Thin Solid Films 605 (2016) 53–56

Contents lists available at ScienceDirect

Thin Solid Films

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

Comparison study of V-doped ZnO thin films on polycarbonate and quartz substrates deposited by RF magnetron sputtering

Tomoya Suzuki *, Hiroshi Chiba, Tomoyuki Kawashima, Katsuyoshi Washio

Graduate School of Engineering, Tohoku University, Sendai 980-8579, Miyagi, Japan

ARTICLE INFO

Article history:
Received 28 April 2015
Received in revised form 19 November 2015
Accepted 25 November 2015
Available online 26 November 2015

Keywords:
Transparent conductive oxide
ZnO
Vanadium
RF sputtering
Polymer substrate

ABSTRACT

Vanadium (V) doped ZnO (VZO) thin films were deposited on flexible polymer and quartz substrates by RF magnetron sputtering, and influences of deposition parameters of V concentration, RF power and growth temperature on resistivity, transmittance and crystallinity were investigated. For the polymer substrates, both a high heat-resistant polycarbonate (PC) film and a functional-layer-coated PC film were adopted. The resistivity decreased gradually but the transmittance was worsened with increasing V concentration. Low RF power and high growth temperature improved both transparency and conductivity. By over-coating of the functional layers, c-axis orientation was deteriorated while low-resistivity and high-transmittance characteristics were achieved. Resistivity and average visible-transmittance (wavelength = 450–800 nm) of VZO films on untreated PC and over-coated PC substrates were 0.98 mΩ cm and 83.7%, and 1.2 mΩ cm and 80.3%, respectively, at V concentration of 2 at.%, RF power of 100 W and growth temperature of 175 °C. VZO films on the polymer substrates had slightly high resistivity but nearly the same optical transmittance, compared to those on quartz, under the identical deposition parameters. These results indicate that good electrical and optical properties can be achieved for the VZO films on PC substrate.

1. Introduction

Transparent conductive oxide (TCO) thin films deposited on polymer substrate have, recently, attracted attention as flexible TCO films due to the characteristics such as lightweight, large-size, and low-cost [1–3]. These features raise a possibility of applying to touch panel displays, piezoelectric transducers and surface acoustic wave devices [4–6]. Impurity-doped Zinc Oxide (ZnO) is one of the most attractive oxide semiconductors with the features of wide direct band gap of 3.37 eV (that is, transparent to visible light), low resistivity of the order of 10–5 Ω cm, and material abundance [7,8]. To give high conductivity, aluminum or gallium has, in general, been used for the dopant in ZnO [9,10]. Indium tin oxide (ITO) has also been used for the low-resistivity TCO films [11]. However, the growth temperature (T_G) for both ZnO and ITO films, considering getting the lowest resistivity due to good crystallinity, is desirably around 300 °C or more [12,13]. Thereby, their deposition conditions should be changed and optimized to be at least T_G less than glass transition temperature of the polymer.

We previously reported that vanadium-doped ZnO (VZO) thin films grown at low temperature of 175 °C exhibited good crystallinity and low resistivity of about 0.5 mΩ cm, with visible light transmittance of 80%, on quartz substrate [14]. This is originated from that V atoms can incorporate into the ZnO film in various electron configurations. Furthermore, it was confirmed that the V doping acted to eliminate the 30°-twisted domains in the case of growth on c-face sapphire substrate. The effect of the V doping was considered the enhancement of adatoms surface migration, so the random nucleation was suppressed [15]. Therefore, in this study, we investigated electrical, optical, and crystallographic properties of VZO thin films grown on the polymer substrates by RF magnetron sputtering comparing to those on the quartz substrates. Here, the comparison was to examine the effect of large difference in thermal expansion coefficient between the polymer substrates and ZnO film. By adopting both an untreated polycarbonate (PC) film and an over-coated PC film with the specific functional layer as the polymer substrates, influences of the difference in the surface on TCO film characteristics were discussed from the perspectives of the V-doping effect, RF power, and the growth temperature.

2. Experiments

Two kinds of polymer substrates were used. One is an untreated PC film. It has high heat resistance up to 215 °C and high visible light transmittance of about 90%. The other is ELECLEAR®-SS (hereinafter referred to as "SS"), manufactured by TEIJIN Limited. The base polymer of SS is PC film and it is over-coated with functional layers to achieve good visibility, impact resistance, and strong adhesion of TCO film. Therefore, SS is processed well to form TCO film on it. However, the surface of SS film is different from PC film. So, the influences of this

* Corresponding author.
E-mail address: tomoya@ecei.tohoku.ac.jp (T. Suzuki).

http://dx.doi.org/10.1016/j.tsf.2015.11.064
0040-6090/

difference in the surface on TCO film were studied comparing with that on the quartz substrate.

The polymers were cleaned in an ultrasonic bath using ethanol and then rinsed by deionized water. VZO films of 50 nm thick were deposited on two kinds of PC or quartz substrates by RF magnetron sputtering (Eiko ES-350SU). The base pressure of sputtering chamber was less than 10^{-6} Pa and the Ar sputtering gas pressure was kept at 1.0 Pa. V was doped by co-sputtering of V chips (99.9% purity) on an erosion area of a ceramic ZnO target (99.99% purity) placed at a distance of 60 mm below the substrate. V concentration was controlled by changing the number of V chips and was determined by X-ray fluorescence (Rigaku RIX2100 using Rh radiation). RF power (P_{RF}) was ranged from 50 to 200 W and T_G was from room temperature (RT) to 175 °C, respectively.

Film thickness, resistivity and transmittance were evaluated respectively by a stylus profiler (Kosaka Laboratory Ltd. ST4000 M), a four-point probe (MITSUBISHI CHEMICAL ANALYTECH Loresta AX MCP-T370), and a spectrophotometer (Hitachi High-Technologies GLOBAL U-4000). The crystallinity was analyzed by out-of-plane X-ray diffraction (XRD, Rigaku SmartLab using CuK_α radiation). The surface morphology was observed by atomic force microscope (AFM, ASYLUM RESEARCH Cypher ES).

3. Result and discussion

3.1. Dependence on V concentration

The dependence of resistivity on V concentration is shown in Fig. 1. VZO films were deposited at P_{RF} = 150 W and T_G = 150 °C while changing the V concentration from 0 to 3 at.%. Resistivity for all substrates decreased gradually with increasing V up to 2 at.% and kept almost constant up to 3 at.%. Minimum resistivity of the VZO film on PC, SS, and quartz substrates was almost the same as 1.2 mΩ cm at V concentration of 2 at.%. This indicates that the influence of the substrate surface on the V -concentration dependence of resistivity was small. Thereby, it can be considered that resistivity is mainly determined by the concentration of the doped impurity. That is, the decrease in resistivity is attributed to the increase in carrier density induced by the V doping. We think that the saturation of resistivity was affected by both the deterioration of crystallinity (shown below) and the V clustering.

The dependence of average transmittance (wavelength = 450–800 nm) for VZO films on V concentration and the transmittance spectra are shown in Fig. 2(a) and (b). Although the transmittance was about 80% for ZnO films, it decreased with increasing V concentration and became lower than 70% over V of 2 at.%. We think this dependence reflects the change in the density of grain boundary, because it scatters an incident light. This consideration came from the result that the crystallinity of VZO films deteriorated with increasing V concentration, as described below in the XRD evaluation. Here, VZO films on SS substrate had slightly higher transmittance than those on PC or quartz substrate at high V concentration range. This is attributed to the

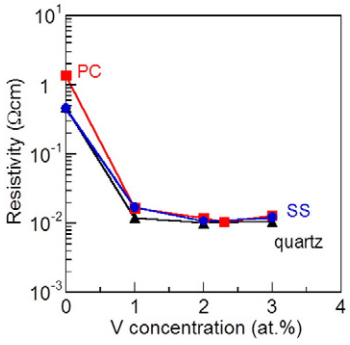

Fig. 1. Dependence of resistivity on V concentration for VZO films grown at P_{RF} = 150 W and T_G = 150 °C.

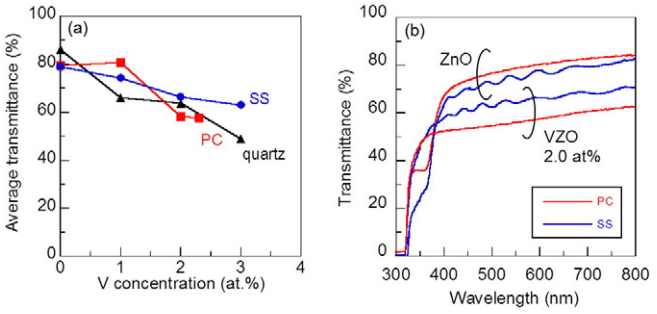

Fig. 2. (a) Dependence of average transmittance on V concentration for VZO films grown at P_{RF} = 150 W and T_G = 150 °C. (b) Transmittance spectra of ZnO and VZO films (V = 2 at.%) deposited on PC and SS substrates.

reduction of reflection by the functional coating layers which act to buffer the difference of refractive index between VZO films and PC substrate.

The dependence of ZnO (002) XRD intensity for ZnO and VZO films on V concentration and the XRD peaks are shown in Fig. 3(a) and (b). The diffraction from ZnO (002) was observed in ZnO and VZO films on

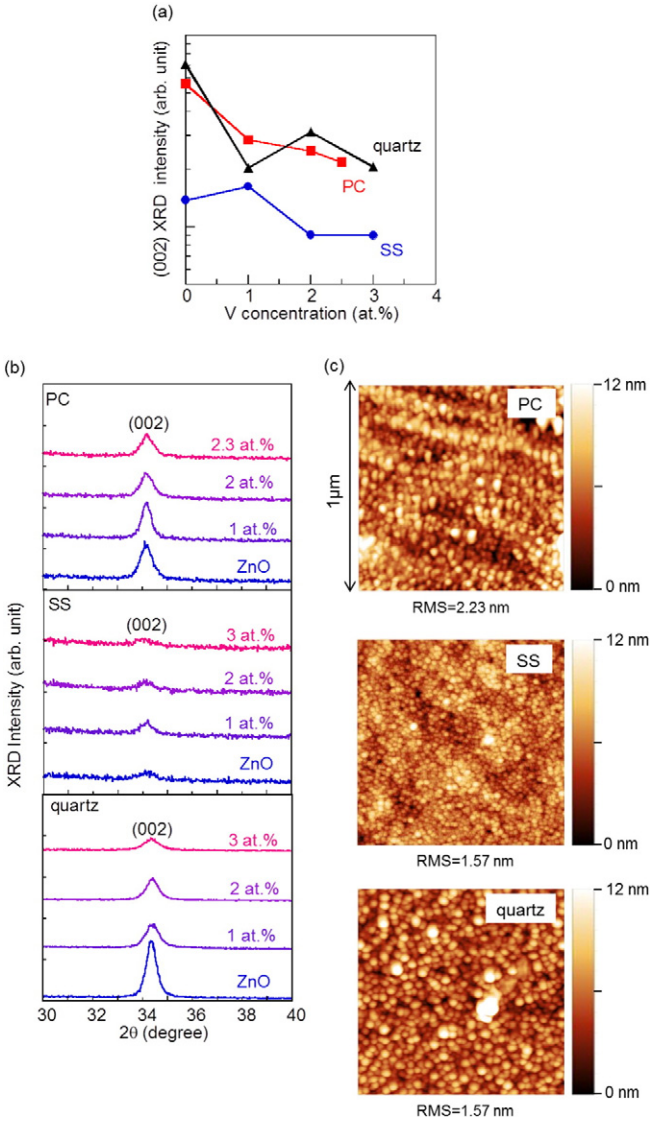

Fig. 3. (a) Dependence of ZnO (002) XRD intensity of VZO films grown at P_{RF} = 150 W and T_G = 150 °C. (b) ZnO (002) XRD peaks of VZO films, and (c) AFM images of VZO (V = 2 at.%) films deposited on PC, SS and quartz substrates.