect of the in-

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trinsic n-type defects, such as oxygen vacancies and zinc interstitials, is needed to realize a p-type ZnO thin film[4], but the problem is that the solubility limits of most elements in ZnO for p-type doping are not high enough. Nitrogen is well known to be the most promising candidate for a p-type dopant for ZnO, although P and As also have been successfully used to make p-type ZnO. N has a much smaller ionic size than P and As, and the energy level of substitutional NO is lower than those of substitutional PO and AsO[10]. 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 NH_3, Zn_3N_2, MMH_y, and NH_3 plasma[11]. Even though it was reported that p-type ZnO may be developed by using nitrogen as p-type dopant, no studies were made to investigate the growth of nitrogen doped ZnO films by using ALE. In this study, the growth of p-type ZnO films by using ALE with NH_3 as a doping source for nitrogen was reported. The effects of the NH_3 gas flow rate and the post-annealing temperature on the carrier concentration and the carrier mobility of the ZnO thin film were investigated.

2. Experimental

Nitrogen-doped ZnO films were grown on sapphire (0001) substrates by using an ALE technique. Diethylzinc (DEZn) and H_2O, which are a precursor for zinc and an oxidant, respectively, were kept in a canister at 0 ℃ for DEZn and 15 ℃ for H_2O. DEZn, H_2O, NH_3 and N_2 purge gases (100 sccm) were fed into the chamber through separate inlet lines and nozzles and purged in an ALE cycle. This cycle was repeated 1000 times. The opening and the closing sequences of the valves were controlled by using a computer. Typical pulse times for the DEZn, H_2O, and NH_3 feeds were 0.1, 0.15, and 0.1 s, respectively, and the purge time between the reactants was 3 s. The substrate temperature was fixed at 150 ℃. Several different kinds of ZnO samples doped with NH_3 were made by using ALE. The NH_3 gas flow rate was fixed to be 5 sccm. The precursors feed sequence was H_2O-NH_3-DEZn. The ZnO thin films in these samples were annealed at 600, 800, and 1000 ℃ in an oxygen atmosphere of 1 atm for 1 h in an annealing furnace. The carrier concentrations, the carrier mobilities, and the resistivities of the ZnO films were investigated by using a Hall measurement system (HMS-2000, Ecopia, Korea). Also, time-dependent Hall effect measurements and low temperature-photoluminescence (PL) analyses were carried out for the sample whose hole concentration was the highest among all the samples prepared in this study.

3. Results and discussion

The electrical properties of the ZnO films grown by using ALE at NH_3 gas flow rates of 5 sccm and annealed at different substrate temperatures were investigated. The carrier concentrations, the carrier mobilities, and the resistivities of the ZnO thin films as functions of the annealing temperature are shown in Fig. 1. The as-grown ZnO films show n-type semiconductor characteristics, but the ZnO films annealed at 800 and 1000 ℃ show p-type semiconductor characteristics.

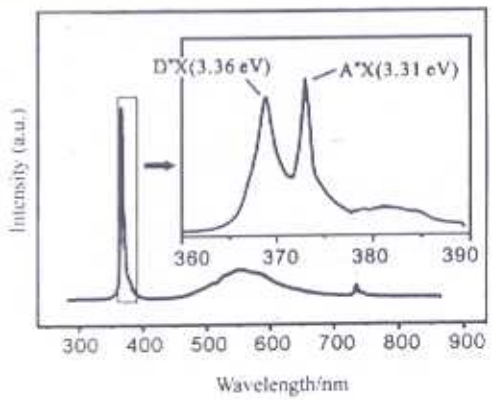

Fig. 1. A PL spectrum at 10 K for nitrogen-doped ZnO thin films grown by using ALE.

The chemical reactions through which a ZnO thin film forms during ALE with a reactant feed sequence of DEZn and H_2O are as follows:
DEZn pulse: S-OH + DEZn ($(C_2H_5)_2Zn$) →

$S\text{-}O\text{-}Zn\text{-}C_2H_5 + C_2H_6$

H_2O pulse: $S\text{-}O\text{-}Zn\text{-}C_2H_5 + H_2O \rightarrow S\text{-}O\text{-}Zn\text{-}OH + C_2H_5$

where the chemical formulae written in bold type denote surface sites for reactions. If the NH_3 gas is supplied to the substrate surface after the H_2O pulse, the -OH radical will be substituted for by $-NH_x$ as follows:

NH_3 pulse: $S\text{-}O\text{-}Zn\text{-}OH + NH_3 \rightarrow S\text{-}O\text{-}Zn\text{-}NH_x + H_2O$

The NH_3 gas flow rate must be limited so that replacement of only some -OH radicals by $-NH_x$ may occur because NH_3 reacts with ZnO very actively. It has been reported that partially decomposed ammonia (NH_x: x = 1, 2) forms, along molecular species, on a Zn-terminated Zn (0001) surface even at 130 K[12].

Post-annealing treatment is known to remove the hydrogen passivation. The dissociation of N-H bonds has been observed by Ogata et al. through post-annealing treatment[13]. It is common for both the carrier concentration and mobility to be increased by increasing the post-annealing temperature in n-type ZnO thin films[14], yet the electrical behaviors of p-type ZnO thin films seem to be quite different from those of n-type ZnO thin films. The electrical resistivity of the ZnO thin film doped with ammonia annealed at 600 ℃ was measured to be infinitely high. In other words, the ZnO films seem to behave as insulators. This may be because the carrier concentrations of the ZnO films are very low as a result of complete compensation and the carrier mobilities are very low, as shown in Fig. 1.

The ZnO thin films doped with nitrogen using ammonia as a doping source became p-type semiconductors with hole concentrations of 2.16×10^{16} cm^{-3} and 3.71×10^{17} cm^{-3} after annealing at 800 and 1000 ℃, respectively. The annealing temperature of 1000 ℃ seems to be high enough for most hydrogen atoms passivating nitrogen atoms to be removed and for the oxygen annealing atmosphere to remove Zn interstitials in the ZnO thin films doped with ammonia. The carrier mobility decreased in the ZnO films as the annealing temperature was increased from 800 to 1000 ℃. This may be attributed to an increase in the hole concentration. Removal of the hydrogen atoms passivating nitrogen atoms is enhanced by annealing at high temperatures. Therefore, the concentration of ionized acceptors (atoms) increases, then, the hole concentration increases as the annealing temperature is increased. It has been reported that free oxygen is generated by annealing at temperatures higher than 900 ℃[15]. Some of these free oxygens will probably act as acceptors.

As the annealing temperature was increased from 800 to 1000 ℃, the resistivity decreased because the hole concentration increased quite a bit although the carrier mobility slightly decreased. The low carrier mobility in the p-type ZnO thin films suggests that acceptor compensation occurred actively [16]. Therefore, it may be concluded that the optimum annealing temperature for p-type ZnO films doped with nitrogen must be 800 ℃ or higher.

Low-temperature PL analyses and Hall-effect measurements were carried out for the sample annealed at 1000 ℃ and the PL spectrum is shown in Fig. 2. The peak located at 3.36 eV is attributed to the near band-edge (NBE) emission of excitions bound to donors (D°X). The peak at 3.32 eV is due to the NBE emission of excitions bound to acceptors (A°X) associated with NO. This result agrees well with Look's report on the low temperature PL of nitrogen-doped ZnO[17].

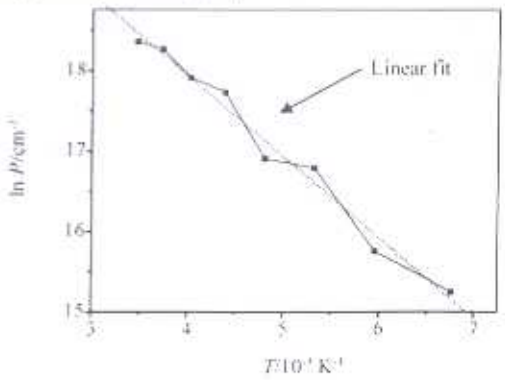

Fig. 2. Arrhenius plot of carrier concentrations for nitrogen-doped ZnO thin films grown by using ALE on basis of time-dependent Hall effect measurement.

Table 1. Carrier concentrations, the carrier mobilities and electrical resistivities of nitrogen-doped ZnO thin films grown by using ALE and annealed at different substrate temperatures along with those of an as-grown ZnO thin film.

Annealing temperature	Type	Carrier concentration/ cm^3	Carrier mobility/ $(cm/(Vs)^{-1})$	Resistivity/ $(\Omega \cdot cm)$
As-grown	n	9.20×10^{15}	13.45	50.5
(((0)	P	–	1.13	–
800	P	2.16×10^{16}	1.08	268.0
1000	P	3.71×10^{17}	0.92	18.3

Fig. 2 shows an Arrhenius plot of the carrier contraction for nitrogen-doped ZnO obtained from time-dependent Hall measurements. A least-squares fit to the Arrhenius plot gave the activation energy of an acceptor as $E_A \approx 86$ meV, which agrees well with the acceptor energy of 90 meV in the dark reported by Claflin *et al.*[18]. According to Alves *et al.*'s report[19], the donor binding energy in ZnO is 50 meV. Therefore, it can be concluded that the dominant carrier in the nitrogen-doped ZnO film grown by using ALE is acceptor. This is another evidence for p-type ZnO.

4. Conclusions

p-type ZnO thin films were grown by using ALE with ammonia as a doping source gas. All the as-grown ZnO thin films doped with nitrogen were found to be n-type, but were converted to p-type by annealing in an oxygen atmosphere. Post-annealing seemed to be indispensable for obtaining p-type ZnO because it removed the hydrogen atoms passivating the nitrogen atoms effectively. The nitrogen-doped ZnO thin films annealed at 1000 ℃ showed p-type semiconductor characteristics, the highest hole concentration of which was 3.71×10^{17} cm^{-3}. The annealing temperature for ammonia-doped ZnO thin films should be 800 ℃ or higher.

The existence of a peak for the near band-edge emission of excitons bound to acceptors (A^0X) at 3.32 eV was confirmed by using low-temperature PL. Also, a least-squares fit to an Arrhenius plot obtained by using time-dependent Hall measurements gave the activation energy of the acceptor as $E_A \approx 86$ meV, which agrees with other reported values.

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