Stable *p*-type ZnO films grown by atomic layer deposition on GaAs substrates and treated by post-deposition rapid thermal annealing

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ABSTRACT

Long-term stable *p*-type ZnO films were grown by atomic layer deposition on semi-insulating GaAs substrates and followed by rapid thermal annealing (RTA) in oxygen ambient. Significant decrease in the electron concentration and increase in the hole concentration, together with the intensity enhancement of acceptor-related A^oX spectral peak and the shift of bound exciton peak from D^oX to A^oX in the low-temperature photoluminescence spectra, were observed as the RTA temperature increased. Conversion of conductivity from intrinsic *n*-type to extrinsic *p*-type ZnO occurred at the RTA temperature of 600 °C. The *p*-type ZnO film with a hole concentration as high as 3.44×10^{20} cm^{-3} and long-term stability up to 180 days was obtained as the RTA treatment was carried out at 700 °C. The results were attributed to the diffusion of arsenic atoms from GaAs into ZnO as well as the activation of As-related acceptors by the post-RTA treatment.

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1. Introduction

ZnO is a very promising material for ultraviolet photonic devices due to its wide direct band gap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature. However, a major obstacle to the development of ZnO-based photonic devices is the difficulty in fabricating stable *p*-type ZnO with high hole concentration. Native crystallographic defects of interstitial Zn (Zn_i), oxygen vacancy (V_O), etc. [1,2] and unintentional incorporation of foreign impurities (such as hydrogen [3]) tend to behave as donors, which result in intrinsic *n*-type conductivity of ZnO. Hence, the achievement of stable *p*-type ZnO with high hole concentration is rather challenging due to compensation of the acceptors by a large amount of electrons supplied by the native defects. Nevertheless, researchers have proposed several ways to realize *p*-type ZnO [4–20]. The crystal growth techniques such as pulsed laser deposition [4–7], radio-frequency magnetron sputtering [8–13], molecular beam epitaxy [14,15], metal-organic chemical vapor deposition [16–18], and atomic layer deposition (ALD) [19,20], have been reported to produce ZnO films. Among these techniques, ALD is a noteworthy technique to grow high-quality ZnO films owing to its self-limiting and layer-by-layer growth features. ALD offers many benefits, such as easy and accurate thickness control, conformal step coverage, high unifor-

mity over a large area, low defect density, good reproducibility, and low deposition temperatures [21]. Our previous study had demonstrated high-quality ZnO films grown on *c*-sapphire substrates using ALD and treated by post-deposition annealing [22]. The results exhibited nearly defect-free photoluminescence (PL) and low-threshold optically-pumped stimulated emission, indicating the high crystal quality of the ZnO films grown by ALD coupled with the post-annealing treatment. In this paper, we present long-term stable *p*-type ZnO films with high hole concentration grown by ALD on semi-insulating GaAs substrates and treated under the appropriate post-deposition rapid thermal annealing (RTA) conditions. The post-RTA treatment was aimed at facilitating the diffusion of arsenic atoms from GaAs to ZnO and activating the As-related acceptors. The *p*-type ZnO film with a high hole concentration of 3.44×10^{20} cm^{-3} and long-term stability up to 180 days was achieved.

2. Experimental procedure

High-quality ZnO films were deposited on commercially available semi-insulating (100) GaAs substrates using the ALD technique. The size of the GaAs substrates was about 2×2 cm^2. $Zn(C_2H_5)_2$ (diethylzinc, DEZn) and H_2O vapor was used as the precursor of zinc and oxygen for the growth of ZnO. The precursors were alternately pulsed into the reaction chamber in an N_2 carrier gas flow during the ALD process. The durations of each DEZn and H_2O pulse were 0.01 and 0.015 s, and each DEZn or H_2O pulse was followed by a 5 s N_2 purge. The deposition temperature was 180 °C at which the ZnO growth rate was about

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0.18 nm per ALD cycle. These deposition parameters have been investigated as the optimal ALD condition for ZnO in our previous reports [22–24]. 1100 ALD cycles were applied to grow the ZnO film and the resulting film thickness was about 200 nm, which was confirmed by an ellipsometry. After deposition of ZnO, the samples were treated by RTA at 500, 550, 600, 650, and 700 °C in oxygen atmosphere for 3 min, so as to improve the crystalline quality, facilitate thermal diffusion of arsenic atoms from GaAs substrates into the ZnO films, and activate the As-related acceptors.

Ecopia HMS-3000 Hall-effect measurement system in the van der Pauw configuration was used to measure the resistivity, carrier density, mobility, conductivity type of the films. The samples were cut into the square size about 0.7×0.7 cm^2 in the Hall-effect measurements. The four corners of the specimens were soldered by small indium blobs for the ohmic contacts. The conductivity type of the ZnO films can also be confirmed by the polarity of Seebeck voltage which is generated by a thermal electromotive force (emf) due to a temperature gradient across materials (called Seebeck test). In Seebeck test, heat was applied to the indium contact on the sample by touching the heated soldering iron on it. A multimeter was used to measure the polarity of voltage difference between the heated and un-heated contacts, and then the conduction type can be determined. X-ray photoelectron spectroscopy (XPS) spectra of the samples were measured by the PHI 5000 VersaProbe Scanning ESCA Microprobe. For the low-temperature PL measurement, samples were placed into a closed cycle helium refrigerator to keep the temperature at 14 K. A 30-mW continuous-wave He–Cd laser ($\lambda = 325$ nm) was used as the excitation source. A computer-controlled SpectroPro 2300i monochromator, conventional lock-in amplifier, and photomultiplier tube were utilized to record the PL spectra. The PL spectra were measured using the standard backscattering configuration, where the light emissions from top surface of the ZnO layers were collected.

3. Results and discussion

Fig. 1(a), (b), and (c) shows the dependence of carrier concentration, mobility, and resistivity on the temperature of post-RTA treatments characterized by Hall-effect measurement. The label "AS" on the horizontal axis of Fig. 1 denotes the as-deposited ZnO sample. In Fig. 1(a), the as-deposited ZnO film shows the intrinsic n-type conductivity with an electron concentration of 3.10×10^{19} cm^{-3}. The high electron concentration in the as-deposited ZnO film might be due to the decomposition of the DEZn at the ALD temperature of 180 °C, resulting in a Zn-rich composition and a lot of oxygen vacancies (which are generally regarded as the donors) in the ZnO films [25,26]. For the specimens treated by the post-RTA, the electron concentration decreased to 1.71×10^{17} cm^{-3} at 500 °C and further dropped to 1.98×10^{16} cm^{-3} at 550 °C, which was 2–3 orders of magnitude lower than that of the as-deposited film. N-type conductivity was converted to p-type as the RTA temperature was greater than 600 °C. One can observe that a hole concentration as high as 3.44×10^{20} cm^{-3} was obtained at the RTA temperature of 700 °C, which was about two orders of magnitude higher than that at 600 °C (4.32×10^{18} cm^{-3}). In addition, the Seebeck test exhibited a positive voltage at the cold end of the samples treated by RTA at the temperatures from 600 to 700 °C, clearly indicating the p-type conductivity. Such significant decrease in the electron concentration and increase in the hole concentration in ZnO of the RTA-treated specimens are mainly attributed to the following mechanisms: (1) Ambiance of oxygen gas in the post-RTA process might effectively convert the Zn-rich composition to ZnO and reduce the oxygen vacancies [11]. Accordingly, the electron concentration decreased. (2) Diffusion of arsenic atoms into the ZnO films from GaAs substrates and activation of As-related acceptors (As$_{Zn}$-2V$_{Zn}$) in ZnO by the RTA treatment [4,8–10,27,28]. For the RTA treatments at 500 and 550 °C, the amount of As-related acceptors was insufficient to supply holes so as to compensate for the plentiful background electrons in ZnO.
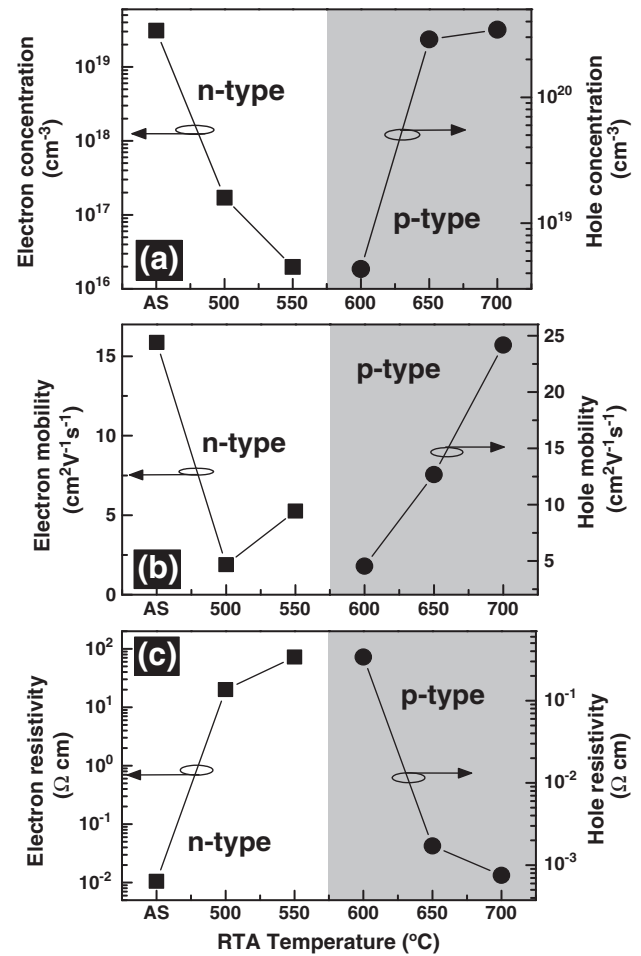

Fig. 1. (a) Carrier concentration, (b) mobility, and (c) resistivity of the ZnO films as a function of the post-RTA temperature.

Thus the conductivity had not been converted to p-type yet. When the RTA temperature further increased, more arsenic atoms gained enough thermal energy to diffuse from GaAs into ZnO. As a result, transformation of the ZnO films from n-type to p-type conductivity was observed when the RTA temperature was greater than 600 °C. The XPS spectra of the as-deposited and RTA-treated (at 700 °C) ZnO films were presented in Fig. 2. As compared with the as-deposited film, an arsenic 2p core-level peak at binding energy of 1325 eV was observed in the RTA-treated samples. It may verify the diffusion of arsenic atoms into the ZnO films by the RTA treatment.
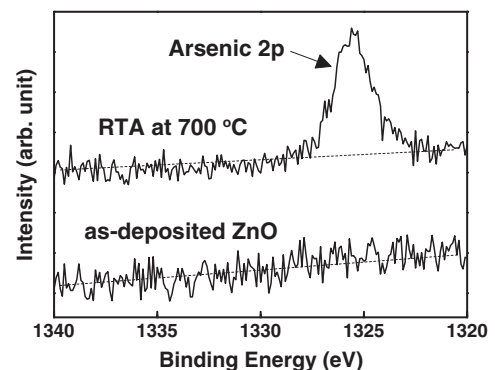

Fig. 2. X-ray photoelectron spectroscopy (XPS) spectra of the as-deposited and RTA-treated (at 700 °C) samples.

Fig. 1(b) demonstrates that when the sample was treated by the post-RTA at 500 °C, the electron mobility decreased to 1.89 cm^2 V^{-1} s^{-1} as compared with that of the as-deposited sample (15.87 cm^2 V^{-1} s^{-1}). Arsenic diffusion into the ZnO films may be responsible for the decrease in the electron mobility. A slight increase in electron mobility was seen at the RTA temperature of 550 °C. One can clearly observe that the hole mobility significantly increased from 4.53 to 24.2 cm^2 V^{-1} s^{-1} as the RTA temperature increased from 600 to 700 °C, which may be attributed to the improvement in crystalline quality of the ZnO films by the RTA treatment. In comparison with the as-deposited sample, significant increase in the resistivity after the RTA treatments at 500 and 550 °C, as shown in Fig. 1(c), results from the drastic drop in the electron concentration. On the other hand, considerable increment of the hole concentration and mobility leads to the remarkable decrease in the resistivity with the increase in the RTA temperature from 600 to 700 °C, achieving a p-type ZnO films with resistivity as low as 7.51 × 10^{-4} Ω-cm. This p-type conductivity in ZnO was further confirmed by the removal of the ZnO films using wet chemical etching. The Hall effect measurement on the remaining GaAs substrate exhibited a very week p-type conductivity with resistivity as high as 1.6 × 10^3 Ω-cm, ascribed to the diffusion of zinc atoms from ZnO into the semi-insulating GaAs substrate. Therefore, it can be deduced that the measured p-type resistivity as low as 7.51 × 10^{-4} Ω-cm mainly originate from the post-annealed ZnO film, not from the GaAs substrate.

Fig. 3 shows the room-temperature PL spectra of the ZnO films treated by RTA at the temperatures from 500 to 700 °C. All the PL spectra exhibited a significant near-band-edge emission and nearly free of the defect-related bands. The absence of light emission from oxygen vacancies and zinc interstitials in the visible region indicates the native donor-type defects were suppressed in the ZnO films grown by ALD and treated by the post-RTA process. The spectral peaks of all samples were around 3.275 eV with fluctuations within 10 meV. The local strain caused by different atomic sizes between the As-related acceptors and the host lattice results in perturbation of the band edge, which accounts for the fluctuations of PL spectral peaks. The great increase in the PL intensity with the RTA temperature could be assigned to the re-crystallization and termination of the defects in ZnO by the RTA treatment.

Fig. 4 shows the low-temperature PL spectra of the RTA-treated samples at 14 K. Two remarkable spectral peaks appear in the spectra. The spectral peak at 3.32 eV can be identified as the transition from free electrons to the acceptor state (FA) [4]. Another spectral peak around 3.36–3.37 eV is attributed to the superposition of radiative recombinations from acceptor-bound excitons (A^{o}X) at 3.36 eV and donor-bound excitons (D^{o}X) at 3.37 eV [4]. With the increase in the RTA temperature, it is clearly seen that the spectral peak around 3.36–3.37 eV gradually shifted from D^{o}X to A^{o}X, suggesting the decrease in the electron concentration and increase in the hole concentration due
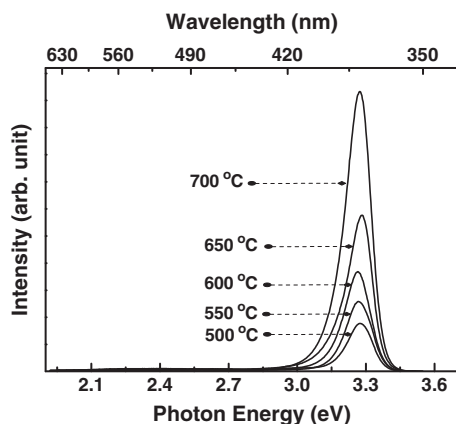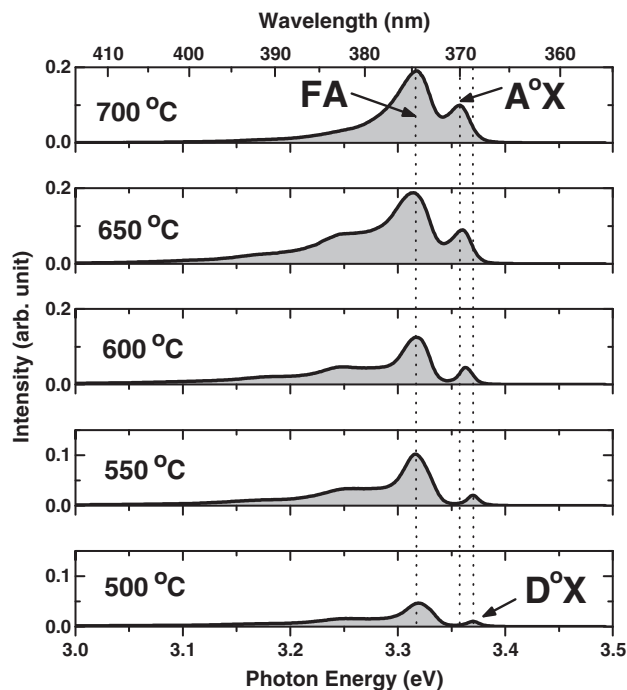

Fig. 4. PL spectra of the RTA-treated ZnO films at a low temperature of 14 K.

to the compensation of the donor states by a great amount of holes. In addition, the PL intensity of A^{o}X spectral peak increased significantly with the RTA temperature, indicating the considerable increase in the amount of acceptors caused by diffusion of arsenic atoms and activation of As-related acceptors in the ZnO films. The results are in good agreement with the electrical characterization of ZnO films as shown in Fig. 1.

Table 1 shows the hole concentration, mobility, and resistivity of the samples treated by RTA at 700 °C at the first day, as well as 30, 60, 90, 120, 150, and 180 days later. One can clearly see that all the electrical characteristics of the samples are stable with time. Noticeable degradation in the p-type conductivity of the ZnO film was not observed in this study.

4. Conclusions

Long-term stable p-type ZnO films were prepared on semi-insulating GaAs substrates using ALD and treated by post-RTA at the temperatures from 600 to 700 °C in the ambience of oxygen gas. The RTA treatment facilitates the diffusion of arsenic atoms from GaAs into ZnO and the activation of As-related acceptors, leading to significant decrease in the electron concentration and increase in the hole concentration, as well as the shift of spectral peaks from D^{o}X to A^{o}X and the intensity enhancement of A^{o}X peak in the low-temperature PL spectra. The presence of arsenic in the ZnO films was confirmed by the XPS spectrum. As the sample was treated by RTA at 700 °C, high-quality p-type ZnO

Fig. 3. PL spectra of the RTA-treated ZnO films at room temperature.

Table 1
Hole concentration, mobility, and resistivity were measured at the first day, and 30, 60, 90, 120 and 180 days later of the sample treated by RTA at 700 °C.

Time (days)	Concentration (10^{20} cm^{-3})	Mobility (cm^2 V^{-1} s^{-1})	Resistivity (10^{-4} Ωcm)
1	3.44	24.2	7.52
30	3.24	25.6	7.52
60	3.24	25.6	7.5
90	3.07	26.8	7.58
120	3.02	27.2	7.61
150	3.05	26.8	7.63
180	3.04	26.6	7.71

films were achieved with a hole concentration as high as 3.44×10^{20} cm^{-3}, resistivity as low as 7.51×10^{-4} Ω-cm, long-term stability up to 180 days, together with a nearly defect-free PL spectrum at room temperature. The study could provide a substantial advancement in fabricating stable p-type ZnO films for the applications of ZnO-based transistors and photonic devices.

Acknowledgment

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