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Effects of hydrogen flux on the properties of Al-doped ZnO films sputtered in $Ar + H_2$ ambient at low temperature

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Abstract

Al-doped ZnO (AZO) transparent conductive thin films were grown by magnetron sputtering with AZO (98 wt.% ZnO, 2 wt.% Al_2O_3) ceramic target in $Ar + H_2$ ambient at a relatively low temperature of 100 °C. To investigate the dependence of crystalline and properties of as-grown AZO films on the H_2-flux, X-ray diffraction (XRD), X-ray photoemission spectrometer (XPS), Hall and transmittance spectra measurements were employed to analyze the AZO samples deposited with different H_2-flux. The results indicate that H_2-flux has a considerable influence on the transparent conductive properties of AZO films. The resistivity of $4.15 \times 10^{-4}\ \Omega$ cm and the average transmittance of more than 94% in the visible range were obtained with the optimal H_2-flux of 1.0 sccm. Such a low temperature growing method present here may be especially useful for some low-melting point photoelectric devices and substrates.

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Keywords: H_2; Al-doped ZnO (AZO); Transparent conductive oxides; XPS; Low temperature deposition

1. Introduction

Transparent conductive oxide (TCO) films have been extensively used in a variety of electronic and opto-electronic applications such as flat-panel displays; low-emissivity, electrochromic, or defrosting windows; organic light emitting diodes. Compared with the most generally used ITO transparent conducting film, Al-doped ZnO (AZO) is emerging as an alternative candidate for ITO thin films due to its cheap and abundant raw material, nontoxic feature, as well as being easy to fabricate and have a good stability in plasma [1,2]. RF magnetron sputtering technique has been widely used to deposit thin films of a broad range of materials because of its advantageous features such as simple apparatus, high deposition rates, and low deposition temperature. Many efforts have been made on the enhancement of the electrical and optical properties of AZO films by sputtering. However, most of the researches have been focused on the dependence of transparent conductive properties of AZO film on such deposition parameters as oxygen flux rate, substrate temperature, post-deposition annealing, and so on [3–9]. These processes suffer one or more disadvantages such as needing a high substrate temperature or a crystalline substrate in order to achieve high transparent conductive AZO films quality for large area coating. Recently, there is particular interest in the properties of hydrogen in ZnO, because of the predictions from density function theory and total energy calculations that it should be a shallow donor [10–12]. The generally observed n-type conductivity, therefore, may at least in fact be explained by the presence of residual hydrogen from the growth ambient, rather than to native defects such as Zn interstitials or O vacancies. Nevertheless, there have been limited studies on the influence of hydrogen on the electrical and optical properties of AZO grown by magnetron sputtering. There have been no definite understood of the role of hydrogen in the growing process of magnetron sputtering.

In this paper, AZO transparent conductive thin films were grown by magnetron sputtering with Al-doped ZnO (98 wt.% ZnO, 2 wt.% Al_2O_3) ceramic target in $Ar + H_2$ ambient at a

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relatively low temperature of 100 °C. The influence of hydrogen on the structural, chemical state, electrical and optical properties of AZO films was investigated by X-ray diffraction (XRD), X-ray photoemission spectrometer (XPS), Hall tester and spectrophotometer.

2. Experimental

AZO transparent conductive thin films were deposited by RF magnetron sputtering on microscope slide glass substrate in $Ar + H_2$ at low temperature of 100 °C. A relatively low deposition temperature of 100 °C was used in this studying because high temperatures may destroy some low-melting point substrates or underlying films. A ceramic disc of ZnO (99.99% in purity) mixed with 2 wt.% Al_2O_3 (99.99% in purity) was used as the target (diameter 52 mm). The target to substrate distance was fixed at 7 cm. Before deposition, the substrate was ultrasonically cleaned in acetone, rinsed in deionized water, and subsequently dried in a flowing nitrogen gas. The chamber was evacuated to an ultimate background pressure lower than 4×10^{-4} Pa. During the AZO deposition, the working gas of Ar and H_2 were independently fed into the reaction chamber through two mass flow controllers, working pressure was maintained at about 0.5 Pa. To investigate the effects of different H_2-flux on the properties of AZO films, the H_2-flow was varied in the range of 0.0–1.6 sccm. Other deposition parameters such as Ar-flow, substrate temperature, RF magnetron working power, and depositional time were fixed at 60 sccm, 100 °C, 200 W and 35 min, respectively. The thickness of all the samples was found to be ~450 nm as measured using a surface profilometer.

The crystalline quality and orientation of ZnO films were determined by X-ray diffraction with a Cu Kα1 radiation ($\lambda = 0.154056$ nm). To identify the chemical state of Zn, O and their ratio, XPS measurements were carried out by an ESCALAB Mark II X-ray photoemission spectrometer with Mg Kα radiation source. In order to avoid the influence of surface absorption in the atmosphere, Ar ion etching was performed about 30 min with an etching rate of 0.5 nm/min. The pressure in the analysis chamber was maintained lower than $\sim 10^{-7}$ Pa. Survey spectra, covering a wide range of energies, have been taken from 0 to 1200 eV in binding energy in a constant pass energy mode of 187.85 eV. Multiregion spectra, for studying narrow energy regions of interest, have been taken of the predominant photoelectron and Auger peaks at higher resolution. The electrical properties were studied by means of room temperature Bio-Rad HL5500 system with the van de Pauw configuration. The transmittance of the films was tested by spectrophotometer in the wavelength range from 300 to 850 nm.

3. Results and discussion

3.1. Structural characteristics

The XRD results are shown in Fig. 1. All the films exhibit around the (0 0 0 2) peak due to a self-texturing mechanism as discussed by Jiang et al. [13]. Park et al. [14] reported that the length of *c*-axis was expected to be shorter if the Al atoms were substituted into the Zn site in the crystal because the ionic radii of Zn^{2+} and Al^{3+} were 72 and 53 pm, respectively. But the XRD results of films prepared in $Ar + H_2$ ambient were inconsistent with that conclusion. These phenomena could be due to that hydrogen atoms were situated in the Zn–O bond center, which meant the lattice parameter of ZnO films would increased, as indicated by the smaller diffraction angle for the sample deposited with H_2-flux [10]. It is also noticed that the full width at half maximum (FWHM) of the films prepared without H_2 and with H_2-flux of 0.4 sccm, 1.0 sccm were 0.30, 0.22, and 0.21, respectively. The decrease in FWHM corresponds to the increase in grain size as deduced from Scheer equation [15]. However, the peak intensity of XRD of AZO film deposited with 1.6 sccm H_2-flux shows a tendency to decrease markedly, almost disappearing, it might be understood when considering

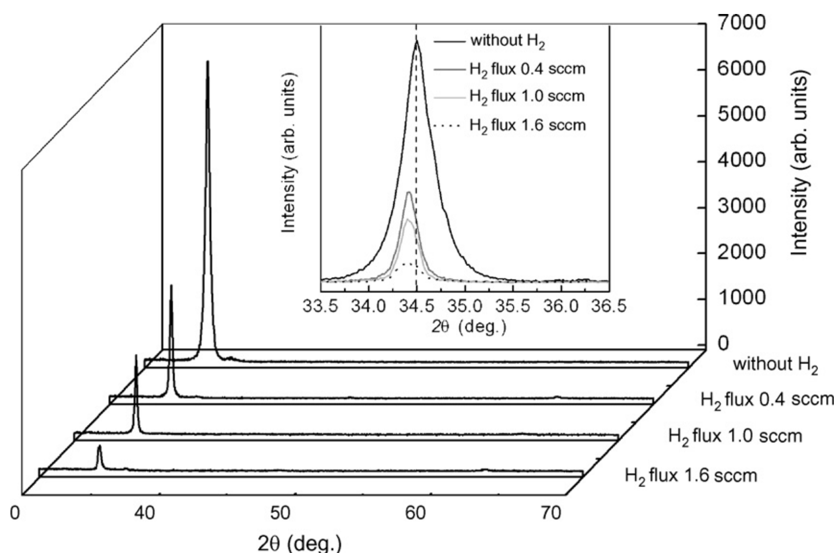

Fig. 1. X-ray diffraction spectrum of AZO films prepared with different H_2-flux.

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