Vacuum 89 (2013) 127–131

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Influence of thickness and annealing temperature on the electrical, optical and structural properties of AZO thin films

F. Wang [a,b], M.Z. Wu [a], Y.Y. Wang [d], Y.M. Yu [d], X.M. Wu [a,b,*], L.J. Zhuge [b,c]

[a] Department of Physics, Soochow University, Suzhou 215006, China
[b] The Key Laboratory of Thin Films of Jiangsu, Soochow University, Suzhou 215006, China
[c] Analysis and Testing Center, Soochow University, Suzhou 215006, China
[d] Wenzheng College of Soochow University, Suzhou 215006, China

ARTICLE INFO

Article history:
Received 20 September 2011
Received in revised form
13 February 2012
Accepted 24 February 2012

Keywords:
AZO
Thickness
Annealing
RF magnetron sputtering
ZnO

ABSTRACT

Transparent conductive Al-doped ZnO (AZO) thin films with various thicknesses between 520 and 1420 nm were deposited on quartz substrates by radio frequency (RF) magnetron sputtering at room temperature for thin film solar cells as transparent conductive oxide (TCO) electrode layers. After deposition, the samples were annealed in a vacuum ambient at temperatures between 250 and 550 °C for a period of 30 min. The structural, electrical, and optical properties of these films have been analyzed as a function of the thickness and the annealing temperature by a series of characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), Hall effect measurements and spectrophotometry. All of these samples exhibited strong (002) diffraction peaks and the visible range transmittance was over 80%. In addition, with the increase of thickness, the Hall mobility increased from 4.88 to 7.86 cm^2/V, the resistivity decreased from 1.2×10^{-2} Ω cm to 4.2×10^{-3} Ω cm. Annealing in vacuum improved the crystallinity together with some changes of the electrical resistance that depended on the annealing temperature. The best characteristics have been obtained at 450 °C, where the lowest resistivity was 2.7×10^{-3} Ω cm for the thickest films.

1. Introduction

Transparent conductive oxides (TCOs) have attracted a great deal of attention in recent years because they play a key role in a number of thin film optoelectronic devices such as thin film solar cells, flat-panel displays, and light emitting diodes [1–3]. Such TCO films are commonly used as electrode layers in thin film solar cells, and they should fit the following criteria: first, to be highly transparent in the visible wavelength range where the solar cell is operating to minimize the photon absorption; second, to have high conductivity to reduce the resistive losses [4]. At present, the incumbent TCO technology is indium tin oxide (ITO), and there are growing concerns regarding its future availability and cost. These concerns are due to its toxicity, along with the limited availability of the metal indium as the production of consumer products using ITO expands rapidly [5]. Because of these shortage concerns, alternative TCO technologies are being developed. Among these alternative technologies, Al-doped ZnO (AZO) film is the particularly attractive one because of its excellent properties, such as non-toxic, high thermal stability, good resistance against damage by hydrogen plasma and low cost of fabrication [6,7]. Therefore, inexpensive AZO becomes a natural selection over costly In-rich ITO, even when its performance does not completely match the expensive counterpart.

Many deposition methods have been used to prepare AZO thin films, including magnetron sputtering [8], pulsed laser deposition (PLD) [9], chemical vapour deposition (CVD) [10], and sol–gel processes [1]. Among them, magnetron sputtering is considered to be a suitable technique owing to its inherent characteristics such as high deposition rate, good controllability and scalability to large area [4,11,12]. It was found that the properties of AZO films are strongly dependent upon the preparation conditions such as the sputtering power, sputtering time, chamber pressure, and substrate temperature, in addition, post-annealing is also found to be an effective method to improve the properties [6,13–15].

Here, we systematically investigated the structure, electrical and optical properties of AZO films prepared by RF magnetron sputtering with various sputtering times. The main purpose is to further understand the relationships between the characteristics of AZO films and their thickness and the annealing temperature.

* Corresponding author. Department of Physics, Soochow University, Suzhou 215006, China. Tel.: +86 0512 6511 2066.
E-mail address: xmwu@suda.edu.cn (X.M. Wu).

0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2012.02.040

2. Experimental details

Deposition of AZO thin films was performed by RF magnetron sputtering from an oxide ceramic target consisting of 98 wt% ZnO and 2 wt% Al_2O_3 at room temperature. Silicon wafers and quartz glasses were chosen as substrates, which were degreased in a dilute detergent solution, rinsed with a large amount of deionized water and dried in a flux of N_2 before they were introduced into the chamber. After vacuum pumping, the sputtering was performed with an Ar pressure of 2 Pa and RF power of 170 W in the chamber evacuated to 7×10^{-4} Pa before argon gas in a flow of 20SCCM was introduced through a mass flow controller. Pre-sputtering for 5 min was done to remove impurities from the target surface. AZO films with various thicknesses were obtained by varying the deposition time from 55 to 120 min. After deposition, the as-grown AZO films were then divided into several groups for vacuum annealing and subsequently structural and physical analyses. Films with the thickness of 1420 nm were annealed at temperatures ranging from 250 to 550 °C in steps of 100 °C for 30 min in vacuum, respectively.

The structure of the films was analyzed by a Rigaku D/Max-2500PC XRD diffractometer using Cu Kα radiation at 40 kV (Cu Kα, $\lambda = 0.15406$ nm). SEM (Hitachi S-4700) was used to determine the thickness via cross-section, top-view SEM imaging was used to determine the surface morphology, and the incidental energy dispersive X-ray spectroscopy (EDX) was used to measure the elemental composition. The surface roughness was evaluated by AFM (NT-MDT Solver P47-PRO). Electrical properties were studied using the Van der Pauw Hall measurement method. Finally, optical properties were measured with a JASCO V-570 spectrophotometer in the wavelength range of 300–800 nm. All the measurements were conducted at room temperature.

3. Results and discussion

3.1. Structural properties

All as-grown samples exhibit a strong peak at about 34°, corresponding to the (002) diffraction peak of hexagonal wurtzite structure, which indicates a c-axis orientation to the surface of the substrates [16]. No Al_2O_3 phase is found, which implies that Al atoms substitute Zn in the hexagonal lattice and Al ions may occupy the interstitial sites of ZnO or probably Al segregates to the non-crystalline region in grain boundaries and forms Al–O bonds [17,18].

The relationship between (002) diffraction angles (2θ) and thickness is shown in Fig. 1a. The thicknesses of AZO films deposited for 55, 70, 80, 95, and 120 min are 520, 660, 790, 930, and 1420 nm, respectively. With the increase of thickness, the value of 2θ increases from 34.34° to 34.42°, indicating that the (002) interplanar spacing of films becomes smaller because of the reduced stress in the crystal grain [19]. Fig. 1(b) shows that the FWHM decreases from 0.465° to 0.312° when the thickness increases from 520 to 1420 nm. Since the grain size is inversely proportional to FWHM, the grain size increase from the smallest value of 17.68 nm to the largest of 26.36 nm, which can be seen in Fig. 1(c).

AFM images are usually used to characterize the morphology, surface roughness and grain size. All samples have a uniform surface morphology like the thickest one in the inset of Fig. 2. However, the surface roughness and grain size gradually enlarge with the increase of thickness. It can be seen from Fig. 2 that, as the thickness reaches 1420 nm, the RMS roughness grows to 22.5 nm, the maximum height fluctuation grows to 205.2 nm and, also, the grain size increases. Such observation is consistent with the conclusion from XRD patterns.

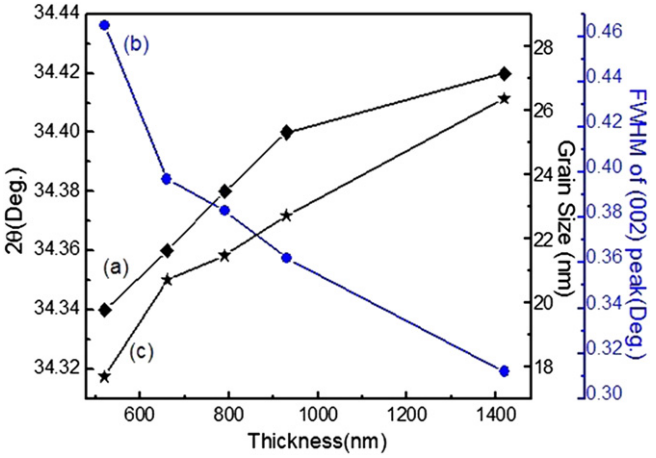

Fig. 1. (002) diffraction angles (a), FWHM (b) and grain size (c) of AZO films as a function of thickness.

It is well-known that the crystal quality will be improved, the dislocations and other defects will move in the material and adsorption/decomposition will occur after post-annealing [15]. As can be seen from Fig. 3, the (002) peak of AZO films becomes sharper, the intensity becomes larger, and the peak position shifts to higher values slightly when the annealing temperature increases to 45 °C, which may imply that more Al ions occupy the lattice position of Zn ions and less stress remains in films after annealing [20].

3.2. Electrical properties

All samples for Hall measurements were sputtered directly over quartz glasses with the size of 10 × 10 mm. Fig. 4 summarizes the dependence of the resistivity (ρ), Hall mobility (μ) and carrier concentration (n) of AZO films on thickness. The resistivity is about 1.2×10^{-2} Ω cm for a 520 nm film, and then gradually decreases to 4.2×10^{-3} Ω cm for a 1420 nm film. This phenomenon is directly related to the change of carrier concentration and Hall mobility according to the formula of resistivity $\rho = 1/(ne\mu)$. All carrier

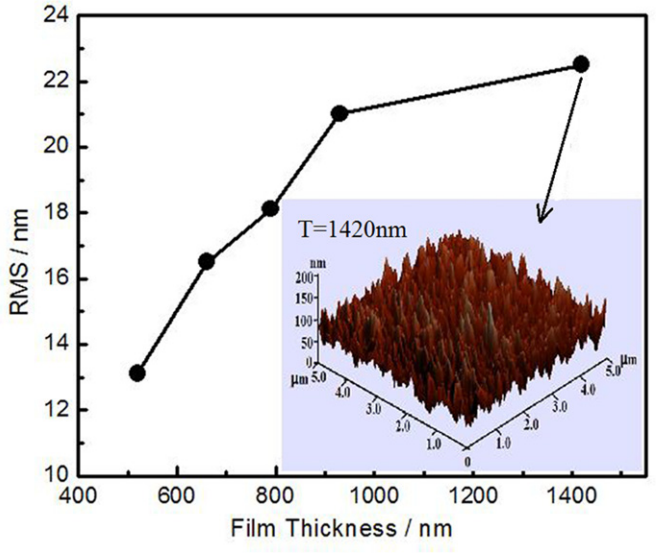

Fig. 2. The relation of RMS and the thickness, the inset is the AFM image of the thickest film.