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Polarity of heavily doped ZnO films grown on sapphire and SiO_2 glass substrates by pulsed laser deposition

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ABSTRACT

The crystalline polarity of undoped and impurity-doped ZnO films grown on SiO_2 glass substrates was investigated with the goal of achieving polarity-selective growth of ZnO films on non-crystalline substrates. We first demonstrated that hard X-ray photoelectron spectroscopy (HX-PES) is an appropriate method for determining the crystalline polarity of ZnO. We then characterized the ZnO films grown by pulsed laser deposition using HX-PES. The resulting films deposited with a 1 mol% Al-doped ZnO target had the (0001) surface, whereas films grown with nominally undoped, 0.1 mol% Al-doped, 1 mol%Ga-doped, and 1 mol% In-doped ZnO targets had the $(000\bar{1})$ surface. Since a clear polarity change due to Al-doping was seen at the ZnO/glass structure, we conclude that the essential parameter governing the polarity of the ZnO films is unlikely lattice matching (alignment of the lattice on the atomic scale) at the heterointerface between the ZnO films and substrates.

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1. Introduction

ZnO has received a great deal of attention due to the wide range of its technological applications. The high optical transparency of ZnO in the visible range along with good electrical conductivity makes it suitable for application as transparent electrodes in flat panel displays and solar cells [1,2]. ZnO-based heterostructures have been extensively investigated for applications in optoelectronic devices such as ultraviolet light emitting diodes (LEDs) [3,4] and transparent field-effect transistors [5,6].

A ZnO crystal has a wurtzite-type structure; hence, it shows spontaneous electrical polarization along the c-axis and thereby has polar surfaces corresponding to the $(000\bar{1})$ face (c(−)-face) and (0001) face (c(+)-face). Furthermore, various properties of ZnO depend on its polarity, including the surface electronic structure [7], chemical stability of the surface [8], interfacial properties [9], and impurity incorporation [10]. Therefore, when designing devices using ZnO, it is important to understand the effects governing the crystalline polarity of ZnO and to develop a crystal growth technology to enable the polarity-selective growth of ZnO films. It has been previously reported that a ZnMgO/ZnO heterostructure with the $(000\bar{1})$ face is more suitable for high electron mobility transistor devices than the heterostructure with the (0001) face [11].

There have been several reports on the surface polarity of ZnO films deposited on sapphire substrates [12–17]. Nominally undoped ZnO films grown on a (0001) sapphire substrate tend to have the $(000\bar{1})$ face [12], and growth of ZnO with the (0001) face on native (0001) sapphire substrates is difficult. To overcome this tendency, the use of a buffer layer has been considered, and deposition of ZnO with the (0001) face on a sapphire substrate has been achieved by inserting thin epitaxial buffer layers of MgO [13], AlN [14], GaN [15], or Cr compounds [16] between the ZnO film and the sapphire substrate. The growth of undoped ZnO films with the (0001) face on native (0001) sapphire substrates has been reported only for film deposition by pulsed laser deposition (PLD) using very specific growth conditions: low growth temperatures (450 °C) with high growth rate on an atomically flat sapphire substrate [17]. These previous studies show that the polarity-selective growth of ZnO on crystalline substrates is possible if very specific growth conditions are used or when a buffer layer is applied. In contrast, polarity-selective growth of ZnO on a non-crystalline substrate has not yet been established, even though the deposition of ZnO on glass substrates is of great importance for industrial applications. Thus, it is crucial that a polarity control technique for ZnO on non-crystalline substrates, such as glass, be developed.

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Recently, we reported that Al-doping into ZnO led to the inversion of polarity of ZnO films on sapphire substrates [18]. Nominally undoped ZnO films grown by PLD have the $(000\bar{1})$ face, as mentioned above, whereas films prepared by PLD using a heavily (1 mol%) Al-doped ZnO target have the (0001) face. This polarity change of PLD-grown ZnO films by using a heavily Al-doped target was observed regardless of the substrate orientation. In fact, ZnO films with the $(000\bar{1})$ face could be deposited not only on (0001) sapphire substrates but also on $(11\bar{2}0)$ sapphire one by using the heavily Al-doped target [18]. These results suggest that the atomic arrangement at a substrate surface is not a major factor for determining the polarity of growing ZnO films, because the atomic configuration at the (0001) sapphire surface is considerably different from that at the $(11\bar{2}0)$ surface. Thus, we speculated that the polarity change induced by Al-doping was a macroscopic phenomenon, and this effect was insensitive to the substrate material. We were therefore motivated to examine the effects of Al-doping on the crystalline polarity of ZnO grown on a non-crystalline substrate such as glass.

For investigating the polarity of ZnO films on glass substrates, we also need to develop a methodology for determining the crystalline polarity of ZnO films with distinct in-plane rotation domains. For instance, ZnO on a non-crystalline substrate shows random orientation of the a-axis, though it is grown along the c-axis. Previously, determining the polarity of ZnO has been carried out using coaxial impact collision ion scattering spectroscopy (CAICISS) [12], convergent beam electron diffraction (CBED) [19], scanning probe microscopy [20], etching by acid [21], and X-ray diffraction using anomalous dispersion [22]. These techniques however have very specific requirements for polarity determination. For example, CAICISS requires a single crystalline sample with sufficient dimensions; CBED requires sufficiently larger grain size than the probe size as well as accurate sample thickness determination and high sample quality. Recently, we found that hard X-ray photoelectron spectroscopy (HX-PES) [23] is also appropriate for determining the crystalline polarity of ZnO [24]. In fact, the spectral profile of ZnO, particularly that in the valence band region, shows strong dependence on the crystalline polarity.

The work presented in this paper examined undoped and heavily doped ZnO films deposited on silica (SiO_2) glass substrates. The films obtained were characterized by HX-PES to reveal the effects of Al-doping on the polarity of ZnO films on non-crystalline substrates. We found that the PLD-grown ZnO films had the (0001) face regardless of the substrate materials when heavily doped with Al, whereas the PLD-grown undoped ZnO films tended to have the $(000\bar{1})$ face. Also, the effects of Ga- and In-doping into ZnO on film polarity were investigated. In our previous paper [18], we only reported the results for 1 mol% Al-doped ZnO films. It is well known that Ga and In act as a donor as well as does Al. It is also important for device applications of ZnO to investigate whether Ga- or In-doping results in a polarity change. In addition, we also studied the polarity of undoped ZnO film with a few-monolayer-thick Al-doped ZnO buffer layer on a sapphire substrate to clarify where polarity inversion occurred. If the growth of the film with the (0001) face starts at the film/substrate interface, the multilayer film should show the (0001) face. Using these data, we discuss a possible mechanism for the observed polarity change due to impurity-doping.

2. Experimental details

Deposition of the ZnO films was carried out by PLD using the fourth-harmonic generation of a neodymium-doped yttrium gallium garnet (YAG:Nd) laser ($\lambda = 266$ nm) with a pulse width of 5 ns, a repetition rate of 5 Hz, and an averaged fluence of about 1 J/cm^2. The growth rate of the films was 0.018 to 0.022 nm/pulse. The film thickness of each sample is shown in Table 1. The substrates used were SiO_2 glass and sapphire with a mirror-polished surface. The sapphire substrate had the $(11\bar{2}0)$ face, which is appropriate for obtaining ZnO films with high crystallinity [25]. The targets used for the PLD growth were nominally pure and doped ZnO ceramics prepared by an ordinary ceramics process. The doped films were grown with a 1 or 0.1 mol% Al-doped target, or a 1 mol% Ga- or In-doped target. It should be noted that the unintentional impurity level in the target was on the order of 10^{16} cm^{-3} or less, according to the results of secondary ion mass spectrometry analysis. The pressure in the growth chamber was kept at 2 mPa by introducing pure oxygen (O_2) gas, and the substrate temperature was kept at 700 °C. The growth process was monitored in situ using reflection high energy electron diffraction. We also examined the effect of a buffer layer by depositing a several-atom-thick doped layer prior to the deposition of undoped ZnO.

Table 1
Electron concentration (n) at room temperature, film thickness (t), FWHM of the ω-scan profile of the 0002 diffraction peak, substrate and chemical composition of typical ZnO films.

Substrate	Doping	t / nm	n / cm^{-3}	FWHM of 0002 / °
Sapphire	Undoped	400	9.6×10^{16}	0.16
Sapphire	Al : 0.1 mol%	170	1.3×10^{19}	0.46
Sapphire	Al : 1 mol%	410	3.2×10^{20}	0.64
Sapphire	Ga : 1 mol%	240	6.5×10^{19}	1.46
Sapphire	In : 1 mol%	510	1.3×10^{19}	1.67
SiO_2 glass	Undoped	460	1.8×10^{18}	1.15
SiO_2 glass	Al : 1 mol%	490	3.0×10^{20}	1.34

The crystallinity of the PLD-grown films was analyzed using X-ray diffraction (XRD) (PANalytical X'Pert Pro MRD) equipped with a hybrid 2-bounce asymmetric Ge (220) monochromator and a Cu Kα source. The morphology of the films was characterized using atomic force microscopy (AFM) (SII SPA400) operated in tapping mode. Si probes having a spring constant of 14 N/m (SII SI-DF20) were used at a resonance frequency of 144 kHz. The electrical resistivity (ρ) of the films was measured by the van der Pauw method using ohmic Al or In electrodes formed on the sample surface, and Hall measurement was performed under a magnetic field of 0.5 T for determining the electron concentration (n) and mobility (μ). The temperature dependencies of ρ, n, and μ were measured over the range 80–350 K.

The polarity of the films deposited on the sapphire substrates was determined using CAICISS and CBED. Since CAICISS is a method for observing atomic arrangements close to the top-most surface, CBED was used to observe the polarity of the film close to the film/substrate interface. The experimental procedure for CAICISS has been published elsewhere [12,26]. The CBED experiments and simulations were performed by NTT Advanced Technology, Ltd., Atsugi, Kanagawa, Japan. For reference, their corresponding literature can be found elsewhere [27]. A bulk ZnO single crystal with known polarity was used as a standard sample for CAICISS analyses.

HX-PES measurements were performed at the undulator beamline BL15XU of SPring-8. The X-ray photon energy was fixed at 5.95 keV, and spectra were obtained at room temperature using a VG Scienta R4000 electron energy analyzer. The total energy resolution was set to 250 meV, as verified with the Fermi cut-off of an evaporated Au thin film. The take-off angle (TOA) of the photoelectrons from the surface was set to 85–88° to perform bulk-sensitive measurements. This high TOA was used for determining the crystalline polarity of ZnO from the HX-PES spectra. The angle between the incident X-rays and the analyzer was fixed at 90°. Details of the experimental setup and procedures of the HX-PES measurements are described elsewhere [23,26,28–30].

3. Results

3.1. Structural and electrical properties of ZnO films on sapphire and glass substrates

All the films on the sapphire and glass substrates were grown along the c-axis. The films on the sapphire substrate showed six well-

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