Thin Solid Films 545 (2013) 106–110

Contents lists available at ScienceDirect

Thin Solid Films

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

Influence of growth temperature on the electrical and structural characteristics of conductive Al-doped ZnO thin films grown by atomic layer deposition

Cheol Hyoun Ahn [a], Sang Yeol Lee [b,*], Hyung Koun Cho [a,*]

[a] School of Advanced Materials Science and Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon, Gyeonggi-do, Republic of Korea
[b] Department of Semiconductor Engineering, Cheongju University, Cheongju, Chungbuk, 360-764, Republic of Korea

ARTICLE INFO

Article history:
Received 27 December 2012
Received in revised form 15 July 2013
Accepted 17 July 2013
Available online 24 July 2013

Keywords:
Atomic layer deposition
Al-doped ZnO
Transparent electrode
Doping
Growth temperature

ABSTRACT

Al-doped ZnO thin films (AZO) were deposited by atomic layer deposition at various temperatures (100–300 °C) with a frequency ratio of 19/1 (Zn–O/Al–O), and their properties were evaluated. With increasing growth temperature, the Al contents in the AZO thin films were continuously increased, because of the rapid increase in the incorporation efficiency of the Al–O layer with respect to the Zn–O layer. Although low-temperature deposition resulted in the abnormal [100]-preferred orientation of the AZO films, they had a high carrier density of ~10^{20} cm^3. However, the Hall mobility showed a low value of 1.5 cm^2/Vs due to the high density of impurities such as C–O or O–H caused by incomplete reaction for precursors. In contrast, the electrical and structural properties of the AZO thin films were enhanced by increasing growth temperature, due to the increased Al doping level and reduced residual impurities, which was confirmed by X-ray diffraction and X-ray photoelectron spectroscopy.

1. Introduction

Recently, ZnO-based semiconductors have been extensively investigated for application in optoelectronic devices, due to their superior optical and electrical properties [1,2]. In particular, doped ZnO thin films have attracted strong attention for practical applications, such as flat panel displays, solar cells, thin-film-transistors, thermoelectric, and various sensors, because their electrical properties can be tuned through the incorporation of metal cations, such as Al, Ga, In, and Hf [3–10].

Intrinsic ZnO is known to naturally be an n-type semiconductor due to oxygen vacancies or zinc interstitials. The control of the electrical and optical properties of the ZnO films is an important issue for industrial applications. However, the intrinsic ZnO thin films are not electrically stable in atmospheric conditions that include oxygen and H_2O. In addition, doped ZnO has emerged as a promising alternative to In–Sn–O, because it shows high conductivity, mobility, and transparency in the visible region. Among metal-doped ZnO (AZO) thin films, AZO is strongly considered as a transparent electrode for application in photovoltaic devices, based on its electrical properties, visible transparency, lower cost, and non-toxicity [11]. AZO has also shown high stability in hydrogen plasma compared with other transparent conducting oxide (TCO) materials. Moreover, the AZO films can be used as efficient antireflection coatings, because of its intermediate refractive index (~1.89) [12]. The growth of AZO thin films has been investigated using a variety of techniques, such as radio frequency magnetron sputtering [4], pulsed layer deposition [13], atomic layer deposition (ALD) [3,13–16], plasma chemical vapor deposition [17], and sol–gel methods [18]. Among these, ALD has unique advantages, such as highly precise thickness control, excellent uniformity over a large area, high conformity, high mass production, and easy control of the doping level. The merits of the ALD process have resulted from the self-limited reaction process of the precursors used, allowing delicate control of the thickness and compositions at the monolayer level.

Recently, several groups have used ALD under various process conditions to deposit transparent oxide semiconductors with high conductivity [3,13–16]. Our previous study revealed that the electrical and structural properties of the AZO films grown by ALD at 200 °C were strongly dependent on the Al contents, and the lowest electrical resistivity of 6.5×10^{-4} [Ω cm] was observed in the AZO film containing 5 at % Al [3]. The deposition of TCO films at low temperature is required to produce electrodes in flexible devices. The growth temperature in an ALD process is an important parameter, because it affects the reaction behavior. However, the influence of growth temperature in AZO thin films grown by ALD has not yet been discussed detail. In this work, we investigate the effect of deposition temperature on the structural, optical, and chemical properties of AZO thin films grown by ALD.

2. Experimental details

AZO thin films of ~200-nm thickness were deposited on (001) Si and corning glass substrates by ALD at various growth temperatures (100–300 °C). Diethylzinc (DEZn), trimethylaluminium (TMA), and high-purity H_2O were used as precursors of zinc, aluminum, and oxygen, respectively. The temperature of cooling circulators for all precursors was held at 10 °C. Nitrogen gas with a flow rate of 100 SCCM was

* Corresponding authors. Tel.: +82 31 290 7364; fax: +82 31 290 7410.
E-mail addresses: sylee@cju.ac.kr (S.Y. Lee), chohk@skku.edu (H.K. Cho).

0040-6090/$ – see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.tsf.2013.07.045

injected directly into the reaction chamber as a carrier and purging gas. One cycle of ALD deposition consisted of exposure to DEZn (or TMA) (0.1 s), a 10 s purge, exposure to H_2O (0.1 s), and another 10 s purge. According to the process optimized in a previous study, the frequency ratio of Zn–O and Al–O cycles was held at the 19/1 for growth of highly conductive AZO thin films. The structural properties of AZO thin films were characterized by X-ray diffraction (XRD, Bruker AZS D8 discover) in θ–2θ scan mode with a copper X-ray source, and secondary electron microscopy (SEM, JEOL JSM6700F) under 15 kV. For chemical analysis, X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA2000) measurements with Al K_a radiation (1486.6 eV) were carried out and were calibrated with C 1 s peak (284.6 eV). The raw XPS spectra were fitted with Gaussian–Lorentzian functions for the quantitative analysis. The electrical properties of AZO thin films deposited on glass substrate were analyzed by room-temperature Hall-effect measurements (Ecopia HMS 3000 system, 0.55 T) using a van der Pauw configuration. Transmittance measurements were also carried out by UV/visible/near-IR spectroscopy (Cary5000) to examine the optical properties of the films.

3. Results and discussion

The structural properties of the AZO thin films grown on Si substrates at various temperatures by ALD were investigated by XRD and SEM. Fig. 1(a) shows the XRD patterns of the AZO thin films. The AZO thin films deposited by ALD generally showed hexagonal wurtzite structure with diffraction peaks at 31.7, 34.4, and 36.2° corresponding to the (100), (002), and (101) planes, respectively. All the AZO films show polycrystalline behavior, irrespective of growth temperatures. However, interestingly, the preferred orientation of these AZO films showed significantly different appearance depending on growth temperatures, as shown in the Fig. 1(a). At the growth temperature of ≤150 °C, the films predominantly exhibit [100]-preferred orientation. Further increase in growth temperature induces a change in the preferred orientation from a-axis to c-axis. It is generally accepted that the un-doped ZnO thin films have a c-axis preferred orientation, because the c-axis is the most densely packed and thermodynamically favorable plane in the wurtzite structure. In addition, because the (002) plane of ZnO consists of one ions among Zn^{2+} and O^{2-}, the thin films have a high growth rate along the c-axis with high polarity. However, it has often been reported that the ZnO thin films grown by ALD showed a-axis preferred orientation due to low growth temperature or doping [6,14,16,19,20]. Recently, Banerjee et al. studied the characterization of AZO grown on glass substrate by ALD with various Al contents at 150 °C [15]. They found that the films showed a-axis preferred orientation when Al doping in ZnO. Although the (100) plane is a charge-neutral surface, the origin of a-axis preferred oriented AZO film suggested that layer-by-layer growth during ALD may cause Al^{3+} ions to disturb the charge neutrality of the (100) plane, thereby affecting its surface energy and causing its preferential growth. In contrast, our studies revealed that the preferred orientation of AZO films grown on Si substrate were strongly dependent on the growth temperature. This means that the preferred orientation of the films is attributed to the chemical reaction of precursors as a function of growth temperature. Fig. 1(b) shows the growth rates of ZnO and Al_2O_3 films deposited by ALD for 400 cycles, evaluated by α-step as a function of growth temperature to compare growth behavior. In a low temperature (<150 °C) region, the growth rate of ZnO and Al_2O_3 films is relatively low, which indicates that the reactants composed of DEZn and H_2O or TMA and H_2O have insufficient energy for active chemical reaction. On the other hand, the growth rate is found to be constant at increased growth temperature regions (150–200 °C for ZnO, 200–250 °C for Al_2O_3). However, further increase in growth temperature results in a significant reduction of the growth rate due to precursor desorption/dissociation. As a result, acceptable ALD windows differ between Zn–O and Al–O. At a low growth temperature (<150 °C for ZnO and <200 °C for Al_2O_3), ethyl groups such as $CH_3CH_2^-$ and CH_3^- originating from precursors can be included within the films due to incomplete reaction, because these anions can be adhered to the Zn-polar surface of the (002) plane, which can interfere in the formation of the c-axis preferred orientation. The ALD window for the stable deposition of the Al_2O_3 film requires higher temperature than that for the ZnO film, as shown in Fig. 1(b). At relatively high growth temperature (200–250 °C), the AZO thin films show stronger (002) diffraction than other planes. The c-axis growth direction was suppressed in the low temperature region due to the incomplete reaction of precursors and residual ethyl groups, resulting in nonpolar (100) preferential growth. As a result, we found that the growth direction by ALD is highly sensitive to the growth temperature reaction process of precursors. Also, this trend is in agreement with the references [19,20]. Pung et al. also suggested that the origin of a-axis growth of the ZnO grown at low temperature is related to ethyl groups [20]. The morphologies of AZO thin films grown on Si substrates depending on growth temperatures were observed by SEM, as shown in Fig. 1(c). The AZO thin films show anisotropic surface morphologies with wedge shape at ≤200 °C and ≥300 °C. At ≤200 °C, the wedge shape

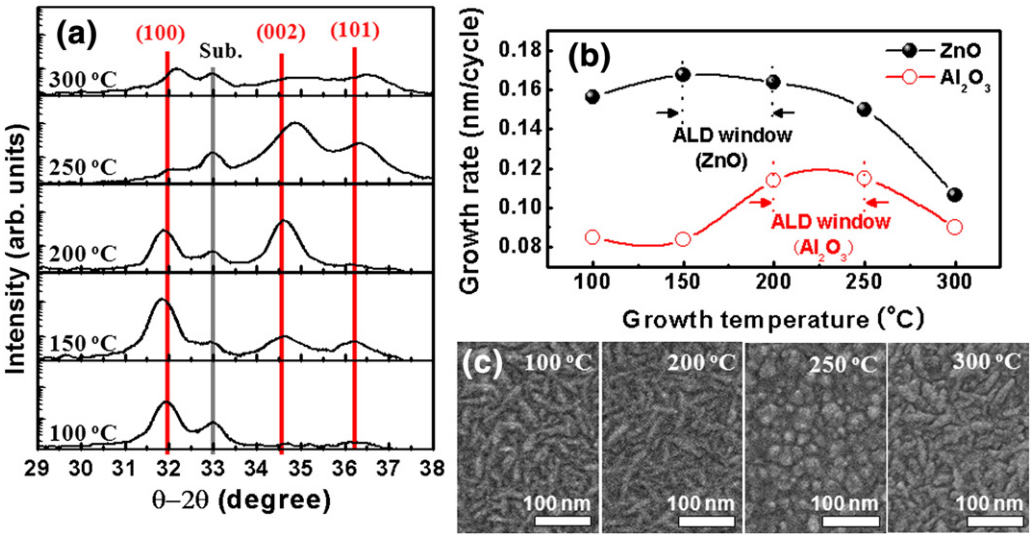

Fig. 1. (a) XRD patterns in θ–2θ scan mode of the AZO thin films deposited at various growth temperatures. (b) Comparison of growth rates for ZnO and Al_2O_3 thin films as a function of growth temperature. (c) SEM images of the AZO thin films deposited at various growth temperatures.