Polarity control of intrinsic ZnO films using substrate bias

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The structures and properties of zinc oxide thin films deposited by radio-frequency magnetron sputtering were investigated for different substrate biases applied during deposition. The electrical bias determined the crystalline polarity of a nominally undoped film on an amorphous substrate: films with a (0001) surface and a (000$\bar{1}$) surface were produced under positive and negative biases, respectively. Moreover, the polarity of the films was determined at an early stage of the deposition and could not be reversed by switching the substrate bias. © 2013 AIP Publishing LLC.
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Polar crystals, i.e., ferroelectric, piezoelectric, and pyroelectric crystals with permanent electric polarization, are of great importance for electronic devices such as sensors and actuators.[1] Furthermore, well-controlled arrangements of such polar domains can be used to produce useful optical devices. For example, quasi-phase-matching (QPM) devices, which are efficient optical wavelength convertors, consist of periodically arranged polar domains.[2]

Wurtzite-type (WZ-type) semiconductors, including zinc oxide (ZnO) and gallium nitride (GaN), are classified as polar crystals.[3–6] Unlike zinc-blend-type semiconductors with cubic lattices, WZ-type semiconductors are composed of alternating cation layers and anion layers along the c-axis, the $\langle 001 \rangle$ direction. Consequently, the WZ-type structure retains cation termination on one c-face and anion termination on the opposite c-face. Films grown with cation termination are denoted as having the (0001) surface, and those with anion termination are denoted as having the (000$\bar{1}$) surface. Because of this polarity, WZ-type semiconductors exhibit interesting anisotropic behaviors.[7–9] For example, the permanent polarization and piezoelectricity of WZ-type semiconductors are utilized to construct high-electron-mobility current transport devices with two-dimensional electron gas (2DEG) at the heterostructure interfaces.[10,11] As for optical applications, attempts to develop QPM devices consisting of polarity-controlled ZnO films have been reported.[12,13] In addition, the chemical durability of the surface[8,14] and the adhesion strength at the heterostructure interface[9] are affected by the crystalline polarity. Hence, controlling the crystalline polarity of WZ-type semiconductor films is an important technology for further development of devices and structures involving WZ-type semiconductors.

In this study, we concentrated on polarity-selective crystallization of ZnO films. Prior studies on controlling the polarity of ZnO films fall into two categories: those that use crystallographic restriction by the substrate[15] or a template layer[12,16,17] and those that use nucleation of films with a favorable polarity due to doping.[18,19] Each of these polarity-controlling techniques imposes certain restrictions on the design of device structures. For example, polarity control induced by the substrate or a template layer requires a crystalline substrate with a specific atomic arrangement. In the case of polarity control by selective nucleation due to doping, a very high dopant concentration, e.g., more than 1 mol. % Al, which results in high n-type conductivity, is required to obtain the desired polarity.[13,18,19] These restrictions sometimes prevent the construction of desirable device structures.

In this context, we were motivated to develop a polarity-selective film deposition process with fewer restrictions on the choice of substrates and film compositions. To this end, under the assumption that an external electric field will interact with the electric dipoles of ZnO nuclei, we examined the effect of an electrical bias applied to the substrate on the polarity of WZ-type ZnO films deposited by radio-frequency (RF) sputtering. In this letter, we describe the effects of the external electric field applied to the substrate during film deposition from the viewpoint of the film polarity.

The homemade experimental setup, shown in Fig. 1, was used for film deposition. With this setup, an intentional electrical bias (V_{sub}) with reference to the ground level could be applied to the substrate using a DC potential source. Note that V_{sub} was applied prior to ignition of the sputtering plasma, and the electric current induced by V_{sub} (I_{sub}) was monitored during deposition. The configuration in which the substrate holder was disconnected from the ground is referred to as the floating condition, under which an unintentional substrate bias of approximately +5 V appeared.

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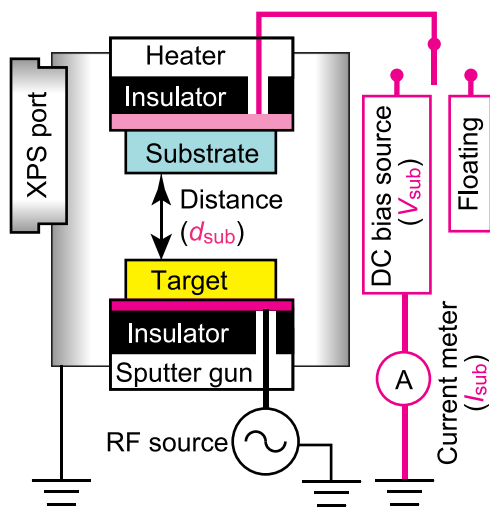
FIG. 1. Illustration of the experimental setup.

A nominally undoped ZnO ceramic (99.99% in purity) was used as the target. The background pressure in the deposition chamber was of the order of 10^{-8} Torr, and the pressure during deposition was kept at 10^{-3} Torr by the introduction of pure Ar gas as the sputtering agent. The RF input power was set to 40 W. Amorphous silica (a-SiO_2) was used as the substrate to avoid any structural restrictions due to the substrate, and the substrate was heated to 500 °C during the deposition. Note that the distance between the substrate and the target is referred to as d_{sub} hereafter, and two different d_{sub} values, 100 and 150 mm, were examined. The larger d_{sub} resulted in a lower growth rate; i.e., the growth rate was ca. 100 nm/h for $d_{sub} = 100$ mm and ca. 40 nm/h for $d_{sub} = 150$ mm. Beyond the different V_{sub} and d_{sub} values, all other parameters remained constant.

Figure 2 shows the θ–2θ XRD scans of the ZnO films obtained under different V_{sub} conditions. Here, the XRD patterns were obtained in an out-of-plane geometry using a Cu-Kα radiation source. Only peaks corresponding to the (00l)

planes of ZnO were found, although all the films deposited in this study showed polycrystalline grain morphologies in atomic force microscopy (AFM) images, as shown in the inset. This indicates that the films possess c-axis-oriented out-of-plane texture and randomly oriented in-plane texture. Therefore, the surfaces of the films must be either Zn-terminated or O-terminated, i.e., the films must have (0001) or (000$\bar{1}$) surfaces. Here, it is also worth noting that the sign and magnitude of V_{sub} produced no obvious changes in the angle and width of the XRD peaks or in the surface morphology as observed by AFM.

X-ray photoemission spectra (XPS) were measured to determine the polarity of the wurtzite-type ZnO, since it has been demonstrated that only the (0001) polar surface of the lattice gives a characteristic sub-peak in valence band (VB) spectra under normal emission geometry.[3,4] It is note worthy that very limited techniques are available for polarity determination of the c-axis textured films with in-plane rotation domains as discussed elsewhere.[6] The usefulness of the VB spectra for polarity determination has been proven by comparing XPS with other techniques like chemical etching,[3,4] convergent beam electron diffraction,[19] ion scattering,[18] and x-ray photoelectron diffraction.[6] A Σ Probe spectrometer (Thermo Fisher Scientific K.K., Yokohama, Japan) equipped with a monochromated Al-Kα X-ray source (1486.6 eV) was used for the XPS study. Note that the XPS spectrometer was connected to the deposition chamber, which facilitated *in situ* XPS measurements without ambiguity due to surface contamination from exposure of the sample to air. The VB spectra were obtained in normal emission geometry to allow the polarity to be determined.[4]

The VB spectra of the films deposited at $d_{sub} = 100$ mm are compared to those of ZnO single crystals in Fig. 3. As can be seen in the spectra obtained from a ZnO single crystal, the subpeak at a binding energy of ~4.5 eV is enhanced only for the (0001) surface and therefore can act as the
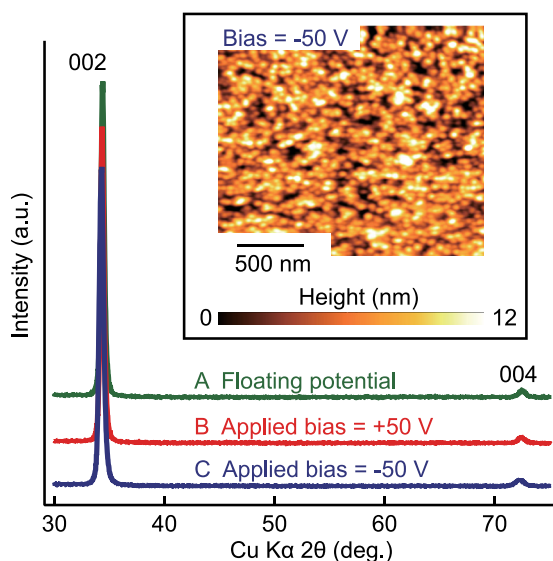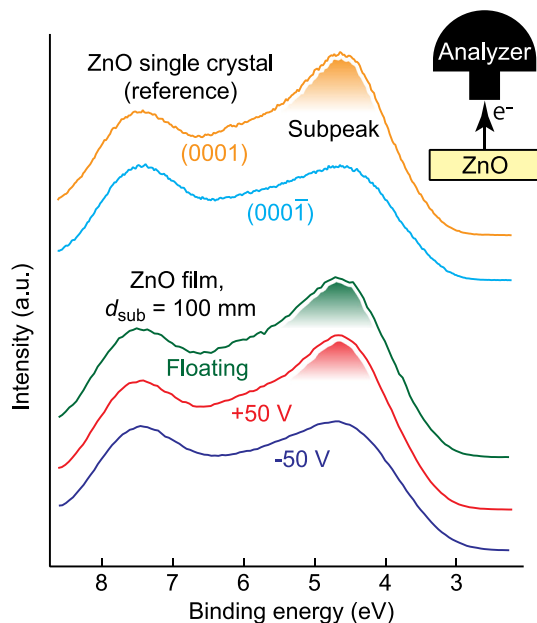

FIG. 2. XRD patterns for ZnO films deposited with (A) floating bias, (B) intentional positive (+50 V) bias, and (C) intentional negative (−50 V) bias. The inset shows an AFM image of the film deposited under negative (−50 V) bias.

FIG. 3. XPS valence band spectra of a ZnO single crystal (upper two) and films deposited under different substrate bias (V_{sub}) conditions (lower three) at $d_{sub} = 100$ mm.

fingerprint of the (0001) surface.[3,4] Spectra with enhanced subpeaks were obtained from the films deposited under a floating potential and under $V_{sub} = +50$ V, but the subpeak was absent in the film deposited under $V_{sub} = -50$ V. This indicates that the positive V_{sub} or floating potential conditions (with an unintentional bias of $+5$ V) resulted in films with a (0001) surface, while the negative V_{sub} resulted in a film with a (000$\bar{1}$) surface. Therefore, the polarity can be controlled successfully by applying V_{sub} when d_{sub} is 100 mm. In contrast, all the obtained films had a (0001) surface regardless of the sign of V_{sub} when d_{sub} was set to 150 mm. This means that d_{sub} is also a major parameter related to polarity control under an applied bias V_{sub}. The essential parameter governing such d_{sub} dependence is unclear at the present stage, but we suppose spatial distribution of charged or excited species and/or kinetic energy distribution is the causes of V_{sub} and d_{sub} dependent film structure.

In order to examine the effect of V_{sub} in detail, multilayered samples were also deposited. To obtain these multilayered samples, a seed layer was deposited under a certain V_{sub} and an overlayer was subsequently deposited under a different V_{sub}. In these experiments, the seed layer was characterized by *in situ* XPS prior to the deposition of the overlayer. The XPS results for one of the bilayer samples are shown in Fig. 4. Here, the seed layer, of 50 nm in thickness, was initially deposited on an a-SiO$_2$ substrate at $V_{sub} = -50$ V, and the overlayer was subsequently deposited at $V_{sub} = +50$ V. The seed layer was identified as having a (000$\bar{1}$) surface because of the absence of the enhanced subpeak at 4.5 eV, which is consistent with the results for single layers. However, the (000$\bar{1}$) surface termination was preserved in the overlayer despite the V_{sub} of $+50$ V. Other V_{sub} sequences were examined, as well, and in all cases the polarity of the overlayer was determined by the V_{sub} conditions used to deposit the seed layer. No polarity change was observed between the seed layer and the overlayer for any bias sequence, implying that the polarity is determined in the early stage of film growth.

Table I summarizes the I_{sub} and transport properties of samples deposited at three different V_{sub}. An interesting effect of applying V_{sub} is that the magnitude of I_{sub} depends
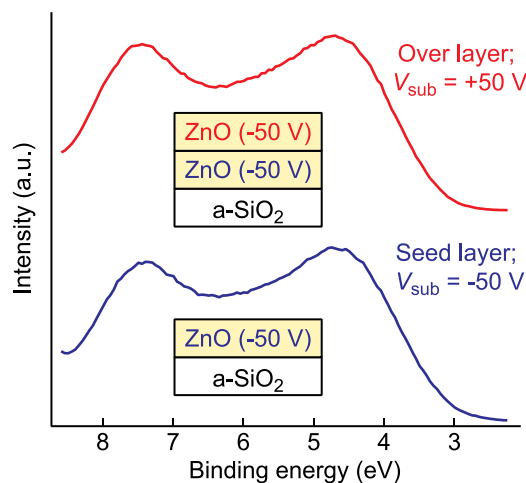
TABLE I. Deposition conditions and physical parameters of deposited films.

Sample ID	ZnO (float)	ZnO (+50)	ZnO (−50)
V_{sub}/V	Float	50	−50
I_{sub}/mA	0	50	−3
d_{sub}/mm	100	100	100
Polarity	(0001)	(0001)	(000$\bar{1}$)
$n_e/10^{19}$ cm^{-3}	1.1	2.8	0.7
μ_e/cm^2 V^{-1} s^{-1}	6.5	9.2	12.0

on the sign of V_{sub}. For example, $I_{sub} = 3$ mA at $V_{sub} = +50$ V and $I_{sub} = -50$ mA at $V_{sub} = -50$ V. These currents were only present when the sputtering plasma was ignited, indicating that the kind and flux of charged species (ions and electrons) arriving to the substrate (or growing film) was changed by V_{sub}.

The electric transport properties in the obtained films determined by Hall effect measurements were affected mildly by V_{sub} (see Table I). A slight variation in electron concentration (n_e) was observed. However, this behavior was not systematic but rather due to unintentional fluctuations in the experimental conditions. Indeed, the n_e of the film deposited at $d_{sub} = 150$ mm was in the same range and varied from sample to sample, while the films deposited at $d_{sub} = 150$ mm were much thinner than the films deposited at $d_{sub} = 100$. Thus, we tentatively conclude that the magnitude of V_{sub} is not a primary reason for the variation of n_e. It is also noted that the electron mobility (μ_e) fluctuated in the range of 10^0 cm^2 V^{-1} s^{-1}, which means that the magnitude of the resistivity was not significantly affected by the sign and magnitude of V_{sub}.

The photoluminescence (PL) spectra of films excited with a 325 nm continuous wave laser were also measured to examine the effect of V_{sub} on the defect structures in the films. The PL spectra of the samples did not display any obvious changes with sign and magnitude of V_{sub}. The spectra consisted of a broad-band visible luminescence resulting from defects, and the shape and intensity of this luminescence was nearly unchanged by the substrate bias. Therefore, the concentrations of non-radiative and radiative recombination centers did not change with V_{sub}.

In summary, we have shown that the crystallographic orientation of ZnO films deposited by RF sputtering can be controlled by applying V_{sub} at $d_{sub} = 100$ mm but not at 150 mm. We also observed that the crystalline polarity of the film is determined in the early stages of the deposition. In particular, the orientation of the formed film is irreversible in the sense that further changes in the crystallographic orientation for subsequently deposited layers are hindered. These findings enable us to speculate on possible mechanisms behind these phenomena. Some processing parameters, such as the substrate temperature and gas pressure, were not varied in this study, but it is evident that the polarity of ZnO films can be controlled using V_{sub} under certain deposition conditions at the nucleation stage. In a study on wurtzite-type AlN film deposition,[20] polarity change by substrate bias was explained by the concept of electric poling[21] under assumption that AlN is a ferroelectric compound where field

FIG. 4. XPS valence band spectra of a bilayer film where the seed layer and overlayer were deposited under different bias conditions.

induced displacement of atom/ion can take place. In the following paragraph of this letter, another possible role of V_{sub} in determining the film polarity is discussed.

Sputter deposition is characterized by energetic fluxes of atoms, ions, and electrons arriving at the sample surface at a wide range of angles and kinetic energies. This might result in many kinetic phenomena (selective resputtering, competitive grain growth, etc.). Since charged species, ion, and electrons contribute to these phenomena, the deposition kinetics might change with V_{sub}.[22] In such cases, the deposition rate and/or the defect type and density of the deposited film would change with V_{sub} as well. Since we did not observe any obvious change in the deposition rate or quality of the films in the XRD, Hall effect, and PL results, we can assume that changes in V_{sub} in the examined range ($\pm 100\,\text{V}$) resulted in negligible variation of these parameters. Instead, the nucleation itself must have been altered by the applied substrate bias.

Heterogeneous nucleation theory predicts the nucleation rates in terms of the surface and interface energies. Since the WZ structure possesses a dipole moment, a nucleus in an electric field will have an additional energy term that depends on the orientation of the dipole with respect to the field, and one of the two orientations of the crystal, showing the (0001) or (000$\bar{1}$) surface, would be energetically favorable while the other is unfavorable. The ratio between the nucleation rates for the favorable (n^*_{fav}) and unfavorable polarity (n^*_{unfav}) is expressed as

$$\frac{n^*_{fav}}{n^*_{unfav}} = \exp\left(-\frac{dG^*_{\text{homo}}}{kT} \cdot \left[S_{\text{unfav}} - S_{\text{fav}}\right]\right), \qquad (1)$$

where dG^*_{homo} is the nucleation barrier for homogeneous nucleation, k is the Boltzmann constant, T is the absolute temperature, and the S parameters ($0 \leq S \leq 1$) are the nuclei shape functions defined by the contact angles of the nuclei.[23] For nuclei with dipoles, S depends on the polarization vector in the nuclei. According to this equation, the exponential dependence can result in important rate differences even if the S functions differ only slightly. Tentatively, we attribute the observed phenomenon to variation of the S functions with V_{sub}.

In conclusion, the ability to impose a crystallographic polarity on ZnO films using an external control parameter was demonstrated by applying a DC substrate bias during RF sputtering. This method enables polarity-selective deposition of undoped ZnO without any crystalline templates. We argued that the selection of the orientation occurs at the nucleation stage, where the energy of the lattice dipole in the electric field is added to the overall formation energy of the nuclei. An external electrical field can potentially be used to control the polarity of other materials possessing dipole moments, which opens an approach to tailoring the polarization of materials for optoelectronic and micromechanical devices.

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