Thin Solid Films 517 (2009) 3048–3052

Contents lists available at ScienceDirect

Thin Solid Films

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

Electrical and optical properties of Al-doped ZnO films deposited by hollow cathode gas flow sputtering

Hiroshi Takeda [a], Yasushi Sato [a], Yoshinori Iwabuchi [b], Masato Yoshikawa [b], Yuzo Shigesato [a,*]

[a] Graduate School of Science and Engineering, Aoyama Gakuin University, 5-10-11 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan
[b] Chemical and Industrial Products Technology Division, Bridgestone Corporation, 3-1-1 Ogawahigashi, Kodaira, Tokyo 187-8531, Japan

ARTICLE INFO

Available online 27 November 2008

Keywords:
ZnO
Al-doped ZnO (AZO)
Transparent conductive oxide (TCO)
Hollow cathode discharge
Gas flow sputtering (GFS)

ABSTRACT

Al-doped ZnO (AZO) films were deposited on glass by hollow cathode gas flow sputtering using Zn–Al alloy targets. Sputtering power for all the depositions was fixed at 1500 W. Resistivities of $0.81–1.1\times10^{-3}$ Ω cm were obtained for AZO films deposited at room temperature with an O_2 flow from 38 to 50 standard cubic centimetre/minute (SCCM), while static deposition rates were almost constant at 270–300 nm/min. On the other hand, lower resistivities of $5.2–6.4\times10^{-4}$ Ω cm were obtained for AZO films deposited at 200 °C with an O_2 flow from 25 to 50 SCCM, while the static deposition rates were almost constant at 200–220 nm/min. Average transmittances in the visible light region were above 80% for both sets of films.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Al-or Ga-doped ZnO [1,2] are regarded to be promising candidates as alternatives to the indium-based transparent conductive oxides (TCOs), such as Sn-doped In_2O_3 (ITO) or amorphous In_2O_3–ZnO (IZO) [3–5], due to advantages of resource availability and non-toxicity. For the industrial applications, including applications in various kinds of flat panel displays and solar batteries, there are strong demands for transparent conductive oxides to be produced with a high deposition rate, with a higher stability and at lower costs. Reactive magnetron sputtering processes using metal or alloy targets have a high potential for low cost deposition of transparent conductive oxides at a high deposition rate. However, the conventional reactive sputtering depositions are usually highly nonlinear processes where the deposition rate and the film stoichiometry show hysteresis loops, called "transition region", as a function of the reactive gas flow, caused by poisoning of the target surface [6]. Already in 2002, 2003 we reported on the high rate depositions of Al-doped ZnO (AZO) by reactive magnetron sputtering in such a "transition region", using a dual cathode pulsing system with plasma emission or plasma impedance feedback systems [7,8].

Gas flow sputtering (GFS), which was already reported by Ishii [9] in 1989, is a high rate deposition technique. In recent years, a number of studies have been reported on metal oxide or metal thin films deposited by GFS [10–16]. This technique is based on a hollow cathode discharge and a gas flow driven material transport. The hollow cathode discharge can occur in a tube or a pair of facing rectangular plates with gas pressures at 10–100 Pa, which results in a high plasma density without the presence of a magnetic field near the target surface. Thereby, the utilization efficiency of a sputter target can be highly improved. Furthermore, a large amount of inert gas flows from the two cathodes to the substrate and reactive gases are feeding into the space between the hollow cathode and the substrate in order to prevent the oxidation of the target surface, so a transition region is not observed. Using metal targets, this deposition method has specific advantages over conventional reactive magnetron sputtering in terms of the high deposition rate. We recently reported on the high rate deposition of TiO_2 photocatalyst with very high activity by GFS [16].

This paper reports on AZO film depositions with a very high deposition rate by GFS using Zn–Al alloy target and O_2 reactive gas. The results obtained indicate that the GFS depositions enable to prepare high-quality AZO films with 10^{-4} Ω cm resistivity and more than 80% transmittance in the visible light region, without using any special feedback systems or strong magnetic field.

2. Experimental details

A GFS system was used for the deposition of AZO films on alkali-free glass substrates (#1737, Corning) with a size of 50 mm × 50 mm. A schematic illustration of the GFS system is shown in reference [16]. This system consists of two Zn–Al alloy targets (Zn:Al = 98.5:1.5 wt.%) with a size of 160 mm × 80 mm, mounted on water-cooled copper, in parallel facing each other. A hollow cathode discharge was generated in the space between the facing targets. The Ar gas stream of 3000 SCCM, where SCCM denotes cubic centimetre/minute at standard temperature and pressure, was introduced from the bottom of the system and went through the space between the faced targets. The size of the orifice of the deposition source was 160 mm × 30 mm

* Corresponding author. Tel.: +81 42 759 6223; fax: +81 42 759 6493.
E-mail address: yuzo@chem.aoyama.ac.jp (Y. Shigesato).

0040-6090/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2008.11.114

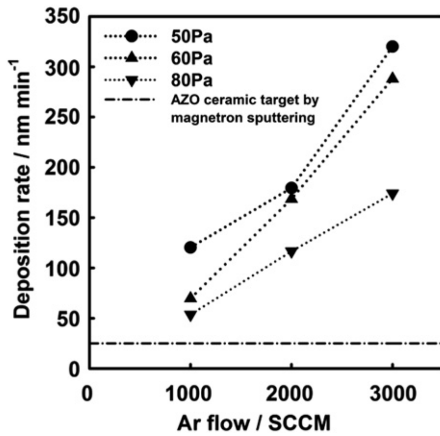

Fig. 1. Deposition rates of Zn–Al alloy films by GFS on unheated substrates as a function of Ar gas flow, without O_2 introduction, at various total gas pressures of 50 (●), 60 (▲) and 80 Pa (▼). For a comparison, a typical AZO deposition rate by conventional magnetron sputtering using an AZO ceramic target (target power density of 1.1 W/cm^2) is also shown by a dash–dot line.

approximately, corresponding to the uniform coating area. O_2 reactive gas was supplied to the vicinity of the substrate to deposit the AZO films. Zn and Al sputtered atoms are transported to the substrate by the forced Ar stream to react with O_2 molecules near the substrate, and the AZO products thus formed are deposited on the substrate. The O_2 flow was varied from 0 to 50 SCCM. Total gas pressure during the depositions was maintained at 50, 60 or 80 Pa by controlling a vacuum exhaust value. The evacuating system consisted of the combination of a mechanical booster pump and a rotary pump. Sputtering power for all the depositions was fixed at 1500 W, i.e., 5.9 W/cm^2. AZO films were deposited on the substrates, unheated and heated at 200 °C, where the temperature of the unheated substrate was less than 50 °C.

The thickness of the films was measured using a surface profiler (Dektak 6M, Veeco). The crystallinity of the films was analyzed by X-ray diffraction (XRD, XRD-6000, Shimadzu) using 40 kV, 20 mA CuK$_{\alpha1}$ radiation. The film structures and surface morphology of the AZO films were observed using a transmission electron microscope (TEM, JEM-4010, JEOL) operating at 400 kV and an atomic force microscope (AFM, SPM-9500J3, Shimadzu).

Resistivity, Hall mobility and carrier density of the films were analyzed by four-point probe method and Hall-effect measurement in the van der Pauw geometry (HL-5500PC, Nanometrics). Transmittance and reflectance of the films were measured from 250–2500 nm using a spectrophotometer (UV-3100, Shimadzu).

3. Results and discussion

Fig. 1 shows the deposition rates of Zn–Al alloy films by GFS on the unheated substrate as a function of the Ar gas flow, without O_2 introduction, at various total gas pressures of 50, 60 and 80 Pa. The deposition rate increased with decreasing total gas pressure and increasing Ar gas flow. The maximum deposition rate of 320 nm/min was obtained at 50 Pa and an Ar gas flow of 3000 SCCM. This deposition rate is about 10 times as high as the deposition rate of conventional magnetron sputtering. The deposition rate was found to depend on the transport process, especially on the gas flow and gas speed of Ar, acting as the carrier gas for the sputtered atoms. The gas flow and gas speed are related to the number of gas particles passing through a given area in a time unit. Since the total gas pressure was adjusted by a throttling valve, the residence time of the Ar gas atoms in the vacuum chamber should be shorter at the lower pressure. Therefore, the gas flow speed at the lower pressure should be faster than the one at higher pressure. Consequently, the sputtered atoms could be carried toward the substrates more effectively and the deposition could increase under the lower gas pressure and the higher gas flow conditions. Such deposition rates have decreased by about 40% with increasing substrate temperature to 200 °C during the depositions. The typical AZO deposition rate at RT by conventional magnetron sputtering with a power density of 1.1 W/cm^2 is also shown, by a dash–dot line, in Fig. 1. Although the power densities in the magnetron sputtering could not be directly compared by those in GFS, the deposition rate of GFS could be expected to be much higher than that of the magnetron sputtering.

Fig. 2 a and b show XRD patterns of the AZO films deposited by GFS on (a) unheated and (b) heated substrates at 200 °C with an Ar flow of 3000 SCCM, a total gas pressure of 50 Pa and an O_2 flow from 10 to 50 SCCM. The thicknesses of the AZO films deposited on unheated glass were adjusted to 500–600 nm whereas the thicknesses of films deposited on glass substrate heated at 200 °C were 250–350 nm. The AZO films deposited with O_2 flow at more than 20 SCCM clearly

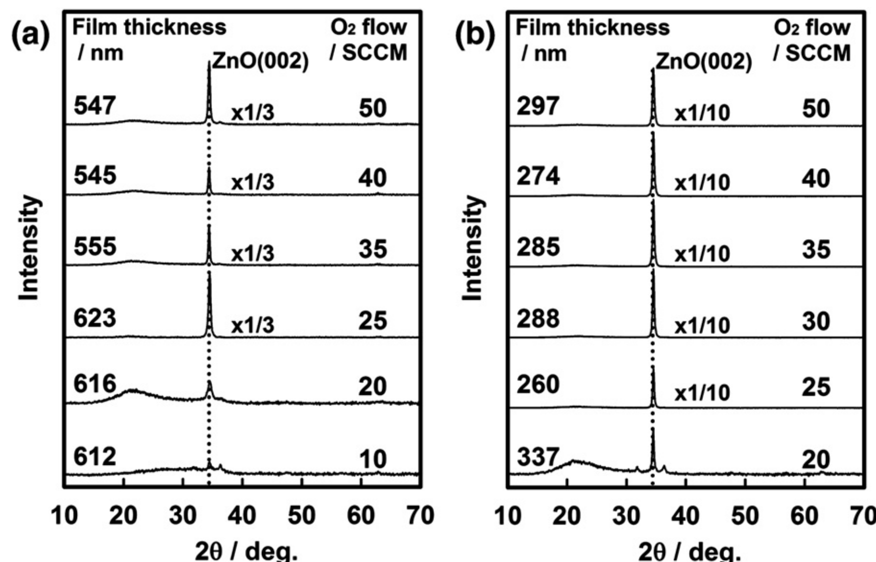

Fig. 2. XRD patterns of AZO films deposited by GFS on (a) unheated (<50 °C) and (b) heated substrates (200 °C), with an Ar flow of 3000 SCCM, a total gas pressure of 50 Pa and an O_2 flow from 10 to 50 SCCM. The thicknesses of all the films are illustrated in the figure.

Download English Version:

https://daneshyari.com/en/article/1669821

Download Persian Version:

https://daneshyari.com/article/1669821

Daneshyari.com