Journal of Vacuum Science & Technology A

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Citation: Journal of Vacuum Science & Technology A **28**, 1307 (2010); doi: 10.1116/1.3484138
View online: http://dx.doi.org/10.1116/1.3484138
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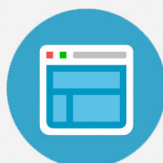

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Intrinsic *p*-type ZnO films fabricated by atmospheric pressure metal organic chemical vapor deposition

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(Received 5 February 2010; accepted 9 August 2010; published 23 September 2010)

The structural, electrical, and optical properties of ZnO films fabricated by atmospheric pressure metal organic chemical vapor deposition (AP-MOCVD) under various gas flow ratios of $[H_2O]/[DEZn]$ (VI/II ratio) ranging from 0.55 to 2.74 were systematically examined. Hall effect measurements exhibited an evident effect of the VI/II ratio on the conduction type of the intrinsic films. An *n*-type film was fabricated at the VI/II ratio=0.55; however, *p*-type ZnO films with the hole concentration of the order of 10^{17} cm^{-3} could be achieved at VI/II ratios higher than 1.0. In particular, the highest mobility of 91.6 cm^2/V s and the lowest resistivity of 0.369 Ω cm have been achieved for the specimen fabricated at the VI/II ratio=1.10. Moreover, room-temperature photoluminescence (PL) measurements demonstrated an interstitial Zn (Zn_i) donor defect related emission at 2.9 eV for the *n*-type film, while a Zn vacancy (V_{Zn}) acceptor defect related one at 3.09 eV for the *p*-type films. The existence of material intrinsic defects was further confirmed by low temperature PL measurements conducted at 10 K. Conclusively, the conduction type of undoped ZnO films deposited by AP-MOCVD is resolved by the VI/II ratio used, which causes the formation of various kinds of intrinsic defects, Zn_i otherwise V_{Zn}. *p*-type ZnO films with the hole concentration in the range of $(1.5-3.3)\times 10^{17}$ cm^{-3} can be achieved with good reproducibility by modulating a VI/II ratio the range 1.0–2.2 for the AP-MOCVD process. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3484138]

I. 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 applications in highly efficient and stable room-temperature ultraviolet lasers and light emitting diodes.[1–3] To achieve such goals, the growth of high-quality *p*-type ZnO is necessary. 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: As,[6] P,[7] and N,[8,9] but an explicit mechanism justifying these results is still lacking and the issue of reproducibility becomes the bottleneck in the development of related devices. In addition, some groups showed intrinsic *p*-type behavior in the ZnO films fabricated by different methods, such as pulsed laser deposition,[10,11] magnetron sputtering,[12,13] low pressure metal organic chemical vapor deposition,[14] plasma-assisted low pressure metal organic chemical vapor deposition,[15] and inductively coupled plasma enhanced chemical vapor deposition.[16] For all the intrinsic films mentioned in Refs. 10–16, the conduction type was changed from *n*-type to *p*-type by varying the oxygen pressure in the growth environment[10,12,14,16] or by conducting the film growth or postannealing at suitable temperatures[11,13,15] in O_2 environment.

In this work, we report on the fabrication of intrinsic *p*-type ZnO films by atmospheric pressure metal organic chemical vapor deposition (AP-MOCVD). We examine the effect of gas flow ratio of $[H_2O]/[DEZn]$ on the conduction

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type of the ZnO films by comparing their electrical and optical properties systematically and by analyzing the possible mechanisms responsible for the results.

II. EXPERIMENT

Undoped ZnO thin films were deposited using a custom-made, one-flow AP-MOCVD system. The substrates are 2 in. (111)-oriented, *p*-type Si wafers with a resistivity of 1–3 kΩ cm. 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 the top surface by a chemical vapor deposition technique. Diethylzinc (DEZn) and de-ionized water (H_2O) were used as the sources of Zn and O, respectively, and N_2 was used as the carrier gas. The growth of ZnO layer was conducted at 400 °C with the gas flow ratio of $[H_2O]/[DEZn]$ (VI/II ratio) being varied from 0.55 to 2.74. The growth time duration for all specimens was set for 40 min to achieve a thickness of about 500–600 nm, recognized by their cross-sectional scanning electron microscopy (SEM) images.

The crystal structure of the ZnO thin films was analyzed by powder X-ray diffraction using Cu K_α line as the x-ray source ($\lambda = 1.540\,56$ Å). Electrical resistivity, carrier concentration, and mobility of the ZnO thin films were evaluated by Hall effect measurements performed at room temperature using the four-probe van der Pauw configuration. The optical properties were examined by photoluminescence (PL) measurements performed at room temperature and 12 K. PL spectra were excited by the 325 nm line of a He–Cd laser.

III. RESULTS AND DISCUSSION

All the films produced were found to be of polycrystalline wurtzite structure with a dominant grain orientation of (101) regardless of the various VI/II ratios used for film deposition. However, there were evident effects of VI/II ratio on the electrical and optical properties of film as described below.

Before the Hall measurement, the current-voltage (*I-V*) characteristics of our specimens had been measured with two Ohmic contacts formed on the top ZnO film and the bottom *p*-Si substrate, respectively, to gain initiative knowledge of the conduction type of ZnO films fabricated. Figure 1 displays the *I-V* characteristics of the specimens examined and the inset in the lower right shows the schematic of the measurement structure. As shown, a rectifying behavior is found only for the specimen fabricated with the VI/II ratio of 0.55, demonstrating an *n*-type conductivity of the deposited film. However, nonrectifying behavior is observed for the specimens fabricated with the VI/II ratio equal to and higher than 1.1. On the same figure, the *I-V* characteristics of the *p*-Si substrate are also displayed for a reference. Obviously, the *p*-type conductivity has been achieved for the specimens fabricated with the VI/II ratio higher than 1.1. Note that all the nonrectifying *I-V* characteristics except that from *p*-Si substrate demonstrate a slight deviation from a straight line, manifesting that a weakly conducting heterojunction has been formed between the ZnO film and Si substrate. Hall effect measurements were then carried out to characterize in more detail the electrical properties of the films deposited at various VI/II ratios and the results are depicted in Fig. 2. Generally, the *p*-type substrate used would influence the Hall measurement of the *p*-type deposited film. However, this influence seems negligible here for the relatively low resistivities obtained in Fig. 2, probably because of the presence of the weakly conducting heterojunction mentioned above. The intrinsic *p*-type conductivity of ZnO was initially found in 1992 by Butkhuzi *et al.*[17] and confirmed later by some other groups.[12–16] All these findings have been completed through the adjustment of oxygen content in the growth/heat-treatment environment, leading to the conversion of conduction type. As is known, the *n*-type conductivity for ZnO can readily be achieved if the intrinsic (undoped) materials are deposited under zinc-rich conditions, or if they are extrinsically doped with group-III elements such as Al and Ga. However, it also depends on the deposition temperature and/or VI/II ratio for the ZnO films prepared. It is quite difficult for the undoped films to have definite *p*- or *n*-type conductivity. Usually, undoped ZnO films show *n*-type electrical properties due to the native point defects of oxygen vacancies (V_O) and Zn interstitials (Zn_i), which may be produced due to a low oxygen content in the film deposition

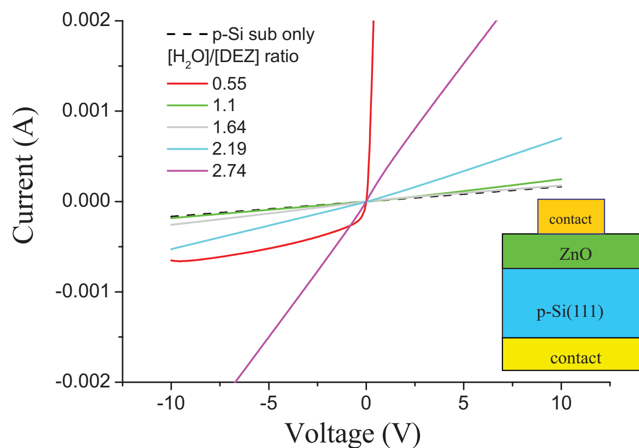

FIG. 1. (Color online) *I-V* characteristics taken from the Ohmic contacts to *p*-Si(111) and ZnO films produced with different VI/II ratios.

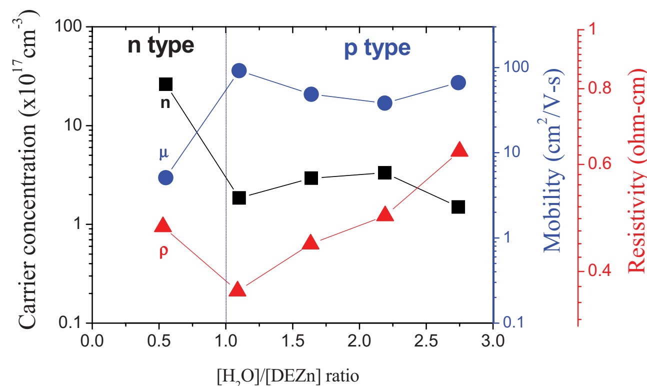

FIG. 2. (Color online) Carrier concentration, mobility, and resistivity of ZnO films deposited at various VI/II ratios.

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process. On the contrary, the intrinsic *p*-type conductivity of ZnO films can be expected for the film deposition to be conducted in an oxygen-rich condition because the sufficient content of oxygen included might produce native Zn vacancies (V_{Zn}), which would act as acceptors. It should be mentioned that the *p*-type doping effect of nitrogen originated from the deposition atmosphere of N_2 can be excluded according to the results of the specimen with the lowest VI/II ratio (0.55) and our previous study on glass substrate.[18] It is therefore considered that both V_O and Zn_i are the main native donor defects for the ZnO films deposited at VI/II ratio=0.55, which consequently featured the *n*-type conductivity for the ZnO films deposited. On the other hand, when the VI/II ratio was increased to higher than 1.0, namely, an oxygen-rich condition for the film deposition, the ZnO film converted its conduction to *p* type due to an increase in the concentration of the acceptor type defect V_{Zn}. The increase of hole concentration from 1.85×10^{17} to 3.33×10^{17} cm^{-3} for the films deposited at the VI/II ratios varying from 1.10 to 2.19 might suggest that more and more V_{Zn} defects have been produced in the films fabricated. It should be noted that the resistivity of the films produced at VI/II ratio =1.10–2.19 also increases from 0.369 to 0.491 Ω cm. This variation tendency is considered to be dominated by the Hall mobility, which decreases from 91.6 to 38.2 $cm^2\ V^{-1}\ s^{-1}$ with increasing the VI/II ratio from 1.10 to 2.19. However, the hole concentration of the film deposited at the highest VI/II ratio of 2.74 decreased. This is probably because the introduction of too many excess oxygen atoms might cause the formation of some complex defects involving V_{Zn}, the divacancy, $V_{Zn}V_O$, and the O-related defects, which either reduce the concentration of V_{Zn} itself or behave as a deep donor to compensate the effect induced by V_{Zn}.[19]

Figure 3(a) displays the room-temperature PL spectra of ZnO films with the PL intensity being normalized. Two emission lines are observable in the PL spectrum of the ZnO film fabricated at VI/II ratio=0.55. The near band edge emission at 3.33 eV is ascribed to free exciton recombination[20] and the deep level emission band at 2.9 eV is attributed to Zn_i.[21] This suggests that donors were formed in the ZnO film, as demonstrated in the Hall effect measurement above, an *n*-type conductive behavior. However, the PL spectra of the specimens fabricated with the VI/II ratio over 1.0 changed evidently as indicated in the same figure. The deep level emission was absent and a much sharper band with the energy ranging from 3.0 to 3.5 eV appeared instead. The luminescence peak energies involved in this emission band could be assigned after one of the spectra (VI/II ratio=2.19) was convoluted with Gaussian fittings. As illustrated in Fig. 4(b), three emission lines are resolved at around 3.28, 3.25, and 3.09 eV, which signify the emissions from free exciton,[22] free electron neutral acceptors,[22] and V_{Zn},[14] respectively. The presence of the weak V_{Zn}-related peak on the low-energy side of the PL spectra might suggest that V_{Zn} defects exist in the ZnO films fabricated with the VI/II ratio over 1.0, which played the role of acceptors and resulted in a compensation

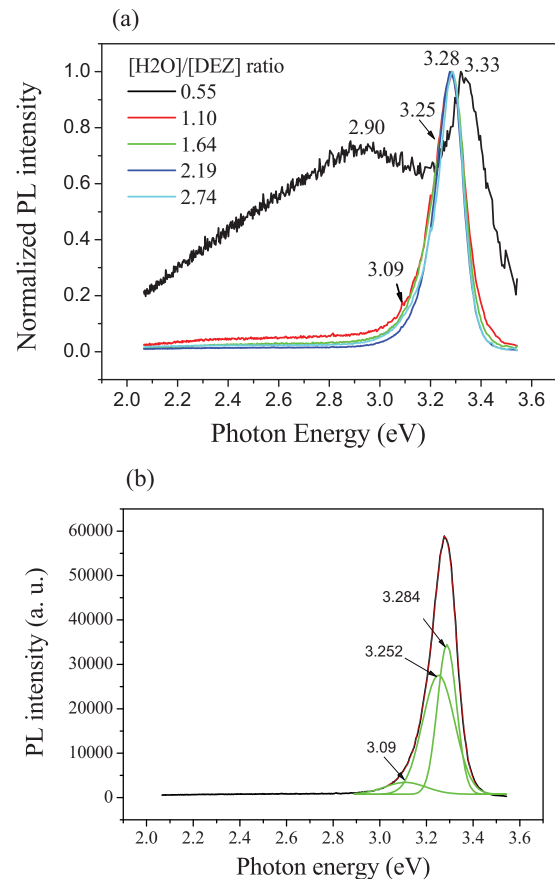

FIG. 3. (Color online) (a) Room-temperature PL spectra from ZnO films fabricated at various VI/II ratios. (b) Gaussian fitting to the PL emission of ZnO film produced at the VI/II ratio=2.19.

effect for electrons. This result is consistent with what have been obtained from the Hall effect measurements described above.

To investigate in some more detail the influence of VI/II ratio on the optical properties of the films fabricated, low temperature PL measurements were performed at 12 K. As demonstrated in Fig. 4(a), the PL spectrum of the ZnO film deposited at the VI/II ratio=0.55 is dominated by a broad line at 3.368 eV, probably due to the high concentration of electron concentration ($>10^{18}$ cm^{-3}). This emission was reported to feature a neutral donor bound exciton ($D\,^0X$) emission.[23] In addition to the $D\,^0X$ line, there are also emission lines related to the two-electron satellite (TES) transitions of $D\,^0X$ and the donor-acceptor-pair (DAP) transition peaking at 3.332 eV[24] and 3.230 eV,[25] respectively. In the effective-mass approximation, the difference between the energy of $D\,^0X$ line ($E_{D\,^0X}$) and that of TES related emission (E_{TES}) can be used to obtain the donor ionization energy (E_D) from $E_D=4/3(E_{D\,^0X}-E_{TES})$.[23] Using this equation, the E_D was estimated to be 48 meV, which is close to the energy level presented by donor energy Zn_i (50 meV).[26] Therefore, the ZnO film fabricated at the VI/II ratio=0.55 exhibits *n*-type conductivity originated from Zn_i donor-type defects, as regularly recognized. On the other hand, for the films deposited at the VI/II ratios ranging from 1.0 and 2.19, the

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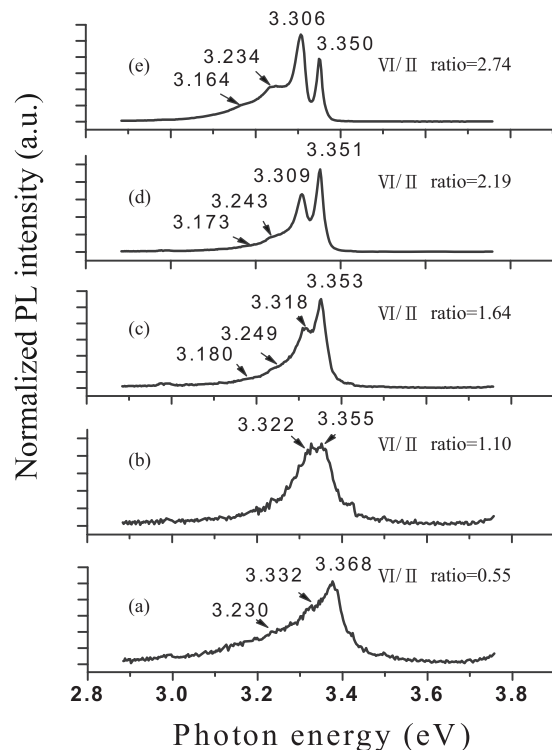

FIG. 4. 12 K PL spectra of undoped ZnO films deposited with different VI/II ratios.

PL spectra [Figs. 4(b) and 4(c)] were dominated by the line at 3.350–3.355 eV, characteristic of the exciton bound to neutral acceptor (A^0X) emission.[23,25,27,28] In addition, the peak situated at 3.306–3.322 eV is assigned to the free electron to neutral acceptor (eA_0) transition.[25,29] The line at 3.249–3.234 eV is considered to be due to the DAP transition.[23,25,29] Also, the line at 3.180–3.164 eV is assigned to the longitudinal optical (LO) phonon replica of DAP transition since a deviation between them is about 69–70 meV, approximating the energy of a LO phonon for ZnO (about 72 meV).[23,29] Moreover, it can be seen that when the VI/II ratio=2.19, the intensity of the A^0X line comes to a maximum and the Hall measurement also demonstrates a highest hole concentration. Then, both the A^0X emission line intensity and hole concentration decrease once the VI/II ratio is increased to 2.74. On the other hand, the eA_0 line intensifies all the way with the VI/II ratio and ultimately even surpasses the A^0X line. The results described above might manifest that modulating the VI/II ratio to an oxygen-rich condition for the AP-MOCVD process would essentially produce large quantities of native defect V_{Zn}, and V_{Zn}-related acceptors consequently result in the *p*-type conductivity of the undoped ZnO films. However, too heavily the excess oxygen atoms introduced into the ZnO film might somewhat cause oxygen interstitial atoms, oxygen antisite atoms beside the V_{Zn}. These defects may weaken the interaction between the free excitons and the neutral acceptors, and also possibly form some complex defects as described above, which therefore impede a further elevation of hole concentration by VI/II ratio. Nevertheless, there are still more efforts required to clarify the details of defect structures and their connections to the VI/II ratio used for the ZnO deposition.

IV. CONCLUSIONS

The effects of VI/II ratio on the conduction type of undoped ZnO films fabricated by AP-MOCVD have been investigated. The ZnO film fabricated at the VI/II ratio=0.55 exhibits *n*-type conductivity. However, the ZnO film fabricated at a VI/II ratio over 1.0 demonstrates *p*-type conductivity. In particular, an intrinsic *p*-type ZnO film with the highest mobility of 91.6 $cm^2/V\,s$, the lowest resistivity of 0.369 Ω cm, and a hole concentration of 1.85×10^{17} cm^{-3} have been achieved at the VI/II ratio=1.10. The origin of the conversion of conduction type for ZnO films produced was confirmed by PL measurements. Room-temperature PL measurements demonstrated a Zn_i donor defect related emission at 2.9 eV for the *n*-type film, while a V_{Zn} acceptor defect related emission at 3.09 eV for the *p*-type films. Moreover, the low temperature measurements performed at 10 K exhibited that the PL spectrum of the *n*-type film was dominated by the neutral donor bound exciton emission at 3.368 eV while those of *p*-type films were dominated by the neutral acceptor bound exciton emissions at 3.350–3.355 eV. Conclusively, the conduction type of undoped ZnO films deposited by AP-MOCVD is resolved by the VI/II ratio used, which causes the formation of various kinds of intrinsic defects, Zn_i otherwise V_{Zn}. Intrinsic *p*-type ZnO films with the hole concentration in the range of $(1.5-3.3)\times10^{17}$ cm^{-3} can be fabricated by AP-MOCVD by modulating the VI/II ratio in the range 1.0–2.2.

ACKNOWLEDGMENTS

The authors earnestly appreciate the Institute of Nuclear Energy Research (INER) for all the technical assistance concerned with this work. The authors are also grateful to the National Science Council of Taiwan, for financially supporting the research under Contract Nos. NSC 99-2221-E-033-030 and NSC 99-2632-E-033-001-MY3.

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