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Highly transparent and conductive Al-doped ZnO films synthesized by pulsed laser co-ablation of Zn and Al targets assisted by oxygen plasma

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ABSTRACT

Highly optically transparent and electrically conductive Al-doped ZnO (AZO) thin films were deposited by pulsed laser co-ablation of a Zn target and an Al target in an oxygen plasma. Zn ablation resulted in the reactive deposition of ZnO films assisted by the plasma, while Al ablation provided the growing ZnO films with Al dopants. The morphology, composition and structure as well as the optical and electrical properties were characterized and the effects of Al doping and annealing treatment were investigated. The deposited AZO films have a hexagonal wurtzite structure with deteriorated crystal quality which can be improved by annealing. The AZO films are highly transparent from ultraviolet up to 1450 nm and present an obvious blue shift in absorption edge and a widening of band gap compared with undoped ZnO. The electrical properties were also improved after annealing with the resistivity decreasing by over two orders of magnitude because of the increase of free carrier concentration. The variation in the carrier concentration also affects the absorption edge and the band gap of the films as well as the transparency in the infrared region. Meanwhile, this method offers an approach for in-situ doping preparation of other doped compound films with different dopant concentrations.

1. Introduction

Transparent conducting oxides (TCOs) have attracted considerable attention and have been studied extensively due to their wide applications in electronics and optoelectronics [1–6]. Indium tin oxide (ITO) is now the most widely used TCO material for optoelectronic devices owing to its combined properties such as high visible transmittance and low electrical resistivity [2]. However, new TCO materials including doped zinc oxide (ZnO) films (for example, ZnO films doped with extrinsic dopants such as Al, In, B, and Ga) have been proposed as alternate TCO materials to replace ITO, because they are inexpensive, abundant and non-toxic. Among them, aluminum doped ZnO (AZO) is most promising since it has the properties similar to those of ITO [7,8] and AZO films have been demonstrated as excellent TCO electrodes in a variety of devices including light-emitting diodes and solar cells [4,5,9–11].

High quality AZO films can be synthesized by various deposition methods such as metal–organic chemical vapor deposition [12,13], sol–gel growth [14,15], spray pyrolysis [16,17], sputtering deposition [7,18], and atomic layer deposition [5,19]. Compared with the methods mentioned above, pulsed laser deposition (PLD) has been established as a versatile technique for preparing thin films of various materials including AZO films [19,20]. In this work, an attempt was made to develop a novel method based on plasma assisted PLD for the synthesis of AZO films by co-ablation of a Zn target and an Al target. In an oxygen plasma generated by electron cyclotron resonance (ECR) microwave discharge and with its assistance, pulsed laser ablation of the Zn target results in the reactive deposition of ZnO film [21]. At the same time, ablation of the Al target provides the growing ZnO film with Al dopants. We have also demonstrated that this method is capable of controlling and varying Al concentration by simply changing the repetition rate of laser pulses ablating the Al target. In addition, this method is most feasible for in-situ doping preparation of various compound films doped with different dopant concentrations.

2. Experimental details

2.1. Sample preparation

Fig. 1 schematically illustrates the experimental arrangement for the synthesis of AZO thin films by co-ablation of a Zn target and an Al target. The homemade

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equipment consists of a PLD system and an ECR plasma source. After being evacuated to a base pressure of $\sim 1 \times 10^{-4}$ Pa, the ECR discharge chamber was filled with flowing high purity (>99.999%) O_2 gas at a working pressure of 3×10^{-2} Pa. A 2.45 GHz microwave was imported into the discharge chamber to generate an oxygen plasma under the ECR conditions. The oxygen plasma was then introduced into the deposition chamber where target ablation and film deposition were carried out. In the environment of the oxygen plasma, the metallic Zn (99.999% in purity) and Al (99.995% in purity) targets were ablated simultaneously by two laser beams from two frequency-doubled Q-switched Nd:YAG lasers (wavelength: 532 nm; pulse width: 5 ns). The laser fluence on the Zn target surface was about 4 J/cm^2, and that on the Al target surface was about 3 J/cm^2. The laser used for Zn ablation (laser beam 1) worked at a constant repetition rate of 10 Hz, while the other laser for Al ablation (laser beam 2) worked at 1 or 2 Hz to provide the films with two different concentrations of Al dopants. Correspondingly, the samples thus prepared are henceforth referred to as AZO1 and AZO2, respectively. Serving as the substrate, a polished single crystalline Si (1 0 0) wafer (5 Ω cm resistivity) or a double-side polished fused quartz plate (UV-grade) was placed 4 cm away from the laser-irradiated spots. The substrate and the targets were kept rotating for depositing films with a homogeneous structure and a well-distributed composition. When laser beam 2 was shut off, only the Zn target was ablated and a ZnO thin film without Al doping was deposited with the assistance of the oxygen plasma [21]. For all the samples, the deposition time was 60 min. The deposited AZO and ZnO thin films were submitted to annealing in a mixed gas (5% H_2 + 95% N_2) atmosphere (6×10^3 Pa) at a temperature of 450 °C for 60 min.

2.2. Sample characterization

The film morphology was examined by field emission scanning electron microscopy (FESEM) with a Hitachi S-4800 microscope. The elemental compositions of the films were analyzed by energy dispersive spectroscopy (EDS) using a Philips XL30FEG* EDAX system. The sample structure was characterized by X-ray diffraction (XRD) with a Rigaku D/MAX 2550 VB/PC X-ray diffractometer using a rotating anode and a Ni-filtered Cu Kα radiation (λ = 0.15406 nm). The structure was also examined through the analysis of vibrational modes by means of Raman backscattering spectroscopy which was carried out with a Jobin Yvon HR-Evolution confocal micro-Raman spectrometer using a 325-nm He–Cd laser beam to excite the samples. For optical characterization, the transmission spectra were measured for the films deposited on quartz plates with a Hitachi UV-3000 ultraviolet-near infrared spectrophotometer. Photoluminescence (PL) measurements were performed at room temperature by exciting the samples at 45° to the sample surface with a 325-nm un-polarized laser beam from a He–Cd laser, collecting the emitted luminescence perpendicular to the sample surface by two fused quartz spherical lenses and recording the spectra using a USB2000 Miniature Fiber Optic Spectrometer. The system for PL measurements had been corrected using a standard light source. Electrical properties were measured using four-probe method in the Van der Pauw configuration with an Ecopia HMS-5000 Variable Temperature Hall Effect Measurement System.

3. Results and discussion

3.1. Morphology and composition

Fig. 2 shows the SEM images of ZnO and AZO1 thin films deposited on Si substrates. It can be seen that the deposited films have a relatively smooth surface without obvious voids and crack. The cross-sectional FESEM images shown in the inset of Fig. 2(a) and (b) reveal that both the ZnO and AZO1 films have a dense structure and a thickness of about 200 nm, with the Al-doped film slightly thicker than the undoped film. The AZO2 film has a thicker thickness of 220 nm. EDS measurements reveal that the AZO2 film contains an Al content of 5.74 at.% and is slightly deficient in O (45.93 at.%). The atomic percent of Al in the AZO1 film was determined to be about 2.87 at.%.

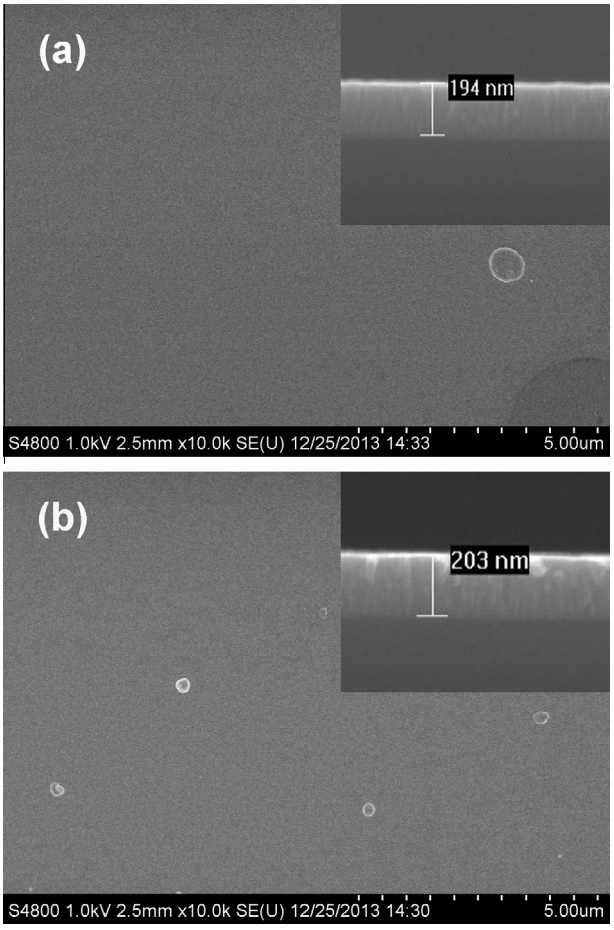

Fig. 2. Top-view SEM images of ZnO (a) and AZO1 (b) film and cross-sectional images (inset).

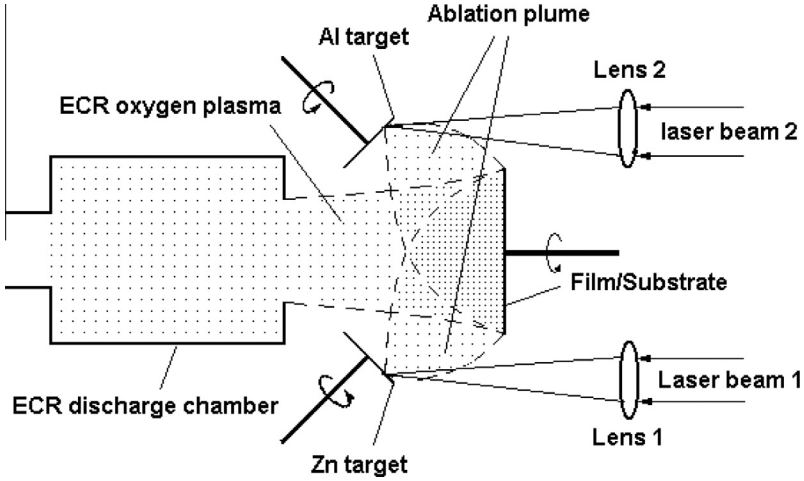

Fig. 1. Schematic diagram of experimental arrangement for AZO film deposition.