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Structural, electrical and optical properties of zirconium-doped zinc oxide films prepared by radio frequency magnetron sputtering

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Abstract

Transparent and conducting zirconium-doped zinc oxide films have been prepared by radio frequency magnetron sputtering at room temperature. The ZrO_2 content in the target is varied from 0 to 10 wt.%. The films are polycrystalline with a hexagonal structure and a preferred orientation along the *c* axis. As the ZrO_2 content increases, the crystallinity and conductivity of the film are initially improved and then both show deterioration. Zr atoms mainly substitute Zn atoms when the ZrO_2 content are 3 and 5 wt.%, but tend to cluster into grain boundaries at higher contents. The lowest resistivity achieved is 2.07×10^{-3} Ω cm with the ZrO_2 content of 5 wt.% with a Hall mobility of 16 $cm^2 V^{-1} s^{-1}$ and a carrier concentration of 1.95×10^{20} cm^{-3}. All the films present a high transmittance of above 90% in the visible range. The optical band gap depends on the carrier concentration, and the value is larger at higher carrier concentration.
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Keywords: Zirconium; Zinc oxide; Sputtering; Transparent conducting oxide

1. Introduction

The use of transparent conducting oxide (TCO) films is becoming more and more necessary due to the development of optoelectronic devices, such as liquid crystal displays, organic light emitting diodes, and solar cells [1–5]. Indium tin oxide (ITO) film is the most widely investigated and used due to its high transparency, low resistivity and high work function [6,7]. In applications involving transparent heaters and chemical sensors, it is required that the films be chemically stable as they cycle through high temperatures. However, ITO is not stable at temperatures above 400 °C [8]. ZrO_2–ZnO is considered to be a kind of potential TCO [9,10] and ZrO_2–ZnO films are stable in chemical and structural properties up to 800 °C [8]. Thus, Zr-doped ZnO (ZZO) is a promising substitute of ITO to work at high temperatures stably. Moreover, ZnO is nontoxic, inexpensive, and abundant compared with ITO [11].

Nowadays, the study on ZZO is very limited. ZZO films have been prepared using pulsed-laser deposition (PLD) [8,11] and sol–gel [12] methods. However, ZZO films have been rarely prepared by sputtering. As a widely used method of depositing films, sputtering can prepare uniform and large area films more easily than PLD method, and can prepare films with higher quality than sol–gel method. Thus, it is necessary to study the ZZO films prepared by sputtering.

We have reported the preparation of transparent conducting ZZO films using radio frequency (RF) magnetron sputtering method and analyzed the properties with the variation of film thickness and deposition pressure in our previous work [13,14]. In this paper, we analyze the effect of doping content on the chemical composition and the structural, electrical, and optical properties of the films in detail.

2. Experimental details

The ZZO films were deposited onto glass (Corning #7059) substrates by RF (13.56 MHz) magnetron sputtering using five ceramic oxide targets ZnO/ZrO_2 (6 cm diameter). The targets

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were prepared from ZnO (purity, 99.99%) and ZrO_2 (purity, 99.99%) powders, and the contents of ZrO_2 were 0, 3, 5, 7, 10 wt.% respectively for different targets. The powders were mixed in a mechanical shaker for 45 min, pressed into pellets at 60 MPa, and then sintered at 1300 °C for 360 min in air. The sputtering was carried out at a pressure of 0.6 Pa in pure argon atmosphere and the RF power was maintained constant at 100 W, for all the films. During the sputtering, the substrates were not intentionally heated. The distance between the substrate and the target was 4 cm. The film thickness was 300 nm in average for all the samples. Prior to deposition, the substrates were cleaned ultrasonically and degreased in acetone. The chamber was initially evacuated to 5.0×10^{-4} Pa, and then pure argon gas was introduced through mass flow controllers to achieve the required pressure.

The film thickness was measured using a XP-2™ profilometer (Ambios Technology Company, USA). The structural properties were analyzed by the X-ray diffraction (XRD) technique using a Philips X' pert MRD diffractometer with a Cu α radiation. The morphology of the surface was observed by atomic force microscope (AFM). X-ray photoelectron spectroscopy (XPS) was performed using an AXIS ULTRA spectrometer (Kratos Analytical Ltd., England) with an Al-K_α radiation source. The XPS measurements were conducted after the films had been etched 30 nm by Ar^+. The electrical properties (resistivity, Hall mobility and carrier concentration) were measured by the four-point probe method and Hall effect measurements using the van der Pauw technique at a constant magnetic field of 0.5 T. The optical transmittance measurements were performed in the range from 300 to 900 nm with a TU-1901 UV–VIS spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZZO films as a function of the ZrO_2 content in the target. For the films of 3 and 5 wt.% ZrO_2, the ZnO (002) and (004) peaks are both observed, and the intensity of the (004) peak is much weaker than that of the (002) peak. However, only the (002) peak is observed for the other films. This indicates that all the films are polycrystalline with the hexagonal structure and have a preferred orientation with the

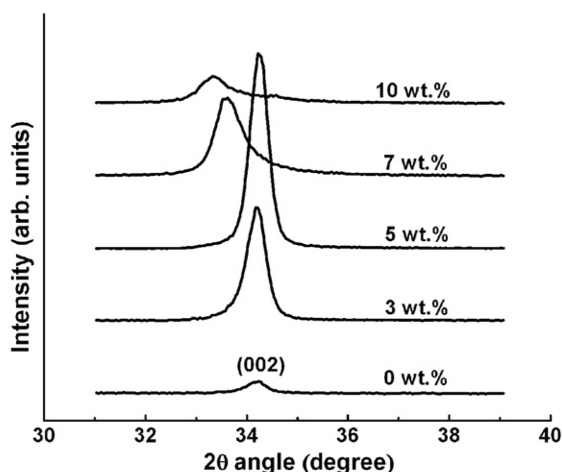

Fig. 1. XRD patterns of ZZO films as a function of the ZrO_2 content.

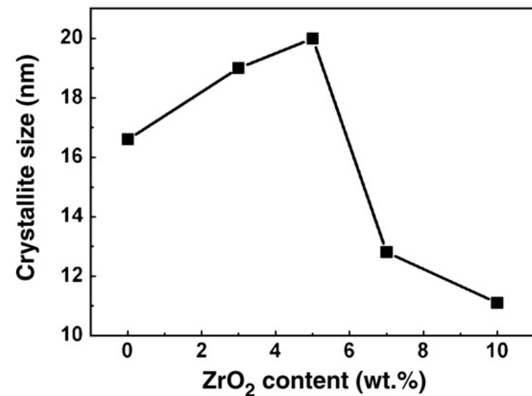

Fig. 2. Dependence of the crystallite size on the ZrO_2 content for ZZO films.

c axis perpendicular to the substrates. As the ZrO_2 content increases from 0 to 5 wt.%, the intensity of the (002) peak increases significantly and the full width at half maximum (FWHM) of the peak decreases from 0.5 to 0.42° implying an improvement of the crystallinity. However, the intensity of the (002) peak shows a sharp decrease and the FWHM of the peak increases to 0.75° when the ZrO_2 content increases further to 10 wt.%, which indicates the deterioration of the crystallinity. The crystallite size can be evaluated by the Sherrer formula [15], and its dependence on the ZrO_2 content is shown in Fig. 2. The crystallite size increases from 16.6 to 20 nm when the ZrO_2 content increases from 0 to 5 wt.%, and then decreases to 11.1 nm with the further increase of the ZrO_2 content to 10 wt.%. The initial increase of the crystallite size should be due to the inhibition of the nucleation caused by the Zr doped into ZnO films. The same results have been found in Cu-doped ZnO films [16]. At higher doping content, however, the excess Zr atoms prefer to cluster into grain boundaries, which will cause the crystal disorder and the consequent decrease of the crystallite size [17].

The *c* axis lattice parameters can be calculated from the XRD patterns. The lattice parameter is 5.24 Å for the film of 0 wt.% ZrO_2 content larger than the value of 5.207 Å for bulk ZnO, which is mainly due to the tensile strain produced within the film during the deposition. Gupta and Mansingh [18] reported that the sputtered ZnO films were in a uniform state of stress with tensile components parallel to the *c* axis, which resulted in the larger lattice parameter. With the increase of the ZrO_2 content from 0 to 5 wt.%, the lattice parameter increases from 5.24 to 5.27 Å. When the ZrO_2 content increases from 5 to 10 wt.%, the lattice parameter shows a significant increase from 5.27 to 5.40 Å. The position of (002) peak shifts to lower angle along with the increase of the lattice parameter. Because the radius (0.59 Å) of Zr^{4+} is very close to that (0.6 Å) of Zn^{2+} in the ZnO structure, the change of the lattice parameter couldn't be attributed to the difference between the radii. The initial increase from 5.24 to 5.27 Å should be due to the increase of the tensile strain in the films [19]. The latter significant increase to 5.40 Å mainly resulted from the incorporation of Zr atoms in the interstitial positions [20], and another reason for the increase may be the formation of ZrO_2–ZnO solid solution [21].

It is also important to investigate the surface morphology of the films, which may affect the properties of the device. Fig. 3

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