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Annealing effects on the p-type ZnO films fabricated on GaAs substrate by atmospheric pressure metal organic chemical vapor deposition

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ABSTRACT

The effects of post-annealing conducted at 500–650 °C on structural, electrical and optical properties of ZnO film fabricated on GaAs (1 0 0) substrate by atmospheric pressure metal-organic chemical vapor deposition are investigated. X-ray diffraction analyses show that the Zn_3As_2 and $ZnGa_2O_4$ phases are produced for the specimens post-annealed at 500 °C and above. Hall measurements indicate that stable p-type ZnO films with hole concentration ranging from 4.7×10^{18} to 8.7×10^{19} cm^{-3} can be obtained by modulating the annealing temperature from 500 to 600 °C. In particular, room-temperature photoluminescence (PL) measurements indicate that the superior-quality p-type film could be achieved by a post-annealing treatment at 600 °C. Moreover, low temperature PL spectra at 10 K are dominated by the acceptor-related luminescence mechanisms for the films post-annealed at 550 °C and above. The ionization energy of acceptor was calculated to be 133–146 meV, which is in good agreement with that theoretically predicted for the As_{Zn}–$2V_{Zn}$ complex in ZnO. The interdiffused arsenic atoms in the film post-annealed at 600 °C are suggested to form the As_{Zn}–$2V_{Zn}$ complex quite effectively, resulting in the most enhanced p-type conductivity and improved material quality.

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1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor with a direct band gap of 3.37 eV at room temperature and a large exciton bind energy of 60 meV, which makes it a good candidate for the applications in highly efficient and stable room temperature ultra-violet (UV) lasers and light emitting diodes [1–3]. To achieve such goals, the growth of high-quality p-type ZnO is required. However, the fabrication of p-type ZnO films by doping is difficult due to the compensation effect of native n-type carriers released by the donor-type defects such as oxygen vacancies and zinc interstitials [4,5].

Recently, several groups have reported the growth of p-type ZnO by doping group V elements N [6], P [7], As [8], and Sb [9]; however, their behavior in the lattice and the corresponding electronic levels are poorly understood. Among the group V elements examined, nitrogen has been regarded as the most suitable impurity for p-type doping in ZnO due to its atomic radius is similar to that of oxygen. However, numerous experimental efforts made by different groups to implement this idea have not resulted in stable and reproducible p-type material yet. Moreover, J.L. Lyons et al. even reported that N is actually a deep acceptor in ZnO with an exceedingly high ionization energy of 1.3 eV based on their theoretical calculations [10]. Therefore, the suitability of N-doping for p-type conductivity in ZnO is required to be examined in more detail.

On the other hand, it seems convincing that the behavior of other group V elements, such as As and Sb, as acceptors in ZnO does not stem from a simple substitution on the group VI-site, but rather from complexes of the type $As(Sb)_{Zn}$–$2V_{Zn}$ with low enthalpies of formation [11]. A direct evidence for arsenic as a zinc-site impurity in ZnO has been presented by U. Wahl et al. using the emission channeling technique [12]. To achieve this purpose, several researchers have prepared ZnO films on GaAs substrates and annealed the specimens to have As atoms diffuse from the substrate into the ZnO films. In this way, p-type ZnO films have been obtained somehow under a strict annealing condition [6,13–15].

This work reports the p-type conductive behavior of ZnO films fabricated on semi-insulating GaAs substrate, regardlessly as-grown or post-annealed, using atmospheric pressure metal organic chemical vapor deposition (AP-MOCVD) technique. In particular, the effects of post-annealing on the p-type characteristics are systematically investigated by analyzing the structural, electrical, and

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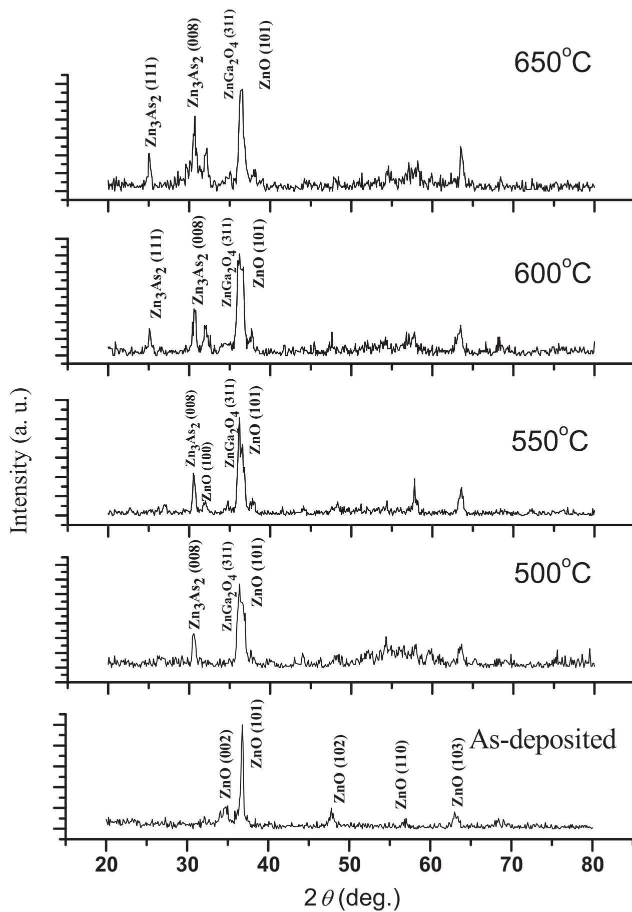

Fig. 1. XRD patterns of ZnO films as deposited and post-annealed at different temperatures from 500 to 650 °C.

optical properties of the films post-annealed at various temperatures. Additionally, the mechanisms responsible for the results obtained are discussed.

2. Experiment

ZnO thin films were deposited on the semi-insulating GaAs (1 0 0) substrate (henceforth, refer to as ZnO/GaAs) by a custom-made one-flow AP-MOCVD system. The growth chamber is a water-cooled vertical reactor. The substrate susceptor is made of graphite, 2 in. in diameter and coated with a SiC film on top surface by CVD technique. Diethylzinc (DEZn) and deionized water (H_2O) were used as the sources of Zn and O, respectively. The growth of ZnO layer was conducted at 450 °C with the flow rates of DEZn and H_2O maintained at 13.4 and 45.7 μmol/min, respectively to have a constant gas flow ratio of $[H_2O]/[DEZn]$ (VI/II ratio) = 3.42. After growth, the 2-in.-diameter wafer was cut into small pieces with the size of 10 mm × 10 mm. Some of the specimens were further annealed in oxygen atmosphere using a rapid thermal annealing system to activate the p-type conductivity of films deposited. The temperature set for post-annealing treatment has been varied from 500 to 650 °C with an increase step of 50 °C. The crystal structure of ZnO thin films was analyzed by x-ray diffraction (XRD, Bruker AXS Diffraktometer D8) using Cu K_α line as the x-ray source (λ = 1.54056 Å) for a 2θ range 20–80°. The resistivity, carrier concentration and mobility of films were measured at room temperature by Hall measurements using the van der Pauw method. The optical properties were examined by photoluminescence (PL) measurements performed at room temperature and 10 K. PL spectra were excited by the 325-nm line of a He-Cd laser with an excitation power of 15 mW.

3. Results and discussion

The XRD patterns of the as-grown ZnO/GaAs(1 0 0) sample and those post-annealed at various temperatures ranging from 500 to 650 °C are shown in Fig. 1. Obviously, all the films show polycrystalline structure with various crystallographic planes being

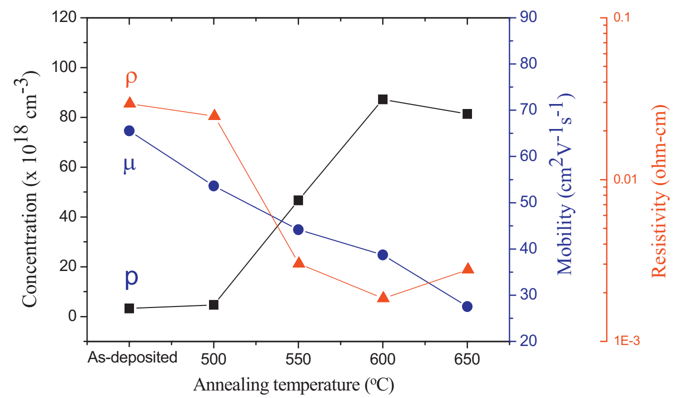

Fig. 2. Resistivity (ρ), mobility (μ), and carrier concentration (p) of ZnO films: as-deposited and post-annealed at different temperatures.

detected. The as-grown film exhibits a grain structure with a dominant plane orientation of (1 0 1). For the samples with the post-annealing conducted at 500 and 550 °C, the intensity of (1 0 1) peak greatly decreases and the XRD patterns become dominated by the other two diffraction peaks at about 30.4° and 35.8° instead. With a further increase in annealing temperature to over 550 °C, another diffraction peak appears at about 25.2°. The presence of XRD peaks at 25.2°, 30.4° and 35.8° demonstrate the formation of Zn_3As_2(1 1 1) [16], Zn_3As_2(0 0 8), and $ZnGa_2O_4$(3 1 1) [17] phases, respectively. These structures were formed due to the interdiffusion of As and Ga atoms into the deposited film, followed by the bonding reactions between them and host Zn and O atoms. The phases of Zn_3As_2 and $ZnGa_2O_4$ mentioned above were not found in previous reports concerned with the thermal diffusion effect on similar ZnO/GaAs material structures fabricated by various methods [6,13–15]. It is also noticeable that the intensities of Zn_3As_2(1 1 1), Zn_3As_2(0 0 8) and $ZnGa_2O_4$(3 1 1) increase with increasing annealing temperature. This manifests that the number of As and Ga atoms introduced into the AP-MOCVD grown film can be controlled by the annealing temperature.

Fig. 2 displays the resistivity (ρ), Hall mobility (μ) and hole concentration (p) of ZnO films as a function of the film annealing temperature. It is noteworthy that even the as-deposited ZnO has already shown p-type conductivity, with ρ, μ, and p measured as 2.954×10^{-2} Ω cm, 65.6 cm^2 V^{-1} s^{-1}, and 3.22×10^{18} cm^{-3}, respectively. As known, the intrinsic conductivity of ZnO is greatly influenced by the point defects produced therein. The p-type conductivity of undoped ZnO has been reported to be possibly due to the formation of Zn vacancies [18]. Our previous investigation also demonstrated that intrinsic p-type ZnO films with the hole concentration 1.5–3.3 × 10^{17} cm^{-3} can be achieved on Si(1 0 0) substrate [19]. In that study, we used the same precursors as now and also conducted the film growth in an oxygen-rich condition (VI/II ratio = 1.1–2.74) to have native defect V_{Zn} related acceptors be the origin of p-type conductivity. However, the elevation of about one order of magnitude in the hole concentration (3.22×10^{18} cm^{-3}) for the as-grown film here seems hard to be completely attributed to the same reasoning. As introduced before, arsenic should also play a part in the p-type doping, which would increase the free hole concentration in this film. Particularly, this behavior is emphasized by the post-annealing as described below. It can be seen that the resistivity of the deposited film decreases initially with increasing annealing temperature and reaches a minimum value of 1.85×10^{-3} Ω cm at the annealing temperature = 600 °C. Then it increases conversely with a further increase of annealing temperature to 650 °C. Whereas, the hole concentration increases gradually with increasing the annealing temperature from 500 to 600 °C and reaches a maximum value of 8.72×10^{19} cm^{-3}. However, a further

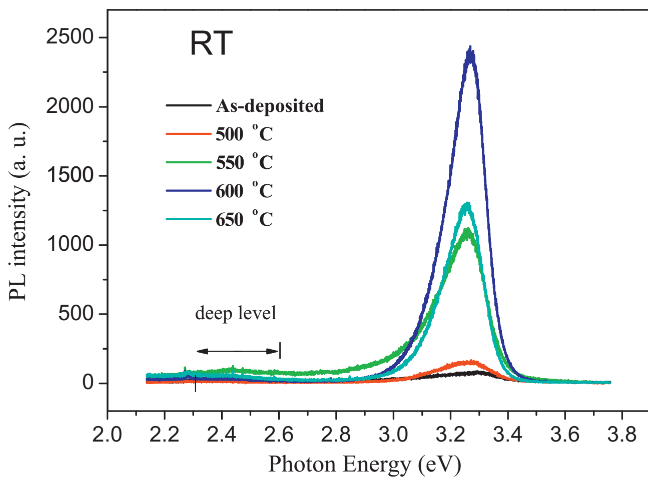

Fig. 3. RT-PL spectra of ZnO films: as-deposited and post-annealed at different temperatures.

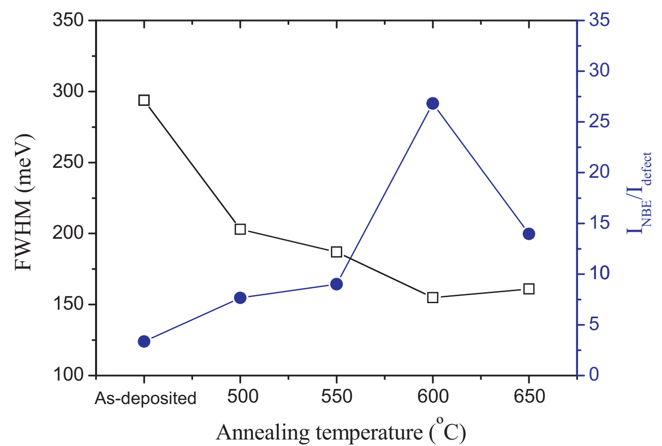

Fig. 4. Variation of $I_{NBE}/I_{deep\text{-}level}$ ratio and FWHM of RT-PL spectrum as a function of post-annealing temperature. The data from the as-deposited sample is also given for comparison.

increase of annealing temperature to 650 °C makes the hole concentration decrease. The reduction of hole concentration may be due to the enhanced interdiffusion of Ga atoms to form the donors of Ga_{Zn}, which induce the carrier compensation phenomenon. Moreover, as the annealing temperature is increased from 500 to 650 °C, the mobility of film monotonously decreases as shown in Fig. 2. This is probably due to that both As and Ga atoms introduced into the ZnO grown film not only contribute to the carrier generation but also introduce the scattering effect on carriers, which therefore reduces the Hall mobility. The reproducibility of the post-annealing effects on p-type conductivity has been recognized for the specimens both from the same wafer and from different growth runs. It should be mentioned that the electrical properties of all the fabricated films have been measured again 30 days later and the stability of electrical properties have been confirmed.

The PL measurements were performed to investigate the influence of annealing temperature on the optical properties of ZnO thin film. Fig. 3 shows the room-temperature PL spectra (RT-PL) of the as-deposited film and those annealed at 500, 550, 600, and 650 °C, respectively. Obviously, the PL results are strongly dependent on the annealing temperature. Both the as-deposited specimen and that annealed at 500 °C exhibit relatively weak near-band-edge (NBE) emissions around 3.291 and 3.278 eV, respectively. However, as the annealing temperature is increased to 550 °C and above, the NBE emission around 3.26 eV intensifies greatly with the intensity arriving at the maximum for the film annealed at 600 °C. This result indicates that the film quality has been improved by elevating the temperature to 550 °C and above for post-annealing treatment. Even an excess structure of $Zn_3As_2(1\,1\,1)$ is demonstrated in the XRD result, the optical property of films seems not to deteriorate. Fig. 4 gives a more clear comparison between the RT-PL spectra obtained. Here, the intensity ratio of NBE emission and deep-level emission ($I_{NBE}/I_{deep\text{-}level}$) as well as the full width at half maximum (FWHM) of NBE emission is plotted as a function of annealing temperature. As shown, the FWHM of RT-PL for the film annealed at 600 °C demonstrates a lowest value of 155 meV. Also, the $I_{NBE}/I_{deep\text{-}level}$ ratio increases with increasing annealing temperature and exhibits the maximum for the film annealed at 600 °C. However, it decreases again with increasing annealing temperature further, which implies that some excess defects are produced in the film when the annealing is carried out at a temperature high to 650 °C. Possible causes of these defects include the decomposition of ZnO film and too many interdiffused As and Ga atoms, which lead to the formation of structural defects causing the deep-level emission [20]. Clearly, the results of RT-PL are in good agreement with those obtained from XRD and Hall analyses.

To investigate further the optical properties and detailed luminescence mechanisms of films, low temperature PL (LT-PL) measurements were performed at 10 K and the results are collected in Fig. 5. As shown in Fig. 5(a), the LT-PL spectrum of the

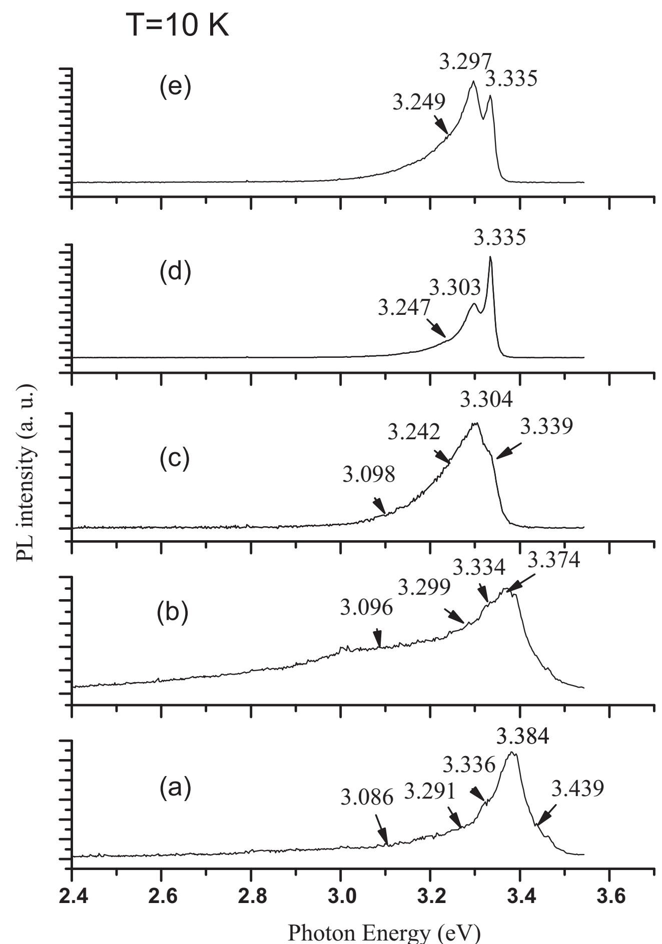

Fig. 5. LT-PL spectra of (a) as-deposited film and those post-annealed at temperatures: (b) 500, (c) 550, (d) 600, and (e) 650 °C.

as-deposited specimen exhibits five emission lines at 3.439, 3.384, 3.336, 3.291, and 3.086 eV, respectively. The lines at 3.384 and 3.439 eV are assigned to the first ($n = 1$) and the second ($n = 2$) excited state transitions of free exciton (FX), respectively [21]. The presence of emissions originated from free excitons might manifest the good quality of film produced. Furthermore, the line at 3.336 eV has been identified as a neutral acceptor bound exciton (A^0X) [14,22] and those at 3.291 and 3.086 eV are assigned to the free electron to neutral acceptor (FA) transition [22,23] and zinc vacancy (V_{Zn}) related emission [24], respectively. These features suggest that the As atom-related acceptors and native defect of V_{Zn} exist in the as-deposited film to induce the p-type conductivity therein. On the other hand, the LT-PL spectra from the specimens conducted with the post-annealing are displayed in Figs. 5(b)–(e). For the specimen post-annealed at 500 °C, the spectrum is still dominated by the line at 3.374 eV related to FX [25] except that the relative magnitude is much reduced. Namely, both the A^0X and FA lines specified for the as-deposited specimen intensify with increasing annealing temperature and situated at 3.334–3.339 and 3.297–3.304 eV, respectively. These two peaks even dominate the whole PL spectrum for the specimens post-annealed at temperatures of 550 °C and above. In particular, as shown in Fig. 5(d), the dominance of a sharp A^0X peak is evident for the spectrum of the film post-annealed at 600 °C. This result associated with that the same specimen has demonstrated the highest hole concentration in previous Hall measurement suggest the superior quality of p-type film has been achieved. Else, the lines situated at energies ranging from 3.242 to 3.249 eV in Fig. 5(c)–(e) are suggested to be induced by the donor–acceptor pair (DAP) recombination [14,23]. It is also worth noting that the intensity of A^0X emission is reversed by that of FA emission for the sample post-annealed at 650 °C. This is considered to be due to the introduction of excess Ga elements, which are easy to become donors in ZnO film, dissociating the A^0X and therefore enhancing both FA and DAP recombination simultaneously. The acceptor energy of As-related dopant can be estimated by [22,23]: $E_A = E_g - E_{FA} + k_BT/2$, where E_g is the intrinsic band gap and E_{FA} the emission energy released by the free electron-acceptor level transition. Using $E_g = 3.437$ eV reported elsewhere [25] and the values specified in the PL spectra for E_{FA}, the value of E_A is estimated to be 133–146 meV. This value is in good agreement with theoretical ionization energy of 150 meV predicted for the As_{Zn}–$2V_{Zn}$ complex [11] as a shallow acceptor in ZnO. Although the microstructures with Zn_3As_2 phase exhibited for the post-annealed samples are also likely to be the origin of p-type conduction, the corresponding activation energy is high to about 930 meV [26]. Therefore, the doping mechanism of the present p-type ZnO film should be much more possible to be the formation of As_{Zn}–$2V_{Zn}$ complex. Here, the As atom is being substituted for Zn site to act as a donor, but is accompanied by two Zn vacancies to have a net effect of supplying one hole per complex defect [11].

As indicated by the XRD analyses, the post-annealing conducted at different temperatures result in the interdiffusion of As and Ga atoms across the ZnO/GaAs interface with different degrees. The diffusion of As atoms into ZnO film is favorable for forming As_{Zn}–$2V_{Zn}$ complex therein. However, the diffusion of Ga atoms into ZnO film is also inevitable, which will result in the compensation effect on doping. The post-annealing treatment performed at 600 °C is thus suggested to have the interdiffused arsenic atoms form As_{Zn}–$2V_{Zn}$ complex quite effectively, which therefore induced the highest p-type conductivity and the superior film quality.

4. Conclusions

Stable p-type ZnO films can be fabricated on semi-insulating GaAs substrate by AP-MOCVD using DEG and H_2O as the source precursors and a gas flow ratio of $[H_2O]/[DEG] = 3.42$. The hole concentration of the as-deposited film is 3.22×10^{18} cm^{-3}, while that of the specimens post-annealed at 500–600 °C ranges from 4.7×10^{18} to 8.7×10^{19} cm^{-3}. The doping mechanism for the p-type ZnO films obtained is suggested to be the formation of As_{Zn}–$2V_{Zn}$ complex. Conclusively, the interdiffusion of As and Ga atoms across the ZnO/GaAs interface is enhanced by the post-annealing treatment. In particular, the post-annealing treatment conducted at 600 °C is found to be beneficial for obtaining the superior-quality p-type ZnO film.

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