

Tailoring of optical and electrical properties of transparent and conductive Al-doped ZnO films by adjustment of Al concentration



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ABSTRACT

Highly optically transparent and electrically conductive Al-doped ZnO (AZO) thin films with varied Al concentrations were synthesized by means of reactive deposition of ZnO host films and in-situ doping of Al by pulsed laser co-ablation of a Zn target and an Al target with the assistance of an oxygen plasma. The optical and electrical properties of AZO films were tailored by the adjustment of Al concentration which was realized by varying the laser fluence on the Al target. The morphology, composition and structure as well as the optical and electrical properties were characterized and the effects of Al doping and post-deposition annealing were investigated. Similar with undoped ZnO, the synthesized AZO films have a hexagonal wurtzite structure with the crystallinity deteriorated, present high visible transparency with the absorption edge blue shifted and show good electrical properties with the electrical conductivity increased. The structural, optical and electrical properties are strongly dependent on Al concentration and are significantly improved after annealing in H₂/N₂ mixed gas. Annealed AZO films containing 3.0 at% Al have optical properties including an absorption edge near 325 nm and an optical band gap of 3.67 eV and electrical properties covering an electrical resistivity of $5.27 \times 10^{-4} \Omega \text{ cm}$ and a carrier concentration of $1.11 \times 10^{21} \text{ cm}^{-3}$ with a Hall mobility of $10.7 \text{ cm}^2/\text{V s}$.

1. Introduction

Transparent conducting oxides (TCOs) are very important in electronics and optoelectronics and have been widely used as materials for conducting window layers or transparent conductive electrodes in many modern optoelectronic devices [1–6]. Nowadays, indium tin oxide (ITO) is the most widely used TCO due to its combined properties such as high optical transmittance and low electrical resistivity [2]. However, ITO has some disadvantages such as high cost and toxicity because indium is rare, expensive and toxic. New TCO materials free of indium have been intensively investigated as candidate TCOs to replace ITO. Among various indium-free TCOs, zinc oxide (ZnO) is considered as one of the most promising TCOs because of its unique nature such as low cost, easy availability, nontoxicity and high chemical stability [7,8]. In addition, ZnO is an attractive metal-oxide semiconductor material whose electronic, optical and optoelectronic properties can be largely tuned by doping with varied elements and concentrations. ZnO is usually *n*-type conductive due to native donor defects, zinc interstitials and oxygen vacancies. However, *n*- or *p*-type conductivity of

ZnO can be controlled by doping [8–10]. ZnO shows high optical transparency which can be further increased by doping [3,11,12]. Undoped ZnO shows high electrical resistivity owing to its low carrier concentration. Doping with various cationic and anionic dopants and annealing at different ambiances can significantly improve the electrical properties of ZnO and can dramatically reduce the electrical resistivity of ZnO. Moreover, the band gap engineering of ZnO by means of doping makes ZnO most promising as an excellent optoelectronic material [8]. It is reported that doping ZnO with Cd decreases the band gap, whereas Al or Mg doping increases the band gap [13–15]. The widening of band gap results in extending the ultraviolet (UV) absorption edge and enhancing the UV response of ZnO, which improves the performance of ZnO-based materials used in the UV region. ZnO doped with extrinsic dopants such as Al, In, B, and Ga has been proposed as alternative to replace ITO. Among them, aluminum doped ZnO (AZO) is most promising since it has the properties similar to those of ITO [16–18]. AZO films have been demonstrated as excellent TCO windows or electrodes in a variety of devices including light-emitting diodes, flat panel displays, thin film transistors, sensors and

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photovoltaic cells as well as in photocatalytic reactions [5,6,17,19,20]. The optical and electrical properties of AZO are strongly dependent on Al concentration and can be largely tailored by adjusting the Al concentration in AZO.

High quality AZO films have been grown by different methods including sol-gel growth [21], spray pyrolysis [22,23], atomic layer deposition [5,24], chemical vapor deposition [25,26], sputtering deposition [16,27,28] and pulsed laser deposition (PLD) [29,30]. In addition, the growth of various nanostructured AZO films including compact polycrystalline and mesoporous films has been achieved by PLD at different gaseous ambiances, and optical and electrical properties were reported structure-dependent [31–33]. We have previously demonstrated a plasma-assisted PLD method to grow AZO films through co-ablation of a Zn target and an Al target by two pulsed laser beams [34]. Just as in most plasma-based or plasma-assisted methods for materials fabrication [35–37], the low-temperature reactive plasma formed in the process of AZO film synthesis plays a vital role. In an oxygen plasma and with its assistance, the ablation of the Zn target results in the reactive deposition of ZnO host, while the ablation of the Al target provides the growing ZnO host with Al dopants. In this in-situ doping method, the Al target is ablated by a separate pulsed laser beam and Al concentration can be easily adjusted by varying the parameters of the laser beam ablating the Al target. In this paper, we report the adjustment of Al concentration in AZO films by varying the laser fluence on the Al target surface and the tailoring of the optical and electrical properties of AZO films by the adjustment of Al concentration.

2. Experimental

2.1. Sample preparation

Deposition of ZnO host films and in-situ doping of Al have been described previously and the experimental set-up used for AZO film deposition was the same as in our previous work [34] (See Fig. S1 in Supplementary material). Pure O₂ gas (purity > 99.999%, pressure 3×10^{-2} Pa) was discharged at electron cyclotron resonance (ECR) by a 2.45 GHz microwave for oxygen plasma generation. In the oxygen plasma, a pure (99.999%) Zn target was ablated by a pulsed laser beam with a wavelength of 532 nm, pulse width of 5 ns and repetition rate of 10 Hz from a frequency-doubled Q-switched Nd:YAG laser to reactively deposit ZnO host films with the assistance of the oxygen plasma. Concurrently, a pure (99.995%) Al target was ablated by another pulsed laser beam with the same wavelength and pulse width, but at a repetition rate of 1 Hz from another frequency-doubled Q-switched Nd:YAG laser, providing Al dopants which were in-situ doped in the growing ZnO host films, forming AZO films. The laser fluence on the Zn target surface was set at about 4 J/cm², and that on the Al target surface was varied at 1, 2 and 3 J/cm², proving the ZnO host films with different quantities of Al dopants and depositing AZO films with different Al concentrations. Correspondingly, the samples thus deposited are referred to as AZO1 AZO2 and AZO3, respectively, in the paper. Polished single crystalline Si (100) wafers (5 Ω cm in resistivity) were supersonically cleaned in alcohol and acetone and dipped in 10% HF solution as film substrates. For the evaluation of optical transparency, films were also deposited on double-side polished UV-grade quartz plates. The substrates were placed 4 cm away from the laser-irradiated spots on the targets and kept rotating during film deposition. For comparison, pure ZnO thin films were also deposited when only the Zn target was ablated while the laser beam ablating the Al target was shut off [38]. All films were deposited for 60 min and then annealed in a mixed H₂/N₂ atmosphere (5% H₂ + 95% N₂, 6×10^3 Pa) at a temperature of 450 °C for 60 min.

2.2. Sample characterization

Field emission scanning electron microscopy (FESEM) was used to

examine film morphology and determine film thickness using a Hitachi S-4800 microscope. Rutherford backscattering (RBS) was performed for the deposited films to evaluate film composition and thickness by bombarding the samples using a 1.7-MeV He⁺ beam at 170° scattering geometry. The He⁺ beam was generated by a 9SDH-2 tandem accelerator at Fudan University and collimated to a diameter of 1.0 mm. X-ray diffraction (XRD) patterns were recorded to characterize film structure by a Rigaku D/MAX 2550 VB/PC X-ray diffractometer equipped with a rotating anode and a Ni-filtered Cu Kα radiation. Optical transparency was characterized by measuring the transmission spectra of the films deposited on quartz plates using a Hitachi UV-3000 ultraviolet-near infrared spectrophotometer. Room-temperature photoluminescence (PL) from the films was measured also for optical characterization. The samples were excited by a 325-nm He–Cd laser beam at 45° to the sample surface, and the emitted luminescence was collected perpendicular to the sample surface by two fused silica lenses and recorded by an Ocean Optics USB2000 miniature fiber optic spectrometer. The system for PL measurements has been calibrated for spectral response using a standard light source. Using an Ecopia HMS-5000 variable temperature Hall effect measurement system, the electrical properties of the films deposited on Si substrates were studied by determining the electrical resistivity, carrier concentrations and Hall mobility with four-probe method in the Van der Pauw configuration.

3. Results and discussion

3.1. Morphology and composition

FESEM observation reveals that the deposited ZnO and AZO films on Si or quartz substrates have a smooth surface (not shown here) [34]. The cross-sectional observation by FESEM images indicates that all the ZnO and AZO films are dense in structure and have a thickness of about 200 nm, with the Al-doped film slightly thicker than the undoped film (See Fig. S2 in Supplementary material).

The film composition was determined by RBS measurements and SIMNRA simulation [39]. Fig. 1 illustrates the measured RBS random spectra of the ZnO and AZO3 films deposited on Si substrates and the simulated one of the AZO3 film. The high and flat peak on the right-hand side in the spectra is the signal scattered from the Zn atoms whereas the oxygen signal superimposes on the Si platform contributed from the Si substrate. The lower energy edge of the Zn peak is very steep, indicating a clear boundary between the film and the substrate. The small step around channel 500 in the spectrum of the AZO3 film is contributed from Al atoms incorporated in the film, which can be clearly seen in the inset in Fig. 1. Fig. 1 also shows that the height of the Zn signal for the AZO3 film is lower than that for the undoped ZnO film by about 6%, which evidences the decrease of Zn due to the

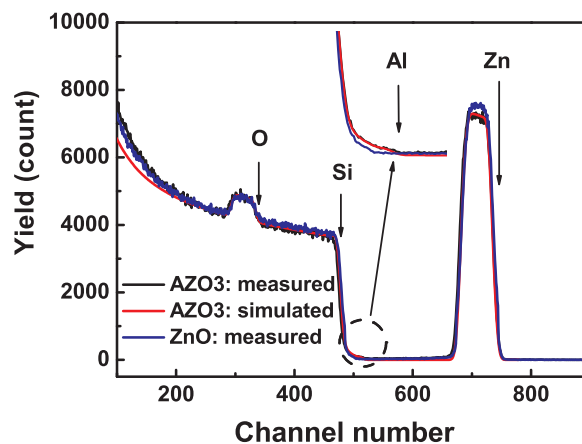


Fig. 1. Measured and simulated RBS random spectra of AZO3 film and measured RBS random spectrum of ZnO film.

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