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The effect of Mg and Al co-doping on the structural and photoelectric properties of ZnO thin film

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ABSTRACT

Mg–Al co-doped ZnO thin films were prepared via radio-frequency reactive magnetron sputtering technique. X-ray diffraction investigation showed all the thin films with different Mg:Al ratio had hexagonal wurtzite structure. All the thin films showed (100) preferential orientation of ZnO. When Al concentration was kept constant but Mg concentration was increased, the grain size decreased at first and then increased. When Mg:Al ratio was 3:1, the grain size reached a maximum. Ultraviolet–visible spectra showed the thin films had a high average transmittance of 80% in the visible range. The optical band gaps of the thin films were obtained as follows: 3.31, 3.32, and 3.37 eV, corresponding to the Mg:Al ratio of 0:1, 1:1, and 3:1, respectively. Photoluminescence spectroscopy showed all the thin films had four main peaks located at 386, 410, 463, and 499 nm. The origin of blue peak is oxygen vacancy. When Mg concentration was kept constant but Al concentration was increased, *I–V* curve presented that for both of the heterojunctions the rectifying behavior was formed. The conductivity of Mg:Al = 1:1 thin film is higher than that of Mg:Al = 1:0 thin film. After illumination, light *I–V* curve deviated from rectifying character.

1. Introduction

Zinc oxide (ZnO), a wide and direct band gap (about 3.37 eV) II–VI semiconductor with a large exciton binding energy (60 meV), has been actively studied for its potential applications [1–3]. ZnO materials are used in solar cells, laser diodes, ultraviolet lasers, surface acoustic wave application, pyroelectric sensor and gas sensor applications [4–6]. Techniques which are used to prepare zinc oxide thin film include chemical vapor deposition [7], pulsed laser deposition [8], sol–gel spin coating [9], radio-frequency (RF) magnetron sputtering [10], molecular beam epitaxy [11], and atomic layer deposition [12]. Compared to other deposition methods, RF magnetron sputtering have the advantages of the simple apparatus, high deposition rate, low substrate temperature, good surface flatness, transparency and the dense layer formation.

The properties of ZnO can be modulated by doping different elements. When ZnO is doped with another material with other band gap, the band gap of result alloy materials can be fine tuned. For example, when ZnO thin film is doped with MgO or Mg, the energy gap of result thin film can vary from 3.7 to 7.2 eV, and the band gap became larger with increase of Mg content [8]. The conductivity of ZnO thin film can be increased by Al-doping, so that the photo-electric efficiency of ZnO-based solar cells will be increased [13]. Suzuki et al. [14] proposed that the co-doping method had the advantage to improve the properties of

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host film, they prepared the V co-doped AZO thin films by magnetron sputtering and obtained high corrosion-resistance and high transmittance film. If Mg and Al are co-doped into ZnO film, the band gap of as-prepared thin film could be tailored, at the same time, the thin film with high conductivity may be obtained by adjusting concentration ratio of Mg and Al. Those excellent properties may have novel effect on the ZnO-based photo-electric devices. Thus, it is necessary to systemically investigate ZnO thin film co-doped with Mg and Al.

In this paper, the Mg–Al co-doped ZnO thin films were prepared via radio-frequency (RF) reactive magnetron sputtering technique. The microstructural, optical and electrical properties of the thin films were investigated. The origins for these properties were also discussed.

2. Experimental

The Mg–Al co-doped ZnO films were deposited on the glass and Si substrates using RF reactive magnetron sputtering technique. A high-purity Zn target (99.999%_ purity, 60 mm in diameter) was used. The glass substrates were ultrasonically cleaned in acetone and alcohol and rinsed in deionized water. The silicon wafers were rinsed in mixed solution of concentrated sulfuric acid and perhydrol for five minutes, hydrogen fluoride solution for 5 min in turn, then were ultrasonically cleaned in acetone and alcohol and rinsed in deionized water, before being putted into the deposition chamber. To conduct Mg and Al doping, Mg and Al foil (purity_99.9%) were pasted to Zn target. The area ratio of Mg, Al foil and effective sputtering area of Zn target, is used to signify corresponding concentration ratio, i.e., Mg:Al:Zn. We separated our experiment into two groups. In the group one, glass substrate was used, Al was kept constant but Mg varied, the above area ratio was 0:1:100, 1:1:100, 2:1:100, 3:1:100, which represented sample AMZO (1), AMZO (2), AMZO (3), AMZO (4), respectively. The target-to-substrate distance was 50 mm. The base pressure in the deposition chamber was 4.0×10^{-4} Pa. High-purity argon and oxygen (purity_99.99%) was used as the sputtering and reactive gas. The Zn target was pre-sputtered in pure Ar for 10 min to remove surface contamination and to maintain system stability. Film growth was carried out for 1.5 h in the ambient with the ratio of O_2: Ar $=$12:8, the working pressure was 2.0 Pa. The substrate temperature and RF power were 100 centigrade and 80 W during sputtering, respectively. The as-deposited thin films were annealed at 400 centigrade in vacuum for 1 h. Under the same ambient, the group two thin films were deposited on glass and silicon wafer. In this group, Mg was kept constant but Al was varied, the above-mentioned area ratio was 1:0:100 and 1:1:100, which represented sample AMZO (5) and AMZO (6), respectively. In order to measure photoelectric property, Al electrode was sputtered on thin film and silicon wafer.

The AMZO thin films were examined by X-ray diffraction (XRD, D/Max-2400) to analyze their crystal structure. A scanning electron microscope (SEM, JSM-6701F) was used to explore surface morphology. The transmittance spectra of the UV–visible light passing through the films were measured by a UV–visible spectrophotometer (Lambda35 UV/VIS). The photoluminescence spectra (PL) were obtained from fluorescent spectrometer by using 325 nm excitation of Xe Lamp (RF-5301, wavelength 325 nm) at room temperature in air. The photoelectric property was measured by electrochemical workstation in dark room, then the heterojunctions were illuminated by ultraviolet lamp to measure light current.

3. Results and discussion

3.1. Structure properties

Fig. 1(a) shows the XRD patterns for the first group of AMZO thin films, i.e., Al concentration was kept constant but Mg concentration varied. Four characteristic peaks of ZnO hexagonal wurtzite: (100), (101), (110), and (002) are observed in all films and no peaks corresponding to other oxide and metal are detected. the diffraction angles of (002) peak are smaller than that of pure ZnO (34.42°), meanwhile the (002) peak tends to larger diffraction angle with the Mg concentration increasing, which can be explained by Mg^{2+} and Al^{3+} substituting Zn^{2+} in the crystal lattice of ZnO. We calculated the *c*-axis lattice parameters and the mean grain size in the four films, which is shown in Table 1, where *D*, *c*, *θ*, and FWHM are the mean grain size, *c*-axis lattice parameters, Bragg diffraction angle, and the full width at

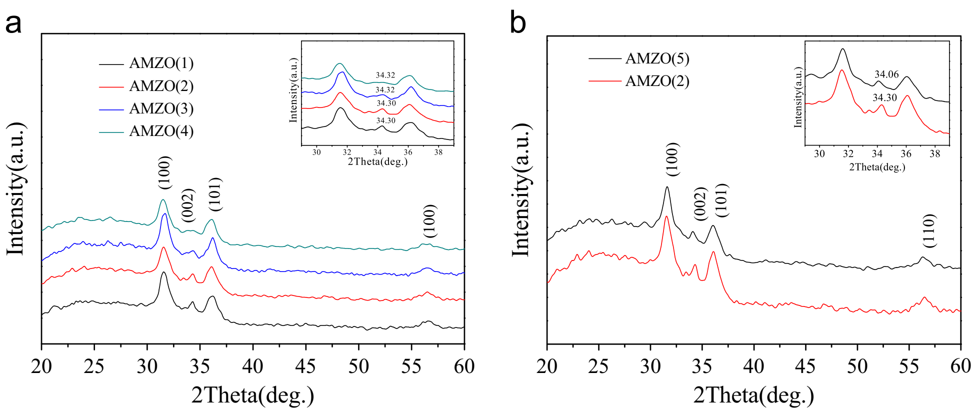

Fig. 1. (a) XRD diffraction patterns for the AMZO thin films at different Mg:Al ratio (AMZO (1): 0:1, AMZO (2): 1:1, AMZO (3): 2:1, AMZO (4): 3:1). (b). XRD diffraction patterns for the AMZO thin films at different Mg:Al ratio (AMZO (5): 1:0, AMZO (6): 1:1).