



Defect-induced optical and electrical property modification in amorphous InGaZnO₄ films



Hyegyong Kim^a, Eunsang Hwang^a, Doo-Yong Lee^a, Ji-Woong Kim^a, Jungseek Hwang^b, Jong-Seong Bae^c, Jeong-Soo Lee^d, Sungkyun Park^{a,*}

^a Department of Physics, Pusan National University, Busan 609-735, South Korea

^b Department of Physics, Sungkyunkwan University, Suwon 440-756, South Korea

^c Busan Center, Korea Basic Science Institute, Busan 618-230, South Korea

^d Neutron Science Division, Korea Atomic Energy Research Institute, Daejeon 305-353, South Korea

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ABSTRACT

We report the physical characteristics of InGaZnO₄ films deposited at various temperatures. The films were deposited on Al₂O₃(0001) substrates using pulsed laser deposition technique. Based on X-ray diffraction and field emission scanning electron microscopy measurements, the crystal structure changed from amorphous to polycrystalline as deposition temperature increased to 550 °C. Furthermore, UV–vis measurements revealed a decrease in tail state i.e. improvement of local ordering, resulting in an increase of optical band-gap energy as deposition temperature increased. The core-level X-ray photoelectron spectra also showed an increase (decrease) in metal–oxide (oxygen deficiency) bond as the deposition temperature increased. The carrier concentration, Hall mobility and conductivity variation with deposition temperature are related to the competition between oxygen deficiency and grain boundary formation.

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1. Introduction

Transparent conducting oxides (TCOs) have generated much interest because of their usage in various applications such as light emitting devices, flexible flat-panel displays, solar cells, electrochromic devices and low emissivity windows [1–3]. In particular, utilizing amorphous transparent semiconductor oxides as thin film transistors has attracted attention due to their larger optical band-gap energy ($E_g \geq 3.5$ eV) and higher mobility ($\mu \sim 10$ cm²/Vs) [4–10]. From the material prospective, the mixture of In–Ga–Zn–O forming amorphous thin film has been extensively studied for TCO applications due to its larger mobility compared with other TCOs. Recently, Hosono et al. reported that the In:Ga:Zn = 1:1:1 mixture of InGaZnO₄ (IGZO) amorphous film exhibited a stable structure with sustainable large mobility, unlike conventional amorphous oxide semiconductors [11,12]. Furthermore, various research has been performed to obtain stable and reliable physical properties of amorphous IGZO by varying partial H₂O pressure during growth [13], *m* composition in InGaO₃(ZnO)_{*m*} films [14–16], oxygen partial pressure and annealing condition [17]. However, most of works have been focused on the correlation between annealing conditions and physical property variations while maintaining amorphous structures [18–20]. On the other hand the deposition temperature-

dependent physical property variation up to the crystallization temperature has not been fully explored [16,21].

In this paper, we examine the deposition temperature-dependent physical properties of IGZO films grown on Al₂O₃(0001) substrates using the pulsed laser deposition method. We found the improved optical properties due to the improved local structural ordering of the films by thermal energy. Furthermore, the electrical property variation of the films can be explained by the grain growth and oxygen deficiency variation of the film with increased deposition temperature.

2. Experiments

For the target material, we sintered a mixture of In₂O₃ (99.99%, Aldrich), Ga₂O₃ (99.99%, Aldrich) and ZnO (99.99%, Aldrich) powders in the ratio of 1:1:2 at 1300 °C for 10 h. The base pressure of the growth chamber was kept at 2×10^{-6} Torr. For the deposition, KrF 248 nm excimer laser (COMPex, Lambda Physik) with 200 mJ energy at 5 Hz repetition rate was used. The deposition time was 35 min for all films. To examine the physical and chemical properties, the films were characterized by X-ray diffraction (XRD, Bruker, D8 Advance) with monochromatic Cu–K α ($\lambda = 1.5406$ Å), field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), X-ray photoelectron spectroscopy (XPS, ESCALab 250, Thermo) and UV–vis spectroscopy (Dongwoo Optron). For the XPS measurement, a monochromatic Al–K α ($h\nu = 1486.6$ eV) with 400 μ m beamsize, 0.1 per step and 50 eV pass energy

* Corresponding author.

E-mail address: psk@pusan.ac.kr (S. Park).

was used. In addition, the electrical properties of films were investigated by measuring Hall mobility, carrier concentration and resistivity (HMS-5000, ECOPIA).

3. Results and discussion

Fig. 1 shows the XRD pattern of the IGZO thin films grown on $\text{Al}_2\text{O}_3(0001)$ substrates at 550°C . Films grown below 450°C (shown in inset in Fig. 1) showed an amorphous phase. On the other hand, the XRD pattern for the film grown at 550°C showed broader diffraction peaks at 30.69° and 35.97° . Comparing the measured diffraction pattern (not shown) to the known bulk InGaZnO_4 (ICSD # 90003), those peaks were indexed as (009) and (105). The surface morphology for the films grown at various temperatures by FE-SEM (Fig. 2) showed no sign of grains until 450°C . The rectangular shapes of grains were observed for the samples grown at 550°C . Based on XRD measurements, these grains are thought to be crystallized. The broadening of the diffraction peaks was associated with the smaller grains shown in Fig. 2(f).

The optical transmittance of the films grown at different deposition temperatures is shown in Fig. 3(a). Films grown above 150°C showed transmittance above 80%. In contrast, films grown at room temperature and 50°C showed poor transmittance due to their relatively poor quality and/or surface roughness, since the slope is related to the quality and/or surface roughness of the films [22,23]. The improved transmittance and increased slope of transmittance at the higher energy region suggest that films had a smoother surface and/or better structural ordering with increased deposition temperature. Fig. 3(b) shows absorption spectra for the films grown at various temperatures. In general, the absorption spectrum can be divided into two regions such as the Tauc and Urbach regions [18,24]. The Tauc region represents the transition between conduction and valence bands. On the other hand, the Urbach region is an absorption tail region where the transition occurred due to the tail state of the amorphous materials. This tail state width (Urbach tail width) can be estimated by fitting the absorption spectra [25–27]. The inset in Fig. 3(b) shows deposition temperature-dependent Urbach tail width of the films. The Urbach tail state for the films grown below 150°C decreased from ~ 550 meV to ~ 320 meV with deposition temperature increase, i.e., reduction of the absorption near the Urbach region. These decreases in the Urbach region are associated with the increase in optical band-gap energy of the films. In contrast, for the films

grown above 250°C , there was no variation of absorption tail (Urbach region).

The deposition temperature-dependent optical band-gap energy of IGZO films obtained from Tauc's relation [28] was shown in the inset in Fig. 3(b). Previously, the optical band-gap energy of the amorphous IGZO film was reported between 3.2 eV and 3.5 eV [29,30]. The measured optical band-gap energy increased from 3.1 ± 0.1 eV for the film grown at room temperature to 4.0 ± 0.3 eV for the film grown at 550°C . The initial increases of optical band-gap energy are associated with the decrease in the Urbach region, which originates from the tail state. With increased deposition temperature, the additional thermal energy will remove the point defects. As a result, the optical band-gap energy will increase. The largest optical band-gap energy appeared for the film grown at 550°C , which could be related to the improved crystallization of the films [20,31].

Fig. 4 shows the O 1s core-level X-ray photoelectron spectra of IGZO thin films grown on $\text{Al}_2\text{O}_3(0001)$ at various deposition temperatures. The vertical lines indicate the reference binding energy of metal-oxide (530.35 eV), oxygen deficiency (531.31 eV) and loosely bound oxygen (532.25 eV) [16,32,33]. The Lorentzian–Gaussian function was used for the peak deconvolution after properly removing background using the Shirley equation and corrected by C 1s peak at 284.5 eV [32,34]. The highest binding energy (531.9 ± 0.1 eV) indicates the loosely bound surface oxygen (oxygen contamination, $-\text{CO}_3$, $-\text{OH}$ and adsorbed O_2). The middle binding energy (531.2 ± 0.1 eV) represents oxygen deficiency [28]. The lowest binding energy (530.0 ± 0.1 eV) is associated with the metal-oxides [16, 35,36]. As deposition temperature increased, the peak areal intensity of the metal-oxide bond increased, while the oxygen deficiency decreased. Table 1 shows the deposition temperature-dependent relative peak areal intensity ratio of O 1s. The increased peak areal intensity of the metal-oxide bond with deposition temperature is related to the improved short-range structural ordering in the film [37]. Similarly, decreased oxygen deficiency (peak area of V_{O}) with increased deposition temperature was observed. This observation is related to the decrease of carrier concentration shown in Fig. 5(a). For the In, Ga, and Zn, the fitted binding energy (not shown) was 444.4 ± 0.0 eV for In $3d_{5/2}$, 1117.5 ± 0.1 eV for Ga $2p_{3/2}$ and 1021.5 ± 0.0 eV for Zn $2p_{3/2}$, which are different from the references. However, they are similar to previously published results [28]. Interestingly, there was no noticeable difference with increased deposition temperature.

The room temperature electrical properties such as carrier concentrations, Hall mobility and resistivity of the IGZO films grown at various temperatures are shown in Fig. 5. The carrier (electron) concentration, shown in Fig. 5(a) increased an order of magnitude as the deposition temperature increased initially (up to 250°C). The largest carrier concentration was $\sim 3 \times 10^{20} \text{ cm}^{-3}$, which is comparable to the known value [21]. On the other hand, the carrier concentration decreased for the film grown above 450°C . The initial increase in carrier concentration despite the reduced oxygen deficiencies might be related to the decreased defect density of the film due to the additional thermal energy. It is known that additional thermal energy reduces the number of defects, which can trap carriers [16,24]. For films grown above 450°C , the decreased carrier concentration is due to the decreased (increased) oxygen deficiency (local structural ordering).

As for the Hall mobility, it increased with deposition temperature until the film became polycrystalline (i.e., up to 450°C). Increase in Hall mobility is related to the additional thermal energy forming conduction paths through intergrains of films [21]. For films grown at 550°C , the Hall mobility dropped abruptly, suggesting the existence of an additional scattering source due to the formation of grain boundaries.

Initially, the electrical resistivity, shown in Fig. 5(c), decreased rapidly as the deposition temperature increased due to the increased Hall

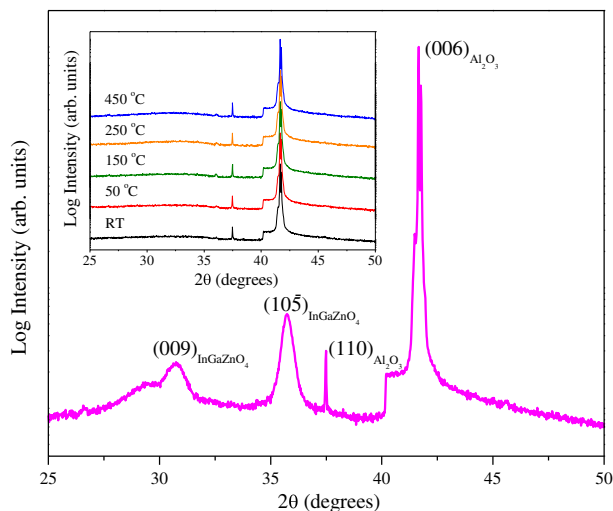


Fig. 1. Normal X-ray diffraction (θ – 2θ geometry) patterns of InGaZnO_4 films grown at 550°C on $\text{Al}_2\text{O}_3(0001)$ substrate. The inset shows the XRD patterns of the films grown at 450°C , 250°C , 150°C , 50°C and RT on $\text{Al}_2\text{O}_3(0001)$ substrate.

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