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Modification of structure and properties of AZO thin film by introducing H_2 in sputtering atmosphere at low substrate temperature

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ABSTRACT

Al-doped ZnO (AZO) thin films were prepared on soda-lime glass at 100 °C by RF magnetron sputtering with different H_2 fluxes. The influences of H_2 flux on structural, electrical, and optical properties were investigated by XRD, Hall Effect measurement, and transmittance spectra. The results show that hydrogen introduction significantly modifies both structure and properties of AZO films. As H_2 flux increases, the increase of unit-cell volume of the films implies that hydrogen is incorporated into ZnO lattice; the obvious decrease of crystallite size indicates that the crystallinity of the films degrades. The resistivity of the films can be continuously decreased with increasing H_2 flux, accompanying with increase of both carrier concentration and Hall mobility. The main factor of increasing carrier concentration and mobility is found to be related to hydrogen incorporation and effective substitution of Zn^{2+} sites by Al^{3+}. The films deposited in Ar + H_2 atmosphere show improved conductive stability in air due to the passivation of intercrystallite by hydrogen. The average transmittance in visible range of the films is hardly dependent on H_2 flux. The E_g of the films increases with increasing H_2 flux, and the blueshift values are close to the theoretical one according to the nonparabolic BM effect.

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1. Introduction

Transparent conducting oxides (TCO) thin films are widely used in flat panel displays, solar cells, touch screens, electrochromic windows, and low-emissivity windows [1,2]. Currently, indium tin oxide (ITO) is the most popular and practical used TCO materials in above applications due to its low resistivity and high transparency [2,3]. In recent years, Al-doped ZnO (AZO) thin films exhibit considerable electrical and optical properties with low material cost, non-toxicity and stability in hydrogen plasma, and thus they are regarded as an alternative material to ITO [3,4]. Many preparation and treatment methods have been carried out to obtain high performance AZO thin films, such as pulsed laser deposition [5], spray pyrolysis [6], magnetron sputtering [7], and post-annealing [8]. However, many studies indicate that high performance AZO thin films are obtained at relatively high substrate temperatures and/or post-annealing temperatures (300–400 °C) [9–11], which are higher than required temperatures for above mentioned applications (<200 °C) [3]. As a result, it is necessary to improve the properties of AZO thin films at low temperature to be compatible with the fabrication of photoelectric device.

In 2000, Van de Walle [12] had predicted that hydrogen occurs exclusively in the positive charge state and acts as a shallow donor in ZnO materials by density functional theory calculations. Experimentally, it has been confirmed that the hydrogen can be intentionally introduced into AZO thin films by H-plasma treatment [13], adding H_2 in growth atmosphere [14], and post-annealing in H_2 [15]. When H_2 is introduced into deposition atmosphere during radio frequency (RF) magnetron sputtering, which is a widely used method to prepare AZO films, hydrogen can be doped into ZnO lattice by hydrogen radicals in plasma to improve the electrical conductivity of the prepared films at low substrate temperatures. However, effect of introduction of H_2 on the structure and properties of magnetron sputtered AZO films is not understood completely.

In this paper, AZO thin films were prepared by RF magnetron sputtering under various H_2 fluxes in sputtering atmosphere at substrate temperature of 100 °C. Effects of hydrogen incorporation on the structural, electrical, and optical properties of AZO films were investigated. The aim is to obtain high performance AZO thin films and explain the behavior of hydrogen in AZO films.

2. Experimental procedures

AZO thin films were prepared on soda-lime glass in a conventional RF magnetron sputtering system with a sintered AZO ceramic target (99.9% in purity, 2 wt.% Al_2O_3, and 60 mm in diameter) purchased from Wuhan Sinotarget Materials Co., Ltd. Before deposition, the glass substrates were cleaned in alcohol, acetone and distilled water by ultrasonic for 15 min successively. The vacuum chamber was evacuated to 1.0×10^{-3} Pa, after that H_2 and Ar were introduced into chamber as sputtering gas. To investigate the influence of H_2 flux on the structure and properties of AZO thin film, the H_2 flux was varied in the range of 0–12 standard-state cubic centimeter per minute (sccm) and the Ar flux was fixed at 95 sccm by using mass flow controllers. The substrate temperature, sputtering power, sputtering pressure, and substrate-target distance were fixed at 100 °C, 150 W, 0.8 Pa, and 65 mm, respectively. To exclude the influence of thickness, all films had a thickness of about 515 nm by varying the deposition time.

Interference microscope (SC57-6JA) was used to determine the thickness of AZO thin films. The crystalline structure of the films was identified by an X-ray diffraction (XRD; Bruker AXS D-8 Advance Model) using Cu Kα radiation. The electrical properties of the films were determined by Hall effects measurement using Van der Pauw method at room temperature. The transmittance spectra of the films were obtained from UV–visible spectrophotometer (UV-2102PC) in the wavelength range of 300–1000 nm.

3. Experimental results and discussion

3.1. Structural characterization

Fig. 1 reveals the XRD patterns of AZO thin films deposited at various H_2 fluxes. It is observed that AZO thin film deposited in pure Ar atmosphere has a relatively strong (100) diffraction peak and a