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FAST TRACK COMMUNICATION

Study of arsenic doping ZnO thin films grown by metal–organic chemical vapor deposition via x-ray photoelectron spectroscopy

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Abstract
Arsenic-doped ZnO (ZnO:As) films were grown by metal–organic chemical vapor deposition (MOCVD) on GaAs layers, which were deposited on sapphire substrates by sputtering using a GaAs target. The As doping was obtained by thermal diffusion. The ZnO:As films were annealed in nitrogen (ZnO:As:N_2) and oxygen (ZnO:As:O_2) atmosphere, respectively. X-ray photoelectron spectroscopy (XPS) measurements showed that annealing in oxygen facilitated even As doping in ZnO films and the content of As remains around 3.4% after Ar^+ bombardment. However, annealing in N_2 leads to the aliquation of As at the surface for ZnO:As films. Core level results show that there are two chemical states of As in ZnO:As:O_2 films including As_{Zn}–$2V_{Zn}$ and As_{Zn}, while four types exist in ZnO:As:N_2 films including As_{Zn}, As_{Zn}–$2V_{Zn}$, As_i, and As_O. The contribution centered at around 43.9 eV of the As 3d peak is ascribed to As_{Zn}–$2V_{Zn}$. The valence band maximum (VBM) spectrum taken by ultraviolet photoelectron spectroscopy (UPS) indicates that the Fermi energy of ZnO:As:O_2 films shifts toward the VBM by 0.37 eV compared with undoped ZnO films, which proves As_{Zn}–$2V_{Zn}$ is an acceptor in ZnO:As:O_2 films, but the ZnO:As films still show n-type conductivity, which is possibly due to the compensation of As-related donor and native defects. Detailed analysis of the chemical states of As may help point toward paths for growing high-quality ZnO:As films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, with a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, is attracting worldwide attention because of its potential applications in short-wavelength optoelectronic devices, such as ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs) operating at high temperatures and in harsh environments [1–3]. However, in order to develop ZnO-based

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optical devices, stable and high-quality p-type ZnO films are required. The major difficulty in fabrication of p-type ZnO films is the self-compensating process on doping and the low solubility of the dopants. To obtain p-type ZnO films, group V elements such as N [4], P [5, 6], and Sb [7] have been tried experimentally as p-type dopants. Some research groups have recently reported that p-type ZnO film can be achieved by As doping using various methods such as ion implantation with post-implantation annealing [8], hybrid beam deposition (HBD) [9], pulsed laser deposition (PLD) [10], thermal diffusion [11–16], etc. Most of them showed a good p-type conductivity with high hole concentration, indicating that As is an efficient dopant for making p-type ZnO [17].

Other researchers have used XPS to try to identify the chemical states of As-related acceptor in ZnO:As films, but they did not draw a conclusion. In the work of Wang *et al*, it was mentioned that interstitial As might play an important role in p-type films [17]. Recently As_{Zn}–$2V_{Zn}$ has been considered to be the most possible acceptor [18]. Some researchers have used XPS to identify the 3d peak of this acceptor, but mixed results were obtained. Kang *et al* [19] and Sun *et al* [20] measure the As 3d peaks centered around 42.6 (42.8) eV, Du *et al* [21] report the As 3d peak around 43.7 eV, Yuen *et al* [22] and Xu *et al* [23] find As 3d peaks at 46.2 (46.4) eV, Yun *et al* report As $3d_{5/2}$ at 45.95 eV [24]. In this work, ZnO:As films were deposited on GaAs/Al_2O_3 by MOCVD, and the GaAs layers were deposited by sputtering on sapphire. The As doping was obtained by thermal diffusion during the high temperature growth and post-annealing. XPS was used in this study to differentiate the species of As found in ZnO:As films. To understand how the electronic properties of the films were affected by As doping, UPS was used to determine positions of the valence band edge with respect to the Fermi level.

2. Experimental details

Firstly a GaAs layer was grown on sapphire by sputtering, the basic pressure of the reaction chamber was 5×10^{-4} Pa. Then ZnO films were deposited on the GaAs layer by MOCVD. Diethyl zinc (DEZn) was used as the zinc source, and ultrahigh purity Ar gas was used as the carrier gas. Highly purified O_2 was used as the oxygen source. The DEZn temperature was kept at $-20\,°C$. The deposition temperature of ZnO films was 610 °C. The deposition was under N_2 atmosphere, which was used to prevent the source gases from upstreaming. The deposition pressure was about 280 Pa. Before deposition the sapphire substrates were cleaned by ultrasound with a sequence of methylbenzene, acetone, and alcohol each for 5 min. After deposition ZnO films were annealed in O_2 and N_2 atmosphere respectively at 600 °C for 30 min. The crystal structure of the ZnO thin film was characterized by a Bruker D8 x-ray diffractometer measurement with Cu Kα radiation. XPS (SPECS XR50) was used to identify the existence and bond states of As in the film. The position of the C 1s peak from contamination was taken as a standard reference with a binding energy of 284.6 eV. UPS (SPECS UV300) was used to analyze the valence band of as-grown films.

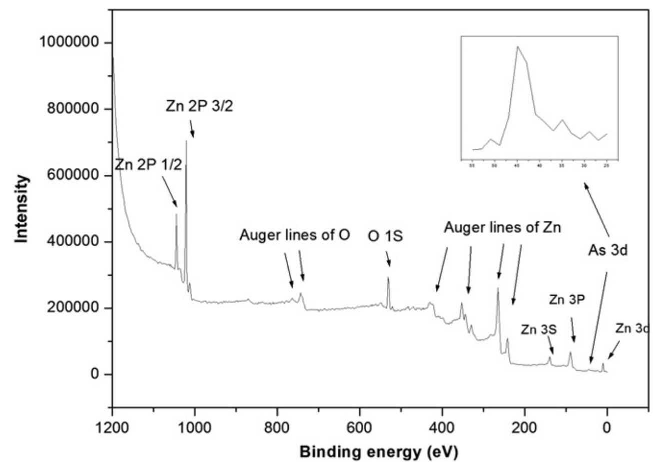

Figure 1. Total XPS spectrum of ZnO:As:O_2 films synthesized on GaAs at a substrate temperature of 610 °C. The inset shows the As 3d peak.

3. Results and discussion

High-quality ZnO films were synthesized on GaAs substrate. Our x-ray diffraction analysis indicates that there is only one strong peak centered around 34.45°, which corresponds to ZnO(002). No obvious change occurs in the crystalline structure due to the incorporation of As in the precursor solution.

Figure 1 shows the total XPS spectrum of a ZnO:As:O_2 film after 30 min Ar^+ bombardment, Ar^+ bombardment was all carried out with a 2 keV ion beam in this work. The As 3d peak is observed around 44.5 eV, as shown in the inset of figure 1. However, no peak related to the Ga core level is detected for all the films in our work, indicating that only the arsenic atoms entered the ZnO layer. Our experimental results also show that the distribution and the chemical state of As in the ZnO:As film is affected by the annealing gas ambient. Figure 2 shows As 3d peaks in ZnO:As films versus Ar^+ bombardment time. As shown in figure 2(a), the As 3d peak shifts from 45.1 eV at the surface to 44.5 eV after Ar^+ bombardment for ZnO:As:O_2 films, then the position of the binding energy remains the same. However, for ZnO:As:N_2 films, another peak at around 40.8 eV is observed with the increase of bombardment time, as shown in figure 2(b). Meanwhile, the As 3d signal of ZnO:As:N_2 films gradually fades to the background with the increase of the Ar^+ bombardment time, this means the aliquation of As at the surface in ZnO:As:N_2 films. Quantitative XPS analyses are carried out by calculation of the area ratios of Zn $2p_{3/2}$, O 1s, and As 3d peaks considering the sensitivity of the detector and the photoionization cross section. For ZnO:As:O_2 films, the content remains at around 3.4% after 90 min Ar^+ sputtering, details are shown in figure 3, but for ZnO:As:N_2 films, the content of As decreases rapidly from 6.2% (at the surface) to 2.0% (after 120 min Ar^+ bombardment). The large oxygen deficiencies (around 10%) shown in figure 3 are not intrinsic but originate from preferential oxygen sputtering during depth profiling with Ar^+ ions [25].

Isolated As in ZnO films may occupy a Zn site (As_{Zn}) an O site (As_O) or an interstitial position (As_i). As_{Zn} acts as a

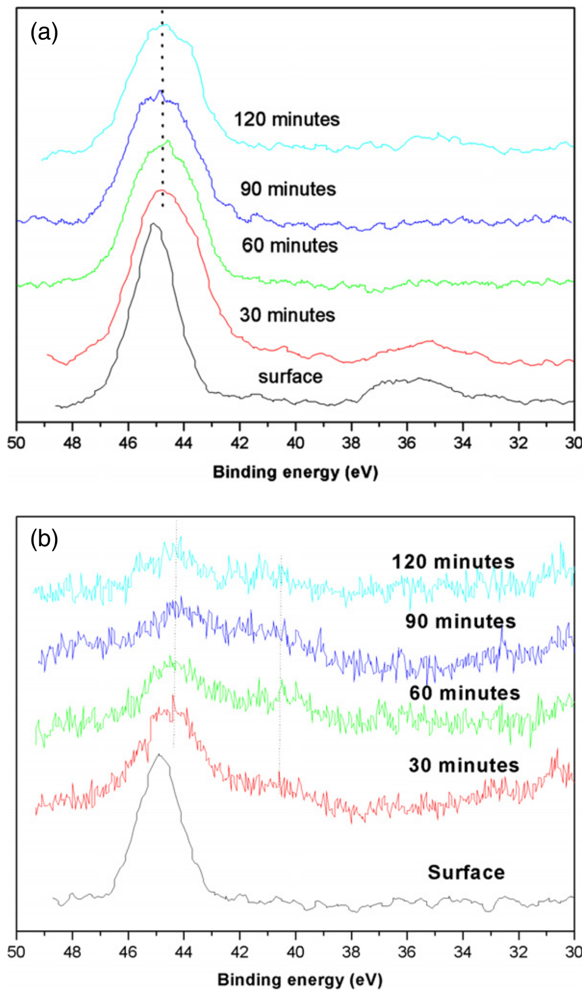

Figure 2. As 3d photoelectron line in ZnO:As films versus Ar^+ bombardment time. (a) ZnO:As:O_2 films, (b) ZnO:As:N_2 films.

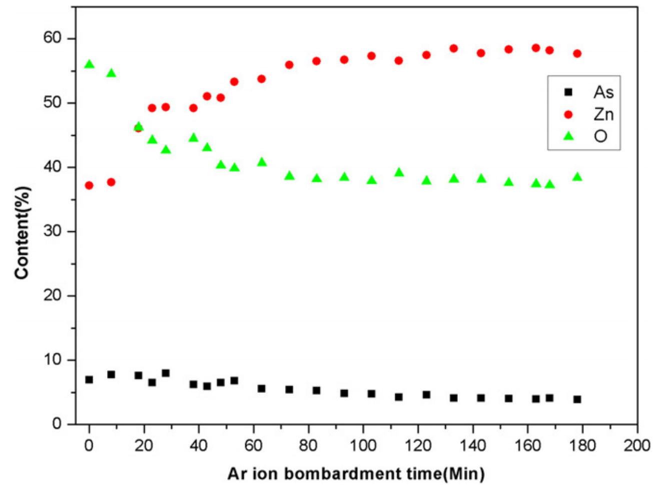

Figure 3. Deep profile of ZnO:As:O_2 films.

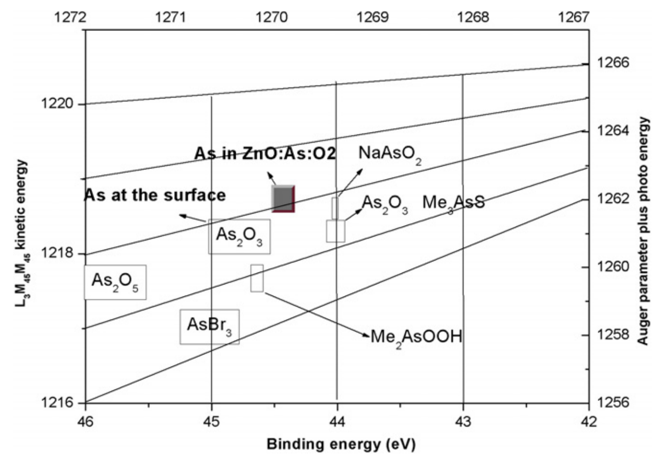

Figure 4. Modified Auger parameter of As.

donor, As_O acts as a deep acceptor, and As_i is amphoteric, so none of them could result in high p-type conductivity. In order to identify the chemical state of As, the modified Auger parameter (α') of As 3d in ZnO:As was measured. α' is defined as the sum of the kinetic energy of the Auger line and the binding energy of the photoelectric line. It is self-compensated from the charge effect and could accurately reflect the chemical state of As. Figure 4 shows modified Auger parameters of As, other data in figure 4 are from the literature [26]. α' of the peak around 45.1 eV in ZnO:As:O_2 films at the surface is 1263.5 eV. According to figure 4 and the results of Hollinger *et al* [27], this peak with a full width at half-maximum (FWHM) of 1.8 eV is ascribed to the oxidized state of As in As_2O_3. The oxide at the surface of ZnO:As films might be formed during the annealing. α' of the peak with a binding energy of 44.5 eV in ZnO:As:O_2 films after 30 min Ar^+ sputtering is 1264.0 eV, as marked by the shading in figure 4. It is clear that the peak is attributed to trivalent As atoms but α' of As 3d is different from that of As_2O_3. Meanwhile this peak with a FWHM of 2.9 eV exhibits two contributions, as shown in figure 5(a). Chemical states with binding energies (FWHM) of 45.2 eV (1.7 eV) and 43.9 eV (1.9 eV) are resolved in the ZnO:As:O_2 films. The contribution at higher binding energy is ascribed to the As–O bond in As_2O_3 as that at the surface before Ar^+ sputtering. The As oxide is formed at a high growth temperature and oxygen-enriched atmosphere during the growth of the films. According to the research of Du *et al* [21], the triple As with a binding energy around 43.9 eV is considered to be an As-related complex As_{Zn}–$2V_{Zn}$, which is a shallow acceptor in ZnO:As films. In this complex, the As atom is a triple donor, donating all of its three electrons to the two V_{Zn}, each of which can accept up to two electrons. The highly electropositive As^{3+} having donated three electrons will sit in a highly electronegative environment with five negatively charged oxygen ions in the geometry of a wurtzite structure [23].

Figure 5(b) shows As 3d contributions in ZnO:As:N_2 films. Chemical states with binding energies of 45.2 and 43.9 eV are resolved, which is the same with ZnO:As:O_2 films. The ratio of As_{Zn}–$2V_{Zn}$ to As_{Zn} is a little bigger in ZnO:As:N_2 films, possibly because it is easier to form As–O bond for ZnO:As annealed in oxygen. The contribution around 42.0 eV can be connected to interstitial As_i, which is amphoteric in ZnO:As films [23]. The peak at 40.8 eV is attributed to the As–Zn bond [27], which forms a deep

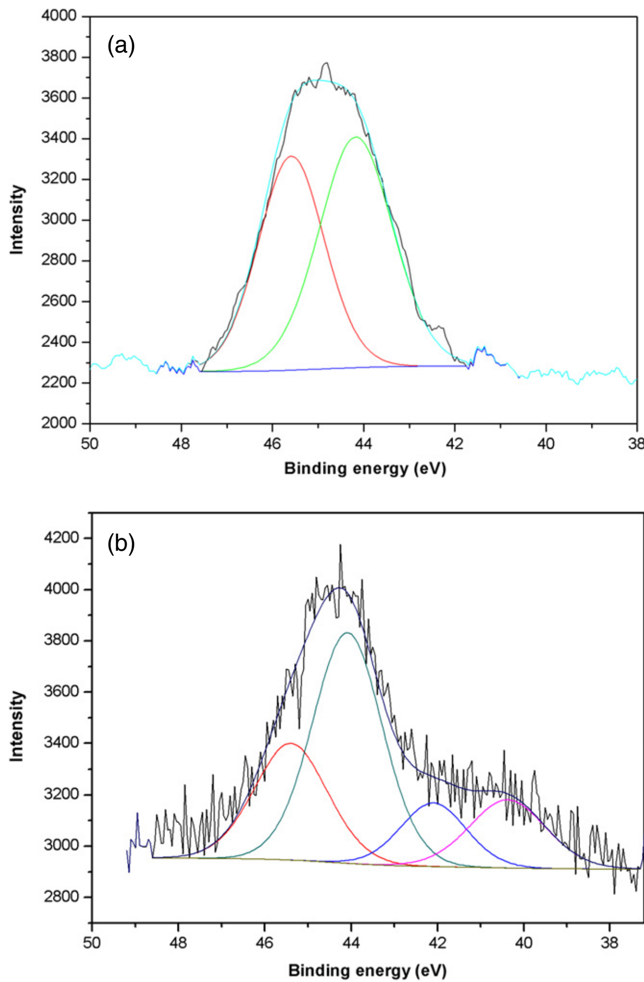

Figure 5. The contributions of As 3d peaks after 30 min Ar^+ sputtering clean (a) ZnO:As:O_2, (b) ZnO:As:N_2.

acceptor level in ZnO:As films [17]. ZnO usually shows n-type conductivities, which might be attributed to an oxygen vacancy induced during the crystal growth. For ZnO:As:N_2 films, As occupy the oxygen vacancies, but As_O does not exist in ZnO:As:O_2 films because As_O has a higher formation energy (9.87 eV) than that of As_{Zn} (1.59 eV), and oxygen-enriched conditions suppress the formation of As_O. As_{Zn}–$2V_{Zn}$ exists in both ZnO:As:N_2 films and ZnO:As:O_2 films, which may be due to the correspondingly lower formation energy of 1.59 eV and lower ionization energy of 0.15 eV [18].

Figure 6 shows the valence band maximum (VBM) spectrum of ZnO:As:O_2 and undoped ZnO films taken with He I radiation (21.2 eV). By extrapolating the leading edge of the valence band to its intersection with the background counts near the Fermi level (E_F), the position of the valence band maximum with respect to the E_F was determined. Compared with ZnO films, the E_F of ZnO:As:O_2 shifts toward the VBM by 0.37 eV [28]. Because undoped ZnO is n-type, this shift of E_F indicates that an acceptor exists in ZnO:As:O_2, and it should be related to As. Because the peak at 45.3 eV is attributed to As_{Zn} and it is a donor in ZnO:As films, then As located around 43.9 eV is the acceptor. The UPS results are in good agreement with the XPS results.

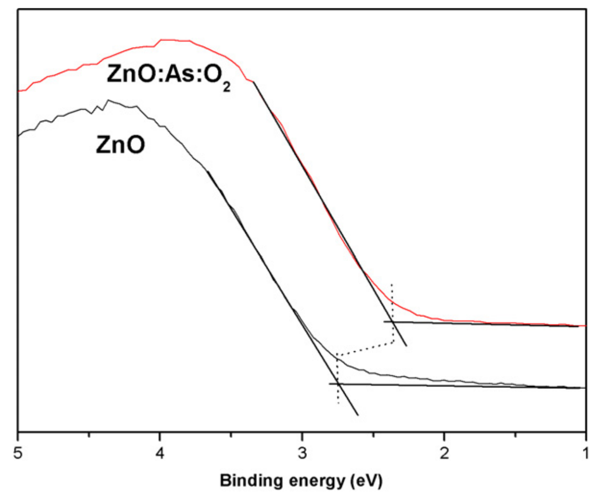

Figure 6. VBM spectra of ZnO and ZnO:As:O_2 thin films cleaned with 2 keV Ar^+ for 120 min. Data were taken with He I radiation (21.2 eV).

4. Conclusions

ZnO:As films were grown by MOCVD on GaAs/Al_2O_3, and the GaAs layer was deposited on Al_2O_3 substrate by RF sputtering using a GaAs target. The As doping was obtained by thermal diffusion. Quantitative XPS analyses show that annealing in oxygen facilitates even As doping in ZnO films. The content of As remains at around 3.4% after Ar^+ bombardment, but annealing in N_2 may lead to the aliquation of As at the surface for ZnO:As films. The arsenic chemical environments in ZnO:As thin films were probed with core level and valence band photoemission. Two different types of arsenic including As_{Zn} and As_{Zn}–$2V_{Zn}$ were found in ZnO:As:O_2 films but four including As_{Zn}, As_{Zn}–$2V_{Zn}$, As_i, and As_O were found in ZnO:As:N_2 films. The peak around 43.9 eV is ascribed to As_{Zn}–$2V_{Zn}$. The valence band maximum spectrum taken by UPS indicates that the Fermi energy of ZnO:As:O_2 films shifts toward the VBM by 0.37 eV compared to that of ZnO films. It proves that As_{Zn}–$2V_{Zn}$ acts as an acceptor in the ZnO:As:O_2 films. But the as-grow ZnO:As films remain n-type, possibly due to the compensation of As-related donors and native defects.

Acknowledgment

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