



Characterizations of arsenic-doped zinc oxide films produced by atmospheric metal-organic chemical vapor deposition



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ABSTRACT

p-type ZnO films were prepared by atmospheric metal-organic chemical vapor deposition technique using arsine (AsH₃) as the doping source. The electrical and optical properties of arsenic-doped ZnO (ZnO:As) films fabricated at 450–600 °C with various AsH₃ flow rates ranging from 8 to 21.34 μmol/min were analyzed and compared. Hall measurements indicate that stable p-type ZnO films with hole concentrations varying from 7.2×10^{15} to 5.8×10^{18} cm⁻³ could be obtained. Besides, low temperature (17 K) photoluminescence spectra of all ZnO:As films also demonstrate the dominance of the line related to the neutral acceptor-bound exciton. Moreover, the elemental identity and chemical bonding information for ZnO:As films were examined by X-ray photoelectron spectroscopy. Based on the results obtained, the effects of doping conditions on the mechanism responsible for the p-type conduction were studied. Conclusively, a simple technique to fabricate good-quality p-type ZnO films has been recognized in this work. Depositing the film at 550 °C with an AsH₃ flow rate of 13.72 μmol/min is appropriate for producing hole concentrations on the order of 10^{17} cm⁻³ for it. Ultimately, by increasing the AsH₃ flow rate to 21.34 μmol/min for doping and depositing the film at 600 °C, ZnO:As films with a hole concentration over 5×10^{18} cm⁻³ together with a mobility of $1.93 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a resistivity of 0.494 ohm-cm can be achieved.

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1. Introduction

Zinc oxide (ZnO) is a II–VI compound semiconductor with a wide and direct bandgap of about 3.37 eV at room temperature and a large exciton bind energy of 60 meV. These features have attracted considerable attention over the applications in highly efficient and stable room temperature ultra-violet (UV) lasers and light emitting diodes [1–3]. To realize these applications, high-quality p-type ZnO films are essential. However, the formation of p-type ZnO films by doping is difficult due to the compensation effect of native n-type carriers caused by the donor-type defects such as oxygen vacancies and zinc interstitials [4,5].

Recently, there have been several reports on the fabrication of p-type ZnO films by doping group V elements N [6], P [7], As [8], and Sb [9]; however, their chemical bonding and physical behavior in the lattice are still not well understood. Among the group V elements examined, nitrogen has been regarded as the most suitable

impurity for p-type doping because of its similar ionic radius to oxygen. Nevertheless, numerous experimental efforts made by different groups to implement this idea have not resulted in stable and reproducible p-type material yet. Moreover, 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 $\text{As}(\text{Sb})_{\text{Zn}}-2\text{V}_{\text{Zn}}$ with low enthalpies of formation [11]. A direct evidence for arsenic as a zinc-site impurity in ZnO has been presented by Wahl et al. using the emission channeling technique [12]. To achieve this purpose, several researchers have prepared ZnO films on GaAs substrates (ZnO/GaAs) 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]. We have also demonstrated that fabricating the ZnO/GaAs structure at 450 °C followed by a rapid thermal annealing treatment at a range of 500–600 °C in oxygen atmosphere would

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achieve p-type ZnO films with a carrier concentration ranging from 4.7×10^{18} to $8.7 \times 10^{19} \text{ cm}^{-3}$ [16].

This work reports the fabrication of p-type conductive ZnO films by performing arsenic-doping (As-doping) during the film growth process without any postgrowth treatment. To the best of our knowledge, related literature on this method has been scarce so far. The effects of As-doping on the films produced are systematically examined from the electrical, optical, and chemical-bonding-structural aspects, respectively. Optimal conditions to carry out the As-doping are analyzed and the mechanisms responsible for the results obtained are also discussed.

2. Experiment

ZnO thin films were deposited using an atmospheric-pressure type metal-organic chemical vapor deposition (AP-MOCVD) system with a water-cooled vertical reactor. The substrates used were cut from just (1 1 1)-oriented Si wafers with a resistivity of 1–3 kohm-cm. Prior to film growth, the Si(1 1 1) substrates were ultrasonically cleaned with trichloroethylene, acetone, then rinsed with deionized water, and finally dried by nitrogen gas. O_2 and diethylzinc ($\text{Zn}(\text{C}_2\text{H}_5)_2$, DEZn) were used as the precursors of oxygen and zinc, respectively. The flow rates of O_2 and DEZn were maintained at 6.66 and 26.71 $\mu\text{mol}/\text{min}$, respectively. To prepare p-type films, As-doping was performed simultaneously with the film deposition and arsine (AsH_3) was used as the precursor of dopant. All the precursors used were transferred using N_2 as the carrier gas. As-doped ZnO (ZnO:As) films were deposited at various temperatures ranging from 450 to 600 °C and with various flow rates of AsH_3 ranging from 8.0 to 21.34 $\mu\text{mol}/\text{min}$ to find an optimal condition for growing ZnO:As films. The growth time duration for all specimens was set for 40 min to achieve a thickness of about 400–500 nm, recognized by the cross-sectional scanning electron microscopy (SEM) images.

The crystalline structure of ZnO:As films was analyzed by X-ray diffraction (XRD, Bruker AXS Diffraktometer D8) with $\text{Cu K}\alpha$ line of the wavelength $\lambda = 1.54056 \text{ \AA}$ as the X-ray source and a 2θ scanning range of 30–60°. The room-temperature resistivity, carrier concentration and mobility of films were analyzed by the Hall-effect measurement system (Ecopia, HMS-5000) using the van der Pauw geometry. The arsenic content in ZnO:As films was measured by energy dispersive spectroscopy (EDS). The optical properties of ZnO:As films were analyzed by photoluminescence (PL) spectroscopy conducted at room temperature and 12 K. A He–Cd laser ($\lambda = 325 \text{ nm}$) with power 8 mW was used as the excitation source for PL measurements. Finally, the elemental identity and chemical bonding information for ZnO:As films were analyzed by X-ray photoelectron spectroscopy (XPS) using Thermo Scientific K-Alpha spectrometer equipped with aluminum $\text{K}\alpha$ 1.2 monochromatized radiation at 1486.6 eV X-ray source.

3. Results and discussion

The specimens examined in the measurements described below are denoted as follows. The undoped specimen is referred to as sample 1. The specimens fabricated at 550 °C with the AsH_3 flow rates of 8.00, 13.72, and 21.34 $\mu\text{mol}/\text{min}$ are referred to as samples 2, 3, and 4, respectively. The ZnO:As films prepared at 450, 500, and 600 °C with a constant AsH_3 flow rate of 21.34 $\mu\text{mol}/\text{min}$ are referred to as samples 5, 6, and 7, respectively. Fig. 1 shows the XRD patterns of the samples mentioned above. The XRD peaks of our grown films were indexed to hexagonal wurtzite (JCPDS card no. 36-1451). Obviously, all the films show poly-crystalline structure with various crystallographic planes being detected. The undoped film exhibits a grain structure with a dominant plane orientation

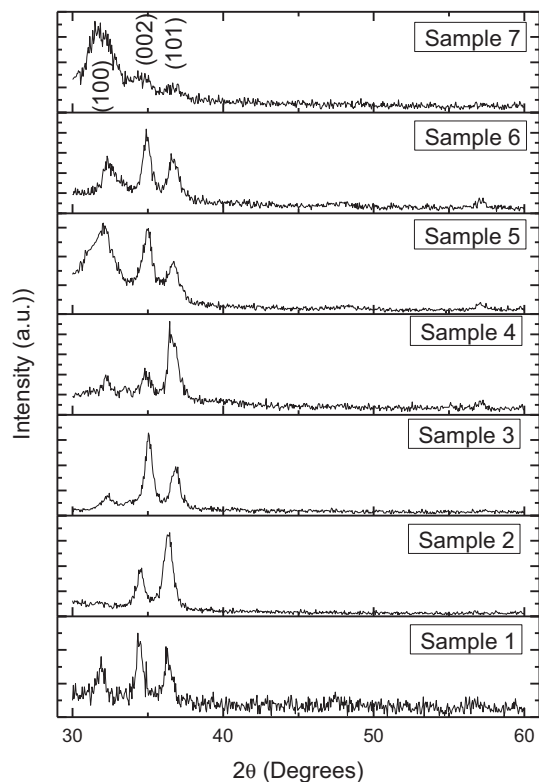


Fig. 1. XRD patterns of ZnO:As films fabricated at 550 °C with different AsH_3 flow rates and those fabricated at different temperatures with a constant AsH_3 flow rate of 21.34 $\mu\text{mol}/\text{min}$.

of (0 0 2). However, the predominant plane changes for the ZnO:As films without a definite correlation between it and the As-doping except that the (100) peak becomes broad to some extent for heavier dopings. This broadening is probably due to strain induced by the activated As atoms and/or the decrease of grain sizes. Besides, some XRD peaks other than the dominant one become quite weak or almost disappear. This result might manifest that the density of the corresponding nucleation crystallites is relatively low or the growth of those kinds of grains is ultimately suppressed by others because of the growth rate anisotropy. Fig. 2 plots the carrier concentration (n or p), mobility (μ), and resistivity (ρ) obtained from the Hall measurements for samples 2, 3, and 4. For comparison, the electrical properties of the sample 1 are also demonstrated in the same figure. The results and the deposition conditions of specimens

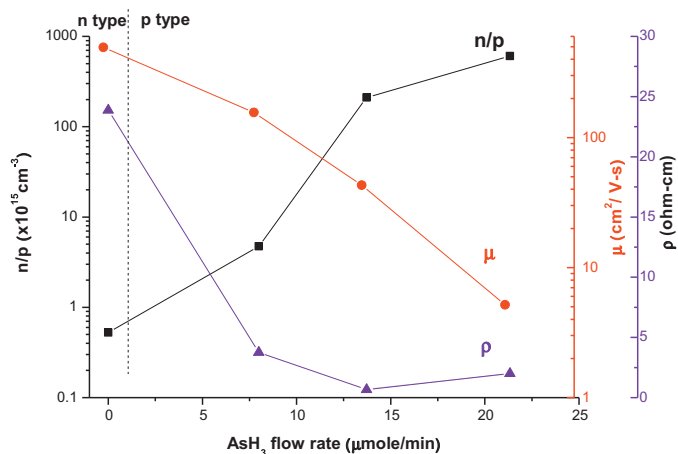


Fig. 2. Electrical properties of ZnO:As films prepared with different AsH_3 flow rates.

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