



Effect of crystalline polarity on microstructure and optoelectronic properties of gallium-doped zinc oxide films deposited onto glass substrates



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ABSTRACT

The effect of crystalline polarity on the microstructure of gallium-doped zinc oxide (GZO) deposited using magnetron sputtering onto glass substrates was investigated. X-ray photoelectron spectroscopy was used to determine the crystalline polarity of *c*-axis textured GZO films. Grains whose radii were more than 1 μm grew abnormally in 0.2 mol% doped GZO when the film was thicker than $\sim 1 \mu\text{m}$, and the radius of the grains was much smaller than 100 nm in the heavily (i.e., 4 mol%) doped GZO, regardless of the film thickness. Such abnormal growth of the grains in the 0.2 mol% doped GZO films coincided with a change in the crystalline polarity: the surfaces of unusually large GZO grains were terminated with the (000 $\bar{1}$) face, and those of normal GZO grains were terminated with the (0001) face. The results indicated that polarity flipping is a very important event for controlling the texture of doped zinc oxide films.

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1. Introduction

Electrodes produced with transparent thin films, including zinc oxide (ZnO) thin films, are one of the key technologies used to fabricate energy saving/harvesting devices [1–3]. Electrodes used for collecting electric charge require low resistance and high transparency in order to be used in high-efficiency photovoltaic cells [1]. Low energy loss in transparent electrodes is also important for low-energy operation of information displays and light-emitting diodes [2]. Further, transparent conductors are important in developing advanced windows for buildings and houses [3]. Toward that goal, several studies have been conducted on ZnO to develop transparent and conductive ZnO-based conductor films [4]. Significant attention has been paid to controlling charge compensation in ZnO in order to increase doping efficiency and decrease optical absorption owing to defects. When we consider the application of transparent electrodes to display devices such as liquid crystal displays and organic electroluminescence displays, transparent conductor films require very flat, smooth surfaces in order to prevent light scattering and inhomogeneity in the distribution of electric potential. However, transparent electrodes must show particular microstructural features such as grains that show large surface areas so that the

transparent electrodes can be used in other applications such as dye-sensitized solar cells [5,6].

Group III impurities doped into ZnO films are widely known as effective donors [7]. There are many more reports to date about Al-doped ZnO films than there are about Ga- and In-doped ones. Most of the Al-doped ZnO films grown for application as transparent electrodes have been sputtered onto α -SiO₂ substrates, and the dependence of their electrical and optical properties including film-surface-texture-induced light scattering on growth conditions such as dopant concentration and film thickness has been investigated [8–10]. Numerous previous studies have focused on the microstructure and electrical properties of ZnO films [6,11,12]. Among the various ZnO films, the “milky white” ones have attracted our interest [12]. It has previously been indicated that milky white ZnO films are appropriate materials for application to the bottom electrodes in solar cells because of the light-scattering properties of the films. Milky white ZnO films have conventionally been prepared using direct current (DC) sputtering, and the preparation procedure is not very specific. Namely, it is uncommon for sputtering to result in irregularly textured films, and the mechanism underlying the formation of the film texture responsible for the milky whiteness is uncertain. In contrast, ZnO films prepared using chemical synthesis routes including hydrothermal [6] and solution deposition [11] often show some irregular or porous structures such as nanoflowers, so it is difficult to use chemical synthesis in order to deposit smooth continuous films. Obtaining chemically deposited ZnO

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films showing high conductivity is difficult because of the gaps that naturally form between grains [11]. It is unlikely that a proper method of depositing ZnO films that show both high surface area and conductivity has been developed, so we are motivated to develop such a method. We used secondary ion mass spectroscopy with a very fine primary beam (NanoSIMS) [13] to distribute impurities in the textured films.

Here, we must also introduce a crystallographic feature of ZnO because its crystalline polarity affects many aspects of its properties. ZnO crystallizes in the wurtzite structure, which is a polar structure that consists of alternating stacks of cation and anion layers along its *c*-axis. Consequently, one *c*-face is the zinc (Zn)-terminated (0001) face and the other is the oxygen (O)-terminated (000 $\bar{1}$) one. For example, the concentration of defects in a ZnO crystal depends on the crystalline sector of the dopant [14–16]. Indeed, donor impurities tend to incorporate into the (000 $\bar{1}$) sector whereas acceptor impurities tend to incorporate into the (0001) one. We recently found that doping affects the crystalline polarity of ZnO thin films deposited using pulsed laser deposition (PLD) [17,18]. In fact, undoped PLD-grown ZnO films grown on sapphire (α -Al₂O₃) and silica glass (a-SiO₂) substrates showed an O-terminated (000 $\bar{1}$) face, and heavily Al-doped ones grown on the same substrates showed a Zn-terminated (0001) one. Changes in the surface morphology of the films have also been associated with the direction of crystal growth. For example, ZnO films homoepitaxially deposited onto the (0001) and (000 $\bar{1}$) faces of substrates show different surface morphologies [19].

Crystalline polarity is a very important aspect of both the microstructure and doping of ZnO thin films; thus, an appropriate method of determining polarity must be developed before the effects of crystalline polarity can be fully understood. There are several methods of determining the polarity of wurtzite structures [20–22]. We recently used X-ray photoelectron spectroscopy (XPS) to demonstrate how polarity is determined. Indeed, X-ray photoelectron diffraction (XPD) measurement [23] of the angle-dependent core-level peak intensity is an established method of determining polarity, and measuring valence band spectra at a normal emission geometry to observe the polarity-dependent valence band profile [18,24] is another appropriate method of determining polarity. In fact, the polarities of the polycrystalline ZnO films that show in-plane rotation domains (i.e., ZnO films deposited onto a-SiO₂ substrates) have previously been determined using the valence band [18] and XPD measurements [25].

In this paper, we report the microstructure and electronic properties of Ga-doped ZnO (GZO) thin films deposited using radiofrequency (RF) magnetron sputtering. We have reproduced the texture associated with milky white GZO and analyzed the properties of the films. We found that the change in the film microstructure correlated with the fluctuation in the concentration of Ga in the films.

2. Experiments

Most of the GZO films were deposited onto a-SiO₂ substrates, and some were deposited onto ZnO single-crystal substrates. All the substrates had very flat surfaces. We examined the (0001) and (000 $\bar{1}$) faces of the ZnO substrates to determine what effect the crystalline polarity of the substrate had on the microstructure of the deposited films. The GZO films were deposited using RF magnetron sputtering with a commercial deposition system. The pressure in the chamber was maintained at 1–2 Pa by balancing pumping with the flow of argon gas. The typical RF electric power loaded to the magnetron head was 150 W. The targets were 3-inch-diameter polycrystalline 0.2 and 4 mol% (molar fraction of Ga/(Ga + Zn)) Ga-doped GZO ceramics prepared using ordinary sintering. A target was fixed ~40 mm below the substrate. The GZO films were sputtered at 30 nm/min for 5–100 min. The substrates were heated in the range 50–150 °C during deposition because they were exposed to the plasma. Hereafter, the 0.2 and 4 mol% Ga-doped GZO are abbreviated as GZO-0.2 and GZO-4.0.

The microstructures of the obtained films were characterized using X-ray diffraction (XRD, PANalytical X'Pert Pro MRD equipped with a

hybrid 2-bounce asymmetric Ge (220) monochromator and a Cu K α radiation source) and scanning electron microscopy (SEM, Carl Zeiss SUPRA 35VP, operation voltage = 7 kV). The distributions of the dopants in the films were analyzed using two secondary ion mass spectroscopy (SIMS) systems: a CAMECA IMS 4f and a CAMECA NanoSIMS-50 spectrometer. ¹³³Cs⁺, whose ion energy was 8 kV, was tuned on the sample surface, and (⁶⁴Zn + ¹⁶O)⁻ and (⁷¹Ga + ¹⁶O)⁻ molecular ions were collected using a multicollection system. The crystalline polarity of the films; i.e., whether the surface was a Zn-terminated (0001) or an O-terminated (000 $\bar{1}$) face, was determined using XPS measured with normal emission geometry [24]. A Σ -probe spectrometer (Thermo Fisher Scientific, K.K., equipped with a monochromated Al K α radiation source (beam energy: 1486 eV) and a sample goniometer) was used for the XPS measurements. The sample surfaces were sputtered using Ar gas before the measurements. The C 1s peak in each spectrum was applied to correct the binding-energy reference. The optical properties of the GZO films were evaluated using regular transmittance measurements (JASCO Corp. V-550) in the range λ = 300–900 nm at room temperature. The electric resistivity (ρ) of the GZO films was measured using the DC four-probe method in which the electrodes were configured in the van der Pauw geometry. Hall measurements (Toyo Corp., ResiTest 8300) were also performed to evaluate the concentration of electrons (n_e) and the Hall carrier mobility (μ_e) of the resultant films. The ohmic electrodes used for the electrical measurements were produced by evaporating indium metal under vacuum.

3. Results and discussion

XRD θ - 2θ patterns typical of the GZO-0.2 and GZO-4.0 films grown on the a-SiO₂ substrates are shown in Fig. 1. The θ - 2θ patterns only show the diffraction peaks assignable to the (0002) and (0004) planes, indicating that the obtained films are well-aligned *c*-axis-oriented ones.

Fig. 2 shows the electric transport properties of the GZO-4.0 films deposited in various thicknesses onto a-SiO₂ substrates. The electric transport properties are plotted as functions of film thickness. The ZnO films often showed decreasing ρ with increasing thickness [7,26]. Although n_e was close to the concentration of Ga atoms in the 4 mol% Ga-doped ZnO target ($1.8 \times 10^{21} \text{ cm}^{-3}$) regardless of the film thickness, μ_e increased with increasing thickness. Thus, the decreased conductivity of the thinner films is attributed to the low crystallinity of the films during nucleation. The GZO-0.2 films showed a similar trend: n_e for the GZO-0.2 films was one order of magnitude less than

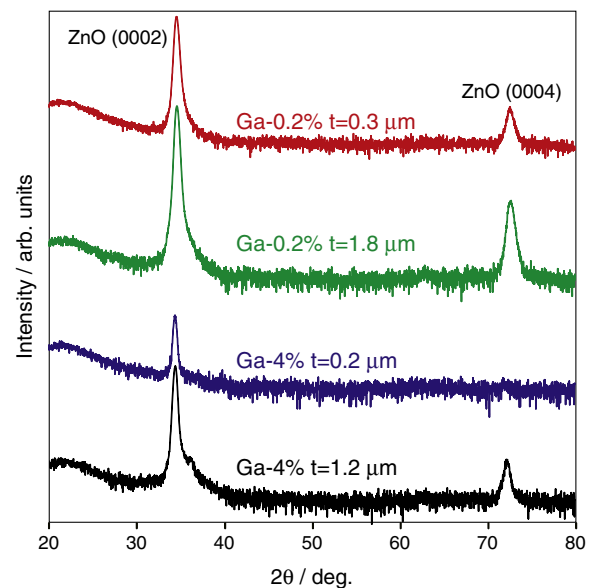


Fig. 1. XRD patterns for Ga-doped ZnO films grown on a-SiO₂ substrates.

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