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Influence of Zn-Sn ratio on optical property and microstructure of Zn-Sn-O films deposited by magnetron sputtering

Yuki Nakanishi [a,*], Kazuhiro Kato [a], Mayuko Horikawa [a], Masaaki Yonekura [b]

[a] Glass Research Center, Central Glass Co., Ltd., 1510 Ohkuchi-cho, Matsusaka City, Mie 515-0001, Japan
[b] Glass Manufacturing Technology Center, Central Glass Co., Ltd., 1510 Ohkuchi-cho, Matsusaka City, Mie 515-0001, Japan

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ABSTRACT

Zinc-tin oxide (ZTO) films can exhibit high visible light transparency, high electrical conductivity and glass-like dense structures; therefore, they are expected to be applied as transparent conductive oxide and barrier layers. In this study, the influence of the Zn-Sn ratio on the optical properties and microstructures of the ZTO films was investigated. The ZTO films were deposited on glass substrates by reactive magnetron sputtering without intentional substrate heating. The chemical state, crystal structure, density, surface morphology and optical properties were evaluated. The ZTO films deposited using lower Sn concentration targets of 0 to 7 at.% had wurtzite structures of ZnO. In contrast, the ZTO films were amorphous when Sn concentrations of 15 to 100 at.% were used. The ZTO films had higher densities at higher Sn concentrations. Additionally, the ZTO films exhibited smooth surfaces compared with the pure ZnO and SnO_2 films. The refractive indices of the ZTO films increased with increasing Sn concentration of the Zn-Sn targets. These results show that the optical properties and microstructures of the ZTO films varied with the Zn-Sn ratio.

1. Introduction

Zinc-tin oxide (Zn-Sn-O or ZTO) films can exhibit high visible light transparency and electrical conductivity. Moreover, they are inexpensive compared to popular transparent conductive oxide (TCO) materials, including rare earth metals, and do not contain toxic elements. Therefore, they have potential applications as TCO electrodes for electronic devices [1–4]. Furthermore, ZTO films can have smooth surfaces and glass-like dense structures [4,5]; hence, they exhibit good thermal and chemical stabilities and they can also be used as barrier layers for electronic devices or optical products [5–7]. For the barrier layer use, amorphous ZTO films without crystal grain boundaries have attracted attention.

ZTO films show different crystal structure in response to the ratio of Zn and Sn. Crystalline $ZnSnO_3$ has the perovskite and ilmenite structures, and Zn_2SnO_4 shows the inverse spinel structure [8–10]. In an elemental composition, ZTO films can be amorphous [4,11]. In addition, ZTO thin films are deposited using various methods, such as thermal evaporation [1], sputtering [2–5,7], hydrothermal synthesis [9] and wet coating [8,12]. It was reported that the ZTO films deposited by the radio frequency (RF) magnetron sputtering using ZTO target showed crystal structure of Zn_2SnO_4 or $ZnSnO_3$ at substrates temperature of no less than 450 °C, on the other hand, they were amorphous at low substrate temperatures [3]. In the case of the ZTO films deposited by RF magnetron sputtering in a combinatorial method using ZnO and SnO_2 targets without intentional substrate heating, the ZTO film with Sn concentration of 16 at.% showed ZnO crystal structure, and then amorphous structure are observed at high Sn concentrations. Additionally, these amorphous films crystallize by heating in vacuum at 650 °C [4]. Other literatures have reported that the ZTO films deposited by reactive magnetron sputtering with a roll-to-roll web coater exhibited the smooth surface and low water vapor transmission [5,7]. The characteristics and microstructures of ZTO thin films can be determined by the deposition conditions. A heating process is necessary to obtain crystalline ZTO thin films [2–4,8,9,12]. Amorphous ZTO films can be obtained without a heating process; therefore, the process is inexpensive compared with the process for crystalline ZTO films [10]. However, the characteristics of ZTO films deposited without a heating process have little been investigated over a wide range of Zn-Sn compositions. In this study, the influence of the Zn-Sn ratio on the optical properties and microstructures of the ZTO films deposited by reactive magnetron sputtering was investigated without a heating process.

2. Experimental details

2.1. Deposition conditions

The ZTO films were deposited on 1.1-mm-thick soda-lime-silicate glass substrates by reactive magnetron sputtering without intentional

* Corresponding author.
E-mail address: yuki.nakanishi@cgco.co.jp (Y. Nakanishi).

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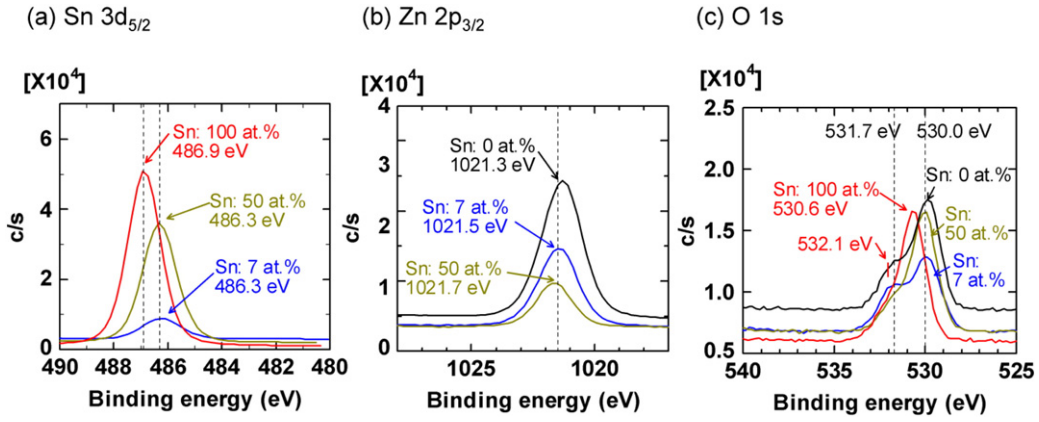

Fig. 1. (a) Sn $3d_{5/2}$, (b) Zn $2p_{3/2}$ and (c) O 1s XPS spectra of the ZTO films deposited using a Zn-Sn target with Sn concentrations of 0, 7, 50 and 100 at.%.

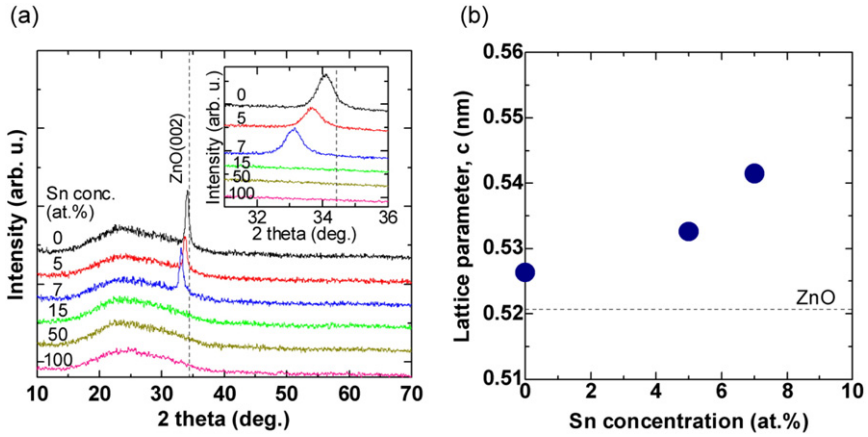

Fig. 2. (a) XRD patterns and (b) c-axis lattice parameter of the ZTO films deposited using the Zn-Sn target.

substrate heating or cooling. The distance between the substrate and the sputter target was set to 90 mm. The coating chamber was evacuated to a back pressure of 1×10^{-4} Pa. The Zn-Sn alloy was used as a sputtering target. The Sn concentrations of the Zn-Sn targets were set to 5, 7, 15 or 50 at.%. These concentrations were selected to obtain both crystalline and amorphous films. For comparison, we also deposited ZnO and SnO_2 films, which are defined as Sn concentrations of 0 and 100 at.%, respectively. Target dimension was 76.2 mm in diameter and 5 mm in thickness. In addition, Zn-Sn targets with Sn concentrations of 15 and 50 at.% were prepared by the sintering method using metallic powder, and the other targets were prepared by the fusion method. Oxygen was used for the reactive gas. The process gases such as argon or nitrogen were not used. The total gas pressure was set to 0.5 Pa. Additionally, the dc power supplied to the Zn-Sn target was maintained at 2.2 Wcm^{-2}. The thicknesses of ZTO films were set to 27–32 nm.

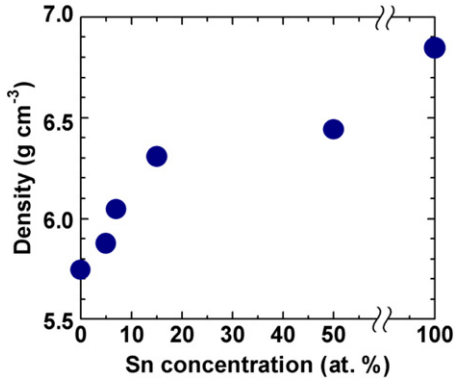

Fig. 3. Density of the ZTO films as a function of the Sn concentration in Zn-Sn.

2.2. Evaluation

2.2.1. Chemical state

The chemical state of the ZTO films was evaluated by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II, ULVAC-PHI) with an Al monochromatic X-ray source. The film surface usually becomes positively charged during X-ray irradiation process; therefore, this positive charge-up was neutralized using electron bombardment system before XPS measurement. Besides, all of the XPS peaks were calibrated with the simultaneously measured C 1s peak. Some of XPS peaks were deconvoluted using Gaussian-Lorentzian fitting model.

2.2.2. Film structure

The crystal structure of the ZTO films was evaluated by X-ray diffraction (XRD, RINT-Ultima III, Rigaku, using CuKα radiation) with the out-of-plane configuration. The density of the ZTO films was estimated by X-ray reflectivity (XRR). The diffraction patterns of the ZTO films were measured in the 2 theta range from 0 to 10° on 2 theta/theta scan; furthermore, the density, thickness and surface roughness were calculated through the computational fitting between measured and ideal