Improvement of the Properties of Direct-Current Magnetron-Sputtered Al-Doped ZnO Polycrystalline Films Containing Retained Ar Atoms Using 10-nm-Thick Buffer Layers

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ABSTRACT: The use of a 10-nm-thick buffer layer enabled tailoring of the characteristics, such as film deposition and structural and electrical properties, of magnetron-sputtered Al-doped ZnO (AZO) films containing unintentionally retained Ar atoms. The AZO films were deposited on glass substrates coated with the buffer layer via direct-current magnetron sputtering using Ar gas, a substrate temperature of 200 °C, and sintered AZO targets with an Al2O3 content of 2.0 wt %. The use of a Ga-doped ZnO film possessing a texture with a specific well-defined orientation as the buffer layer was very effective for improving the crystallographic orientation, reducing the residual stress, and improving the carrier transport of the AZO films. The residual compressive stress and in-grain carrier mobility were responsible for the retention of Ar atoms by the films, as observed using an electron probe microanalyzer.

INTRODUCTION

Magnetron sputtering (MS) is the most commonly used deposition technique for transparent conductive oxide (TCO) films, such as Sn-doped In2O3 (indium tin oxide (ITO)), ITO films deposited by MS are industry standard for numerous applications in photovoltaics, flat-panel displays, organic light-emitting diodes, and smart windows. On the other hand, Al- or Ga-doped ZnO (AZO or GZO), Nb-doped TiO2, and BaSnO3 films as an alternative material to replace the ITO films have been tried by the MS technique. However, one issue concerning magnetron-sputtered TCO films has yet to be resolved, namely, the nonuniform spatial distribution of electrical resistivity (ρ) on the substrate surface. Specifically, the area of the substrate opposite to the erosion zone of the target typically exhibits a relatively high ρ compared to that of other regions farther from this area. At present, the dominant factors responsible for this degradation of the electrical properties of the substrate opposite to the erosion zone of the target are not thoroughly understood. In an effort to address this issue, we have been investigating the influence of the erosion zone of MS targets on carrier transport in magnetron-sputtered AZO films on glass substrates. In our previous study, we detected relatively high amounts of residual argon (Ar) in AZO films deposited using direct-current (DC) MS compared with those deposited using radio frequency (RF) MS, irrespective of the substrate position. It was found that during film deposition recoiling Ar atoms collide with the growing AZO films, especially at the substrate positions opposite to the erosion zone. The impact of Ar atoms increases the contribution of grain-boundary scattering to the carrier transport owing to the deterioration of the crystallographic orientation. The residual Ar atoms present a significant obstacle to the free carriers in the in-grains, leading to a reduced carrier mobility. Our previous and present studies are the first to characterize the effects of Ar atoms on the film deposition, carrier transport properties, and crystallographic orientation in magnetron-sputtered TCO films. Based on these findings, to achieve a uniform spatial distribution of ρ, it is necessary to develop a technology that suppresses the effects of Ar atoms on the crystallographic orientation of as-deposited films grown at the substrate positions opposite to the erosion zone. To reduce the impact of Ar atoms, a two-step deposition process using a buffer layer, which was first explored in the case of gallium nitride (GaN), may be an effective method for fabricating AZO films with little contribution of grain-boundary scattering to carrier transport owing to the enhanced c-axis alignment between the columnar grains. Note that the buffer layers would play an important role in the increase in carrier concentration owing to the reduced local disorder, which also lead to the formation of a grain-boundary-potential barrier with a small energy difference relative to the Fermi level, resulting in a

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decrease in the contribution of grain-boundary scattering to carrier transport.\textsuperscript{31} By a comparison of the amounts of residual Ar atoms between AZO films with a buffer layer, showing a texture with a well-defined (0001) orientation as a result of the control of the crystallographic orientation, and buffer-layer-free AZO films with mixture orientation, we will elucidate the locations of residual Ar atoms such as the sites trapped at the surface of grain boundary and in-grains. The concept of the buffer layer leading to the changes in the locations of residual Ar atoms presented in this study is significantly different from that of the previous reports.\textsuperscript{17,26–29} 

In this study, we used 10-nm-thick Ga-doped ZnO (GZO) films deposited via DC arc discharge ion plating (IP) as the buffer layer. The main features of this buffer layer are a very smooth surface and a texture exhibiting a well-defined (0001) orientation, in contrast to buffer layers fabricated using RF-MS.\textsuperscript{32–34} We previously demonstrated that AZO films deposited on a 10-nm-thick GZO buffer layer using IP exhibited a well-defined (0001) orientation, in stark contrast to the mixture of (0001) and other orientations typically observed for DC-magnetron-sputtered AZO films.\textsuperscript{32–34} Consequently, highly (0001)-oriented AZO films with a marked reduction in the contribution of grain-boundary scattering to the carrier transport were obtained. However, the influence of the buffer layer on the crystallographic orientation, distribution, and carrier transport in the DC-magnetron-sputtered AZO films was investigated at substrate positions distant from the area opposite to the erosion zone of the target.\textsuperscript{32–34} In this study, we examined the influence of the improved orientation distribution due to the buffer layer on the carrier transport in DC-magnetron-sputtered AZO films at substrate positions both in the area opposite to the erosion zone of the target and farther away from this area.

### EXPERIMENTAL SECTION

**Film Deposition.** We deposited AZO films on alkali-free glass substrates (Corning, Eagle XG) with or without a 10-nm-thick buffer layer at a substrate temperature of 200 °C via DC–MS using an MS apparatus (ULVAC, CS-L) operating at a power of 200 W. The target was a high-density sintered ceramic circular AZO (diameter, 8 cm; Toshima Manufacturing Corp.) with an Al\textsubscript{2}O\textsubscript{3} content of 2.0 wt %. The reason that we chose the ceramic target is to limit the supply of oxygen-related species to the films from the target during the deposition process. The reason we chose Al films as eminently suitable for donors, leading to high carrier transport, is as follows. Table 1 lists valence-shell-orbital radii (R\textsubscript{max})\textsuperscript{35} and atomic term values, valence-shell-orbital energies, of Al, Ga, Zn, and O atoms.\textsuperscript{36} It shows that R\textsubscript{max} is the radius at which the magnitude of wave function is greatest, for the valence orbitals, 3s and 3p orbitals, of Al atoms are larger than those for the valence orbitals, 4s and 4p orbitals, of Ga atoms. This implies that larger concentrations of Ga donors are required before their orbits can overlap sufficiently for metallic conduction to occur, compared to those of Al donors. Notice that the energy difference between −\epsilon\textsubscript{s} of Al and Zn atom is smaller than that between −\epsilon\textsubscript{s} of Ga and Zn atoms.\textsuperscript{36} The interaction between Al and Zn atoms owing to an overlap of valence s orbitals will be stronger than that between Ga and Zn atoms, resulting in the formation of an Al-impurity band with a wide bandwidth inserted into the bottom of the host conduction band compared to the bandwidth of a Ga-impurity band located in the vicinity of the bottom of the conduction band of GZO films. Taking into account the features of Al valence orbitals and the Al-impurity band described above, it would be expected that AZO films exhibit high carrier transport in grains compared to that of GZO films.

The substrate was placed parallel to the target surface at a minimum substrate-to-target distance of 10 cm. The properties of the magnetron-sputtered AZO films at substrate positions in the area opposite to the erosion zone of the target and farther away from this area were evaluated at substrate positions of 0.5 and 6.5 cm, respectively, as depicted in Figure 1a (plane view) and Figure 1b (cross-sectional view).\textsuperscript{20} All of the deposition processes were performed under a pure Ar atmosphere at a pressure of 1.0 Pa. Prior to film deposition, the chamber was evacuated until the base pressure reached approximately 2.0 × 10\textsuperscript{-5} Pa.\textsuperscript{20} Following a previous report that the radial distributions of the electrical parameters depend on the erosion depth of the target,\textsuperscript{15} we deposited all of the AZO films at approximately the same time when the erosion depth of the target exceeded 1 mm.

We deposited the 10-nm-thick buffer layer of GZO on the glass substrates using an IP apparatus (Sumitomo Heavy Industries, Ltd.) with a DC arc discharge current of 150 A. We introduced oxygen (O\textsubscript{2}) gas into the chamber at a flow rate of 10 sccm to control the density of oxygen-related point defects such as oxygen vacancies and oxygen interstitials in the resulting film. The evaporation source (HAKUSUI Tech., Sky-Z) used for the deposition of the buffer layer was sintered ceramic ZnO (99.99% purity) containing 4.0 wt % Ga\textsubscript{2}O\textsubscript{3} (99.9% purity).\textsuperscript{37} Additional details regarding the buffer layer are reported previously.\textsuperscript{32–34}

**Characterization.** We measured the film thickness using a surface profilometer (KLA-Tencor, α-Step IQ). The microscopic morphology of the samples was evaluated using field-emission scanning electron microscopy (FESEM; Hitachi, SU9000). Photoluminescence (PL) measurements were performed at room temperature; the films were photoexcited using the 325 nm (3.815 eV) line of a HeCd laser, and the luminescent light was monitored using a spectrometer (Princeton Instruments, SP2500) equipped with a charge-coupled device detector (PIXIS256E).\textsuperscript{38} The carrier concentration (N), Hall mobility (\mu\textsubscript{H}), and \rho were determined using Hall effect measurements (Nanometrics, HL500PC) at room temperature according to the van der Pauw method. The optical properties were measured using a spectrophotometer (Hitachi, U-4100) and two different spectroscopic ellipsometers (J.A. Woollam, M-2000DI and IR-VASE Mark II). The optical transmittance (T) and reflectance (R) spectra of the AZO films in the wavelength range of 200–2400 nm were obtained using the spectrophotometer with an incident angle of 5°. The ellipsometric data (\Psi and \Delta) were acquired in the wavelength ranges of 0.3–1.7 μm (M-2000DI) and 1.7–30 μm (IR-VASE Mark II) at incident angles of 55, 65, and 75°.

| s orbital radius [Å] | p orbital radius [Å] | −\epsilon\textsubscript{s} [eV] | −\epsilon\textsubscript{p} [eV] |
|----------------------|----------------------|-------------------|-------------------|
| Al (3s, 3p)          | Ga (4s, 4p)          | Zn (4s, 4p)       | O (2s, 2p)        |
| 1.11                 | 1.05                 | 1.20              | 0.46              |
| 1.42                 | 1.40                 | 11.37             | 8.40              |
| 10.11                | 4.86                 | 4.90              | 3.38              |

Table 1. Valence-Shell-Orbital Radii and Atomic Term Values of Al, Ga, Zn, and O Atoms
For a comprehensive analysis of the texture, we conducted out-of-plane grazing-incidence (GI) X-ray diffraction (XRD) measurements using a SmartLab XRD system (Rigaku Corp.) with Cu Kα radiation (wavelength $\lambda = 0.15418$ nm, based on the weighted average of Cu Kα$_1$ ($\lambda = 0.154059$ nm) and Cu Kα$_2$ ($\lambda = 0.15444$ nm) in an intensity ratio of 2:1), where the substrate surface was subjected to X-ray irradiation at an incident angle ($\omega$) of 0.35° and only the 2θ axis was scanned. The textures of the bulk AZO films were characterized on the basis of out-of-plane wide-range reciprocal space maps (RSMs) and pole figures by a SmartLab XRD system equipped with a PILATUS 100K/R two-dimensional X-ray detector using Cu Kα radiation. The incorporated Ar content was analyzed using an electron probe microanalyzer (EPMA; JEOL, JXA-8200 or JXA-8500F). The analyzing crystal used for Ar was PETH (interplanar spacing of the reflecting plane: $d = 0.4371$ nm).

The electronic structure was determined by hard X-ray photoelectron spectroscopy (HAXPES) measurements, which were performed at BL46XU in Spring-8. HAXPES can be evaluated the electronic states of the bulk lying at depths of several tens of nanometers due to its large probing depth, compared with photoelectron spectroscopy using soft X-ray. An incident X-ray with a photon energy of 7.939 keV, which was monochromatized with a Si(111) double crystal and Si(444) channel-cut monochromator, was horizontally and vertically focused on a sample surface by Rh-coated mirrors. Photoelectron spectra were observed by an electron spectrometer (VG-Scienta, R-4000). The aperture of the analyzer slit was 0.5 mm with a curved rectangular shape, and the pass energy was fixed as 200 eV. X-ray was incident on films in the direction of the channel length at the incident angle of 5°, and the emitted photoelectrons were detected at the take-off angle of 85°.

### RESULTS AND DISCUSSION

**Crystallographic Orientation Distribution.** Figure 2a,b shows the out-of-plane wide-range RSMs of buffer-layer-free...
500-nm-thick AZO films at substrate positions of 0.5 and 6.5 cm, respectively. Figure 2c shows the out-of-plane wide-range RSM of a 500-nm-thick AZO film grown on a buffer layer at a substrate position of 0.5 cm. \( q_\parallel \) and \( q_\perp \) represent the coordinates of the reciprocal space in the directions parallel and perpendicular to the surface, respectively (\( q = 1/d_{\text{bulk}} = 2 \sin \theta/\lambda \), where \( \theta \) and \( \lambda \) are the X-ray incident angle and wavelength, respectively). The vertical line (i.e., the \( q_\perp \) axis) in the RSMs corresponds to a \( \theta/2\theta \) symmetrical scan of out-of-plane XRD measurements at angles from 10 to 130°. The dashed line corresponds to an orbit of a \( \omega \)-fixed \( 2\theta \) scan of out-of-plane GI-XRD, which will be discussed later alongside Figure 4. The out-of-plane RSMs demonstrate that all of the AZO films possessed a wurtzite structure. No peaks indicating the presence of other phases, such as crystalline Al oxides or other precipitates of Al–O compounds, were observed. From Figure 2, we determined that all of the AZO films had \{0001\} families of planes parallel to the substrate surface, that is, a (0001) orientation.

Figure 2c clearly shows the occurrence of narrow peaks corresponding to the 0002, 0004, and 0006 reflections with very high intensities for the AZO film grown on the buffer layer at a substrate position of 0.5 cm. The same peaks were also observed for the AZO film grown on the buffer layer at a substrate position of 6.5 cm (data not shown). Thus, it is not necessary to consider the influence of the erosion zone of the target on the crystallographic orientation of the textured polycrystalline AZO films deposited on the buffer layer. Analysis of the data revealed that the centers of gravity of the peaks for the 0002, 0004, and 0006 reflections were located approximately on the vertical line, that is, the \( q_\perp \) axis of the RSMs. This indicates that the (0001) plane of the AZO films lay approximately parallel to the substrate surface. No peaks indicating other orientations, such as 1011 diffraction peaks, were observed for these films. This confirms the highly preferential generation of columnar grains with the c-axis orientation owing to the well-defined (0001) orientation throughout the entire AZO film grown on the buffer layer. 32–34

For the buffer-layer-free AZO film at a substrate position of 0.5 cm (Figure 2a), analysis of the data obtained from the RSMs revealed that the centers of gravity of the 1010, 1122, and 1124 reflections, together with those of the 0002, 0004, and 0006 reflections, were located on the \( q_\parallel \) axis of the RSMs. This clearly demonstrates that the buffer-layer-free AZO film at a substrate position of 0.5 cm possessed a (0001) orientation mixed with (1010), (1122), and (1124) orientations. On the other hand, the peaks originating from the (1122) and (1124) orientations disappeared together with that originating from the (1011) orientation for the buffer-layer-free AZO film at a substrate position of 6.5 cm, as shown in Figure 2b. 30,32–34,40

To estimate the texture evolution quantitatively, we examined the variation of the volume fraction of (0001) orientation \( V_{(0001)} \) obtained from the XRD pole figure measurements. Figure 3a–c shows XRD pole figures of the 0002 reflections of the same films in Figure 2, respectively. The upper figure and lower spectra correspond to two-dimensional projections and variation in intensity with \( \alpha \) and \( \beta \), respectively. In these figures, the distribution of the poles for 0002 reflections appears as a spot in the center of the figure, or as a spot together with some rings located at an \( \alpha \) range of 20°–90°. The first peak was attributed to the (0001) orientation. The presence of another peak revealed that AZO films have a mixture of multiple orientations. \( V_{(0001)} \) represents the percentage ratio of the area of the (0001) orientation against whole area. According to this definition, a greater value of \( V_{(0001)} \) corresponds to a stronger (0001) orientation texture. 30,33,34,39 We calculated the values of \( V_{(0001)} \) to be 69.7 and 95.0% for the buffer-layer-free AZO films at substrate positions of 0.5 and 6.5 cm, respectively. The \( V_{(0001)} \) values of AZO films grown on a buffer layer were found to exceed 99%, irrespective of the substrate position, demonstrating that the inclusion of a buffer layer is an effective strategy for enhancing the \( V_{(0001)} \) of AZO films at any given substrate position. 32–34 At a particular substrate position, the \( V_{(0001)} \) of AZO films grown on a buffer layer was higher than that of films grown directly on the substrate, and this effect became very large for substrate positions opposite to the erosion zone of the target.
Texture Evolution. Next, we studied the orientation distribution during the initial deposition stage of the AZO films. We performed out-of-plane GI-XRD measurements to investigate the differences in the deposition mechanism between AZO films with and without a buffer layer at substrate positions of 0.5 and 6.5 cm. Figure 4a,b shows the out-of-plane GI-XRD patterns of AZO films of various thicknesses grown in the absence and presence of a buffer layer, respectively. The upper and lower spectra in each panel correspond to substrate positions of 0.5 and 6.5 cm, respectively.

The out-of-plane GI-XRD patterns of all of the buffer-layer-free AZO films in Figure 4a show 0002 and 1013 reflections. For the 15-nm-thick AZO film at a substrate position of 0.5 cm, as shown in the upper part of Figure 4a, 0002 and 1013 reflections were observed. Upon increasing the thickness to 30 nm, we additionally observed 1011, 1012, and 1120 reflections. Further increasing the thickness to 60 nm led to the observation of additional 1010, 1122, 0004, and 2022 reflections. The 20-nm-thick AZO film at a substrate position of 6.5 cm predominantly exhibited 0002 and 1013 reflections, as shown in the lower part of Figure 4a. Upon increasing the thickness to 40 nm, we additionally observed 1010, 1012, and 1122 reflections. With further increasing the thickness up to 70 nm, the 1011 and 1120 reflections were also observed in addition to the above-described five peaks. The variation of the observed reflections as a function of film thickness may indicate that the buffer-layer-free AZO films possessed a polycrystalline textured structure consisting of some crystallites with a low probability of orientations other than the (0001) orientation during the early stage of film deposition, irrespective of the substrate position. On the other hand, the use of a buffer layer led to AZO films that exhibited a very intense 1013 reflection and the complete absence of the other reflections, indicating the successful deposition of AZO films with a well-defined (0001) orientation. Figure 4b clearly shows that all of the AZO films grown on a buffer layer maintained the same reflection of 1013, irrespective of the film thickness and substrate position. These findings suggest that the AZO films deposited on the buffer layer were highly textured with a preferential c-axis orientation, similar to the results observed for the 500-nm-thick AZO films grown on the buffer layer, during the early stages of film deposition. The use of a buffer layer has therefore been demonstrated to produce AZO polycrystalline films possessing a textured structure with a well-defined (0001) orientation, irrespective of the film thickness and substrate position, resulting in a contribution of grain-boundary scattering to carrier transport of less than 0.04, which will be discussed in Electrical Properties and Carrier Transport section.

Figure 5 shows the in-plane stress ($\sigma_a$) of AZO films with and without a buffer layer at substrate positions of 0.5 and 6.5 cm for film thicknesses ranging from 15 to 500 nm. For hexagonal crystals, the in-plane stress, $\sigma_a$, can be expressed as $\sigma_a = 2C_{13} - C_{13}(C_{11} + C_{12})/2C_{13} \times (l_i - l_c)$ where $C_{ij}$ are the stiffness constants with values of $C_{11} = 208.8$, $C_{12} = 213.8$, $C_{13} = 119.7$, and $C_{13} = 104.2$ GPa (the c-axis lattice parameter of stress-free bulk ZnO ($l_c$) = 5.207 Å). $l_i$ was calculated from the peak position of the 0002 reflection in the out-of-plane $\theta/2\theta$ XRD profiles. Note that negative values of $\sigma_a$ indicate residual compressive stress (i.e., increased $l_i$), whereas positive values indicate residual tensile stress (i.e., decreased $l_i$). We observed only minor variation between the samples in the values of the $a$-axis lattice parameter ($l_a$) calculated from the peak positions of the 1010 reflection in the in-plane XRD profiles, indicating that the unit-cell volume behaved similarly to the tendency of $l_i$. Figure 5 shows that at a substrate position of 0.5 cm the AZO films exhibited residual compressive stress irrespective of film thickness. In these films, increasing the film thickness resulted in a decrease in the magnitude of $\sigma_a$. These experimental results also demonstrate the influence of the buffer layer on reducing the residual compressive stress at a particular film thickness. As described above, the use of the buffer layer was very effective for achieving polycrystalline AZO films possessing a texture with a high concentration of small-angle grain boundaries. In such films, we would expect to find a very low concentration of residual O atoms trapped at
the interatomic forces at the grain boundaries tend to close any existing gaps with the consequence that the neighboring crystallites are strained in tension. We observed the above effects of the small-angle-grain boundaries on the residual stress for AZO films grown on a buffer layer at a substrate position of 6.5 cm, as shown in Figure 5. The film-thickness-dependent $\sigma_t$ exhibited unusual and complex behavior for the buffer-layer-free AZO films at a substrate position of 6.5 cm. For thick AZO films, we found that the tensile stress of the grain boundaries appears to remain the dominant stress mechanism.

Note that the values of $\sigma_t$ for the 500- and 200-nm-thick AZO films with the buffer layer at a substrate position of 6.5 cm were almost zero, indicating a stress-free state. In contrast, the $\sigma_t$ values of the AZO films with the buffer layer at a substrate position of 0.5 cm indicated a large residual compressive stress despite the presence of the columnar grains with the highly preferential $c$-axis orientation. The occurrence of this residual compressive stress may be attributable to the remaining Ar incorporated into the AZO films, which will be discussed in the Quality of In-grains section.

Figure 6a,b shows FESEM images of buffer-layer-free 500-nm-thick AZO films at substrate positions of 0.5 and 6.5 cm, respectively, and Figure 6c,d shows those of 500-nm-thick AZO films with the buffer layer at substrate positions of 0.5 and 6.5 cm, respectively. The left and right sides of each panel show plane and cross-sectional views, respectively. Figure 6 clearly demonstrates the influence of the buffer layer on the microstructure of the AZO films; the use of the buffer layer was very effective for achieving AZO films that grew via columnar grains. Figure 6a,b shows that the buffer-layer-free AZO films apparently grew via columnar grains during the initial stage of deposition and subsequently formed grains of various shapes later in the film deposition process; the lateral grain size of some of the columns appeared to change during film deposition, which may be attributable to the recrystallization process and poor alignment between the columnar grains. Note also that the DC–MS deposition process afforded AZO films possessing a mixed orientation. Some of the adatoms on the deposition surface, especially those at substrate positions opposite to the erosion zone of the target, possess a high energy, and this excess energy may be sufficient to drive these atoms into the grain boundaries. The incorporation of excess atoms into grain boundaries leads to a large residual compressive stress in the film.

Figure 6c,d shows that the dense polycrystalline AZO films grown on the buffer layer exhibited a typical columnar-grain structure with a flat grain surface, and the lateral grain size of each column appears to remain almost constant along the film thickness. We have therefore confirmed the influence of the buffer layer on the microstructure of AZO films deposited using DC–MS. During film deposition on the buffer layer, the adatoms on the deposition surface with excess free energy become incorporated into the hexagonal arrays of Zn and O in the buffer layer. Thus, the buffer layer suppresses the movement of these adatoms with excess free energy to the grain boundaries, resulting in a preferential $(0001)$ orientation and reducing the residual compressive stress in the film.

Quality of In-grains. Figure 7 shows EPMA spectra of 500-nm-thick AZO films with and without a buffer layer at substrate positions of 0.5 and 6.5 cm as a function of photon energy.
The intensity of the signal corresponding to Ar atoms from the inert deposition gas was strongly dependent on the substrate position, whereas the presence or absence of the buffer layer had little effect on the peak intensity. Figure 7 clearly shows that the intensity of the peak corresponding to Ar atoms was higher for the substrate position of 0.5 cm than for the substrate position of 6.5 cm located farther away from the erosion zone of the target. To semiquantitatively estimate the content of retained Ar atoms in the films, we calculated the ratios of Ar Kα/Zn Kα area intensity, and the results are presented in Table 2. At the substrate position of 0.5 cm, the Ar Kα/Zn Kα ratios for the AZO films with and without the buffer layer were 0.19 and 0.12, respectively. On the other hand, at the substrate position of 6.5 cm, the ratios with and without the buffer layer were considerably lower at 0.08 and 0.06, respectively. These findings imply the fact that introduction of Ar atoms primarily results from backscattering perpendicular to the target in the erosion zone, while the sputtered flux is distributed angularly. It should be noted that the content of residual Ar atoms in AZO films with the buffer layer was on the same level with the case of without the buffer layer, although it even had columnar grains with the highly preferential c-axis orientation owing to the well-defined (0001) orientation. The above finding implies that the flying fluxes of recoiling Ar-related species are mainly incorporated in-grain.

We conducted PL measurements to investigate the quality of the polycrystalline AZO films. In general, the PL spectra of ZnO-based films contain two bands, namely, near-band-edge (NBE) emission in the ultraviolet region and defect-related deep-level (DL) emissions in the visible region. For the PL measurements, we used quartz glass as the substrate because the PL spectra of AZO films on alkali-free glass substrates were dominated by bands originating from the substrate. We observed little difference in the structural, electrical, and optical properties between AZO films deposited on quartz and alkali-free glass substrates. Figure 8 shows representative PL spectra of AZO films with and without a buffer layer at substrate positions of 0.5 and 6.5 cm as a function of wavelength. The upper and lower spectra correspond to substrate positions of 0.5 and 6.5 cm, respectively. The NBE emission band at a wavelength of approximately 350 nm dominated the PL spectra of all of the AZO films, with some oscillations, and only a very weak peak corresponding to DL emission was observed in the wavelength range of 450–600 nm. These oscillations are probably attributable to the film thickness. The DL emission can be ascribed to various types of intrinsic point defects, such as oxygen vacancies, oxygen antisites, oxygen located at interstitial sites, Zn located at interstitial sites, and Zn vacancies. A point to be noted here is that all samples exhibited a DL emission intensity with little strength. It means a low density of the intrinsic defect, assuming that the presence of intrinsic point defects of the films is observed as DL emission in the visible wavelength range. Bikowski et al. reported the maximum of the $\rho$, $l_{\rho}$ expansion and the minimum of the crystallite size for AZO films grown at the area of the substrate opposite to the erosion zone of the target, where the maximum of the flux of the high-energy electronegative-oxygen ($O^-$) ions was observed with the plasma process monitor. They explained the above findings thorough the ion-energy-dependent dynamic equilibrium between the formation of oxygen interstitials ($O_i$), resulting in an increase in $l_{\rho}$, and the compensation of carrier electrons donated by donors. In this study, there is no
evidence of the degradation of the properties owing to the damage caused by high-energy O− ions, even for AZO films deposited at substrate positions opposite to the erosion zone. Therefore, we focus on the discussion about the effects of the remaining Ar on the properties.

The intensity of the NBE emission of the AZO films was strongly dependent on the substrate position. As shown in Figure 8, the NBE emission intensity was considerably higher for the substrate position of 6.5 cm than that for the substrate position of 0.5 cm opposite to the erosion zone of the target. This observation suggests that the AZO films should possess a very high density of nonradiative defects at the substrate position of 0.5 cm compared to that at the substrate position of 6.5 cm. Nonradiative recombination centers can originate from numerous sources, such as dislocations, point defects, surface states, and, in particular, interface states in the grain boundaries of polycrystalline films. The intensity of the NBE photoluminescent area and the amount of residual Ar atoms were determined; thus, the residual Ar atoms induce the generation of crystallographic defects in the films, which is expected to be a dominant factor limiting the density of nonradiative recombination centers.20 We also observed a small increase in the NBE emission intensity for the AZO films with the buffer layer relative to those without the buffer layer at the same substrate position. Taking into account the fact that AZO films with the buffer layer exhibit improved flatness and crystallinity compared to that of buffer-layer-free AZO films, it can be explained by a decrease in the additional surface states owing to the adsorption of carbon-related gases at the surface of the in-grains and in Al-related precipitates at the surface of grain boundaries.

Electronic Structure. Figure 9a,b shows valence band (VB) spectra and Fermi-level region spectra of 500-nm-thick AZO films with and without a buffer layer at substrate positions of 0.5 cm and of 500-nm-thick AZO films with the buffer layer at a substrate position of 6.5 cm, respectively. These spectra have been normalized to the Zn 3d peak intensity. From Figure 9b, the density of states (DOS) can be observed in the Fermi-level region for all films. The DOS intensity of AZO films slightly increased by inserting a buffer layer and then drastically increased farther away from the erosion zone of the target. These differences of DOS intensity can be explained by those of N whose values will be discussed in next section.

In Figure 9a, two groups can be observed in the VB: (1) From 10 to 14 eV, there are bands with a strong d character, originating mostly from d states at Zn sites. (2) For the upper valence band located above approximately 8 eV, O p states are dominant. In the energy region from 5 eV to the valence band maximum, the states exhibit complex behavior, namely, they consist of the bonding states between O p and another Zn set of 4p′, p′, and ps with T2 symmetry and the antibonding states between O p and the 3d set with T3 symmetry.62−64 For Figure 9a, subpeak structure at about 4.8 eV in VB spectra is clearly observed from AZO films with a buffer layer, compared with buffer-layer-free AZO films. The appearance of the subpeak is considered as a fingerprint of the Zn-polar surface of ZnO, whereas its absence suggests the existence of an O-polar surface of ZnO.38,65−67 The appearance of the subpeak also depends on the plasmon excitation scattering from the electrons in the conduction band.58 Taking into account that a subpeak can be similarly observed in AZO films with a buffer layer despite the fact that N is different at each substrate positions, buffer-layer-free AZO films may be different in polarity from AZO films with a buffer layer. It should be noted that the electrical and optical properties and σ0 of AZO films with a buffer layer were strongly dependent on the substrate position, whereas the VB spectra were identical at any given substrate position. This finding suggests that degradation of the electrical and optical properties occurs in deep parts that cannot be probed by HAXPES.

Electrical Properties and Carrier Transport. Finally, to clarify the influence of the buffer layer on the electrical properties of AZO films at different substrate positions, we examined the electrical properties and carrier transport characteristics. Table 2 summarizes the determined values of ρ, N, and µf for the AZO films with and without buffer layers at substrate positions of 0.5 and 6.5 cm. Taking into account the fact that the buffer layer thickness was only 10 nm and the total sample thickness was 500 nm, the following discussion is based on a single-layer model. Table 2 also shows the values of V(0001)Ar Kα/Zn Kα area intensity ratio, and σd determined for the AZO films. The results demonstrate that the presence of the buffer layer effectively enhanced both N and µf thereby reducing the value of ρ compared to that of buffer-layer-free AZO films, irrespective of the substrate position. These effects of the buffer layer were more pronounced at the substrate position of 0.5 cm opposite to the erosion zone of the target.

The performance of the TCO material, figure of merit (Φ), can be determined from the sheet resistance (Rs) and T using Haacke’s relation as follows: 69 Φ = (Tvσ/100)10, where Tv is the optical average transmittance in the wavelength range from 400 to 700 nm. According to the definition, a high value of Φ corresponds to a high performance of TCO. Rs, Tv, and
Φ of AZO films in this study are summarized in Table 2. It clearly shows very high Φ of about 42 × 10⁻³ Ω⁻¹ of AZO films with buffer layers deposited at a substrate position of 6.5 cm compared with the previous literature data of ITO films of 28.66 × 10⁻³ Ω⁻¹, 5 Nb-doped TiO₂ films of 5.6 × 10⁻³ Ω⁻¹, and La-doped BaSnO₃ films of 5 × 10⁻³ Ω⁻¹.

To obtain a better understanding of the enhanced μ_H in the presence of the buffer layer, we calculated the optical mobility (μ opt) and the ratio of μ opt to the carrier mobility at the grain boundaries (μ GB). The ratio μ opt/μ GB is an important parameter for quantifying the degree of the contribution of grain-boundary scattering to carrier transport. In this study, we take μ opt as the in-grain carrier mobility. μ opt was calculated on the basis of the Drude theory using the experimental data for T and R determined from the spectrophotometric measurements combined with the experimental data for μ GB of 1.03 and therefore a substantially lower μ GB at a substrate position of 0.5 cm exhibited a μ opt of 29.0 cm²/(Vs) whereas those at a substrate position of 0.5 cm exhibited a μ opt of 28.4 cm²/(Vs) and a μ opt/μ GB of 0.04, leading to a slightly reduced μ_H of 27.3 cm²/(Vs) owing to the small contribution of grain-boundary scattering to carrier transport. The buffer-layer-free AZO film at the same substrate position exhibited a similar μ opt of 29.0 cm²/(Vs) but a considerably higher μ opt/μ GB of 1.03 and therefore a substantially lower μ GB of 14.3 cm²/(Vs). These results provide an important insight into the effect of the buffer layer from the viewpoint of the structural properties. In our previous studies, we found that AZO films possessing textures with complex orientations such as (1010), (1122), and (1124) exhibited high values of μ opt/μ GB and μ H values that were lower than μ opt. To obtain AZO films with high μ H, we calculated the optical mobility for μ opt/μ GB, increasing V opt, which leads to a reduction in μ opt/μ GB.

This study has elucidated the other factors limiting the electrical properties of AZO films deposited using DC–MS. These factors include the retained Ar and residual stress in the films. As shown in Table 2, the AZO films with the buffer layer at a substrate position of 0.5 cm exhibited a μ GB of 27.3 cm²/(Vs) with an N of 4.93 × 10²⁰ cm⁻³, whereas those at a substrate position of 6.5 cm displayed a μ GB of 41.3 cm²/(Vs) with an N of 7.23 × 10²⁰ cm⁻³. Although both of these AZO films possessed a texture with a well-defined (0001) orientation and small-angle grain boundaries, i.e., excellent alignment between the columnar grains, they contained distinctly different amounts of retained Ar and residual stress. As shown in Table 2, similar findings were observed for the buffer-layer-free AZO films. Future studies on other possible factors, such as Ar incorporated in the grains and residual stress including both compressive and tensile stress, are required to further build on the results of this study and our previous studies.

CONCLUSIONS

In this work, we investigated the effects of inserting a very thin buffer layer on the film deposition and structural and electrical properties of polycrystalline DC-magnetron-sputtered AZO films grown on glass substrates at positions in the area opposite to the erosion zone of the target and farther away from this area. We have demonstrated that the use of a 10-nm-thick buffer layer deposited via DC arc discharge IP led to AZO films possessing a texture with a specific well-defined (0001) orientation, effectively improving the crystallographic orientation of the AZO films irrespective of the substrate position. The AZO films grown on the buffer layer exhibited V opt/μ opt values exceeding 99% at both substrate positions. Consequently, these films displayed a marked reduction in the contribution of grain-boundary scattering to the carrier transport, affording a drop to μ opt/μ GB ratio of less than 0.04, whereas we observed no effect on the intrinsic carrier transport μ opt. These findings indicate that the Ar-related obstacles to carrier transport were mainly present in the in-grains. The results of this study clearly indicate that technologies for producing AZO films with a high carrier transport must afford a significant decrease in the amount of Ar incorporated in the in-grains.

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REFERENCES

(1) Ishibashi, S.; Higuchi, Y.; Otá, Y.; Nakamura, K. Low resistivity indium–tin oxide transparent conductive films. II. Effect of sputtering voltage on electrical property of films. J. Vac. Sci. Technol., A 1990, 8, 1403–1406.
(2) Wolf, S. D.; Descoendres, A.; Holman, Z. C.; Ballif, C. High-efficiency Silicon Heterojunction Solar Cells: A Review. Green 2012, 2, 7–24.
(3) Katayama, M. TFT-LCD technology. Thin Solid Films 1999, 341, 140–147.
(4) Salehi, A.; Fu, X.; Shin, D.-H.; So, F. Recent Advances in OLED Optical Design. Adv. Funct. Mater. 2019, 29, No. 1808803.
(5) Granqvist, C. G. Electrochromic tungsten oxide films: Review of progress 1993-1998. Sol. Energy Mater. Sol. Cells 2000, 60, 201–262.
(6) Gogova, D.; Thomas, L.-K.; Camin, B. Comparative study of gasochromic and electrochromic effect in thermally evaporated tungsten oxide thin films. Thin Solid Films 2009, 517, 3326–3331.

(7) Tomina, K.; Yuasa, T.; Kume, M.; Tada, O. Influence of Energetic Oxygen Bombardment on Conductive ZnO Film. Jpn. J. Appl. Phys. 1985, 24, 944–949.

(8) Tomina, K.; Kuroda, K.; Tada, O. Radiation Effect due to Energetic Oxygen Atoms on Conductive Al-Doped ZnO Films. Jpn. J. Appl. Phys. 1988, 27, 1176–1180.

(9) Minami, T.; Sato, H.; Imamoto, H.; Takata, S. Substrate Temperature Dependence of Transparent Conducting Al-Doped ZnO Thin Films Prepared by Magnetron Sputtering. Jpn. J. Appl. Phys. 1992, 31, L257–L260.

(10) Minami, T.; Miyata, T.; Yamamoto, T.; Toda, H. Origin of electrical property distribution on the surface of ZnO:Al films prepared by magnetron sputtering. J. Vac. Sci. Technol., A 2000, 18, 1584–1589.

(11) Minami, T.; Ohtani, Y.; Miyata, T.; Kuboi, T. Transparent conducting Al-doped ZnO thin films prepared by magnetron sputtering with dc and rf powers applied in combination. J. Vac. Sci. Technol., A 2007, 25, 1172–1177.

(12) Kon, M.; Song, P. K.; Mitsu, A.; Shigesato, Y. Crystallinity of Gallium-Doped Zinc Oxide Films Deposited by DC Magnetron Sputtering Using Ar, Ne or Kr Gas. Jpn. J. Appl. Phys. 2002, 41, 6174–6179.

(13) Rieth, L. W.; Holloway, P. H. Influence of negative ion resputtering on ZnO:Al thin films. J. Vac. Sci. Technol., A 2004, 22, 20–29.

(14) Sato, Y.; Ishihara, K.; Oka, N.; Shigesato, Y. Spatial distribution of electrical properties for Al-doped ZnO films deposited by dc magnetron sputtering using various inert gases. J. Vac. Sci. Technol., A 2010, 28, 895–900.

(15) Bikowski, A.; Welzel, T.; Ellmer, K. The correlation between the radial distribution of high-energetic ions and the structural as well as electrical properties of magnetron sputtered ZnO:Al films. J. Appl. Phys. 2013, 114, No. 223716.

(16) Crovetto, A.; Ottsen, T. S.; Stamate, C.; Kjær, D.; Schou, J.; Hansen, O. On performance limitations and property correlations of Al-doped ZnO deposited by radiofrequency sputtering. J. Phys. D: Appl. Phys. 2016, 49, No. 295101.

(17) Nomoto, J.; Oda, Y.; Miyata, T.; Minami, T. Effect of inserting a buffer layer on the characteristics of transparent conducting impurity-doped ZnO thin films prepared by dc magnetron sputtering. Thin Solid Films 2010, 519, 1587–1593.

(18) Yamada, Y.; Kadowaki, K.; Kikuchi, H.; Funaki, S.; Kubo, S. Positional variation and annealing effect in magnetron sputtered Ga-doped ZnO films. Thin Solid Films 2016, 609, 25–29.

(19) Meng, F.; Peng, S.; Xu, G.; Wang, Y.; Ge, F.; Huang, F. Structure of uniform and high-quality Al-doped ZnO films by magnetron sputter deposition at low temperatures. Thin Solid Films 2018, 665, 109–116.

(20) Nomoto, J.; Makino, H.; Inaba, K.; Kobayashi, S.; Yamamoto, T. Effects of the erosion zone of magnetron sputtering targets on the spatial distribution of structural and electrical properties of transparent conductive Al-doped ZnO polycrystalline films. J. Appl. Phys. 2018, 124, No. 065304.

(21) Meng, F.; Ge, F.; Chen, Y.; Xu, G.; Huang, F. Local structural changes induced by ion bombardment in magnetron sputtered ZnO:Al films: Raman, XPS, and XAS study. Surf. Coat. Technol. 2019, 365, 2–9.

(22) Yamada, N.; Higosugi, T.; Hoang, N. L. H.; Furubayashi, Y.; Hirose, Y.; Konuma, S.; Shimada, T.; Hasegawa, T. Structural, electrical and optical properties of sputter-deposited Nb-doped TiO2 (TNO) polycrystalline films. Thin Solid Films 2008, 516, 5754–5757.

(23) Sato, Y.; Sanno, Y.; Tasaki, C.; Oka, N.; Kamiyama, T.; Shigesato, Y. Electrical and optical properties of Nb-doped TiO2 films deposited by dc magnetron sputtering using slightly reduced Nb-doped TiO2,x ceramic targets. J. Vac. Sci. Technol., A 2010, 28, 851–855.

(24) Ganguly, K.; Ambwani, P.; Xu, P.; Jeong, J. S.; Mkhoyan, K. A.; Leighton, C.; Jalan, B. Structure and transport in high pressure oxygen sputter-deposited BaSnO3−x. APL Mater. 2015, 3, No. 062509.

(25) Luo, B.; Hu, J. Unraveling the Oxygen Effect on the Properties of Sputtered BaSnO3 Thin Films. ACS Appl. Electron. Mater. 2019, 1, 51–57.

(26) Itagaki, N.; Matsushima, K.; Yamashita, D.; Seo, H.; Koga, K.; Shiraishi, M. Off-axis sputter deposition of ZnO films on c-sapphire substrates with buffer layers prepared via nitrogen-mediated crystallization. In Oxide-Based Mater. Devices V; Teherani, F. H., Look, D. C., Rogers, D. J., Eds.; 2014; 89871A.

(27) Amano, H.; Sawaki, N.; Akasaki, I.; Toyoda, Y. Metalorganic vapor phase epitaxial growth of a high quality GaN film using an AlN buffer layer. Appl. Phys. Lett. 1986, 48, 353–355.

(28) Nakamura, S. GaN Growth Using GaN Buffer Layer. Jpn. J. Appl. Phys. 1991, 30, L1705–L1707.

(29) Gogova, D.; Larsson, H.; Kasc, A.; Yazdi, G. R.; Ivanov, I.; Yakimova, R.; Momemar, B.; Aujol, E.; Frayssinet, E.; Faurie, J.-P.; Beaumont, B.; Gibart, P. High-Quality 2” Bulk-Like Free-Standing GaN Grown by HydrideVapour Phase Epitaxy on a Si-doped Metal Organic Vapour Phase Epitaxial GaN Template with an Ultra Low Dislocation Density. Jpn. J. Appl. Phys. 2005, 44, 1181–1185.

(30) Nomoto, J.; Inaba, K.; Osada, M.; Kobayashi, S.; Makino, H.; Yamamoto, T. Highly (0001)-oriented Al-doped ZnO polycrystalline films on amorphous glass Substrates. J. Appl. Phys. 2016, 120, No. 125302.

(31) Mickan, M.; Helmersson, U.; Rinnert, H.; Ghanbaja, J.; Muller, D.; Horwat, D. Room temperature deposition of homogeneous, highly transparent and conductive Al-doped ZnO films by reactive high power impulse magnetron sputtering. Sol. Energy Mater. Sol. Cells 2016, 157, 742–749.

(32) Nomoto, J.; Makino, H.; Yamamoto, T. High-Hall-Mobility Al-Doped ZnO Films Having Textured Polycrystalline Structure with a Well-Defined (0001) Orientation. Nanoscale Res. Lett. 2016, 11, No. 320.

(33) Nomoto, J.; Makino, H.; Yamamoto, T. Correlation between carrier transport and orientation evolution of polycrystalline transparent conductive Al-doped ZnO films. Thin Solid Films 2016, 620, 2–9.

(34) Nomoto, J.; Makino, H.; Yamamoto, T. Characteristics of the orientation distribution and carrier transport of polycrystalline Al-doped ZnO films prepared by direct current magnetron sputtering. Thin Solid Films 2017, 644, 33–40.

(35) Mann, J. B. Atomic Structure Calculations II. Hartree-Fock Wavefunctions and Radial Expectation Values: Hydrogen to Lawrencium; LA-3691; Los Alamos Scientific Laboratory, 1968.

(36) Harrison, W. A. Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond; DOVER PUBLICATIONS, INC.: New York, 1989.

(37) Nomoto, J.; Makino, H.; Yamamoto, T. Limiting factors of carrier concentration and transport of polycrystalline Ga-doped ZnO films deposited by ion plating with dc arc discharge. Thin Solid Films 2016, 601, 13–17.

(38) Makino, H.; Shimizu, H. Influence of crystallographic polarity on the opto-electrical properties of polycrystalline ZnO thin films deposited by magnetron sputtering. Appl. Surf. Sci. 2018, 439, 839–844.

(39) Nomoto, J.; Inaba, K.; Kobayashi, S.; Watanabe, T.; Makino, H.; Yamamoto, T. Characteristics of Carrier Transport and Crystallographic Orientation Distribution of Transparent Conductive Al-Doped ZnO Polycrystalline Films Deposited by Radio-Frequency, Direct-Current, and Radio-Frequency-Supervised Direct-Current Magnetron Sputtering. Materials 2017, 10, 916.

(40) Nomoto, J.; Inaba, K.; Kobayashi, S.; Makino, H.; Yamamoto, T. Interface layer to tailor the texture and surface morphology of Al-doped ZnO polycrystalline films on glass substrates. J. Cryst. Growth 2017, 468, 645–649.

(41) Nomoto, J.; Makino, H.; Inaba, K.; Kobayashi, S.; Yamamoto, T. Erratum: “Effects of the erosion zone of magnetron sputtering
targets on the spatial distribution of structural and electrical properties of 
transparent conductive Al-doped ZnO polycrystalline films” [J. Appl. 
Phys. 124, 063504 (2018)]. J. Appl. Phys. 2019, 125, No. 029901.

(42) Kobayashi, K. Hard X-ray photoemission spectroscopy. Nucl. 
Instrum. Methods Phys. Res. 2009, A601, 32–47.

(43) Yasuno, S.; Oji, H.; Kogananezawa, T.; Watanabe, H. Hard x-ray 
photoelectron spectroscopy equipment developed at beamline 
BL46XU of SPring-8 for industrial researches. AIP Conf. Proc. 
2016, 1741, No. 030020.

(44) Cebulla, R.; Wendt, R.; Ellmer, K. Al-doped zinc oxide films 
deposited by simultaneous rf and dc excitation of a magnetron 
plasma: Relationships between plasma parameters and structural 
and electrical film properties. J. Appl. Phys. 1998, 83, 1087–1095.

(45) Hinze, J.; Ellmer, K. In situ measurement of mechanical stress in 
polycrystalline zinc-oxide thin films prepared by magnetron 
sputtering. J. Appl. Phys. 2000, 88, 2443–2450.

(46) Terasako, T.; Nomoto, J.; Makino, H.; Yamamoto, N.; 
Shirakata, S.; Yamamoto, T. Effects of oxygen gas flow rates and Ga 
contents on structural properties of Ga-doped ZnO films prepared by 
ion-plating with a DC arc discharge. Thin Solid Films 2015, 
516, 24–28.

(47) Thornton, J. A.; Tabock, J.; Hoffman, D. W. Internal stresses in 
magnetic films deposited by cylindrical magnetron sputtering. Thin 
Solid Films 1979, 64, 111–119.

(48) Thornton, J. A.; Hoffman, D. W. Internal stresses in amorphous 
 silicon films deposited by cylindrical magnetron sputtering using Ne, 
Ar, Kr, Xe, and Ar+H2. J. Vac. Sci. Technol. 1981, 18, 203–207.

(49) Thornton, J. A.; Hoffman, D. W. The influence of discharge 
current on the intrinsic stress in Mo films deposited using cylindrical 
and planar magnetron sputtering sources. J. Vac. Sci. Technol. A, 
1985, 3, 576–579.

(50) Onai, Y.; Uchida, T.; Kasahara, Y.; Ichikawa, K.; Hoshi, Y. 
Transparent conductive film for top-emission organic light-emitting 
deVICES by low damage facing target sputtering. Thin Solid Films 
2008, 516, 5911–5915.

(51) Shirakata, S.; Sakemi, T.; Awai, K.; Yamamoto, T. Optical and 
 electrical properties of ZnO films prepared by URT-IP method. Thin 
Solid Films 2003, 445, 278–283.

(52) Djurisic, A. B.; Leung, Y. H. Optical Properties of ZnO 
Nanostripes. Small 2006, 2, 944–961.

(53) Pigeat, P.; Esvararakhanthan, T.; Briançon, J. L.; Rinnert, H. 
Optical modelling of photoluminescence emitted by thin doped films. 
Thin Solid Films 2011, 519, 8003–8007.

(54) Vanheusden, K.; Seager, C. H.; Warren, W. L.; Tallant, D. R.; 
Voigt, J. A. Correlation between photoluminescence and oxygen 
 vacancies in ZnO phosphors. Appl. Phys. Lett. 1996, 68, 403–405.

(55) Lin, B.; Fu, Z.; Jia, Y. Green luminescent center in undoped 
zinc oxide films deposited on silicon substrates. Appl. Phys. Lett. 
2001, 79, 943–945.

(56) Chandrimou, C.; Boukos, N.; Stogiou, C.; Travlos, A. PL study 
of oxygen defect formation in ZnO nanorods. Microelectron. J. 2009, 
40, 296–298.

(57) Wu, X. L.; Siu, G. G.; Fu, C. L.; Ong, H. C. Photoluminescence 
and cathodoluminescence studies of stoichiometric and oxygen- 
deficient ZnO films. Appl. Phys. Lett. 2001, 78, 2285–2287.

(58) Ahn, C. H.; Kim, Y. Y.; Kim, D. C.; Mohanta, S. K.; Cho, H. K. A 
comparative analysis of deep level emission in ZnO layers deposited 
by various methods. J. Appl. Phys. 2009, 105, No. 013502.

(59) Fang, Z.; Wang, Y.; Xu, D.; Tan, Y.; Liu, X. Blue luminescent 
center in ZnO films deposited on silicon substrates. Opt. Mater. 
2004, 26, 239–242.

(60) Prucnal, S.; Wu, J.; Benèncin, Y.; Liedke, M. O.; Wagner, A.; 
Liu, F.; Wang, M.; Rebohle, L.; Zhou, S.; Cai, H.; Skorupa, W. 
Engineering of optical and electrical properties of ZnO by 
onequilibrium thermal processing: The role of zinc interstitials and zinc 
vacancies. J. Appl. Phys. 2017, 122, No. 035303.

(61) Bikowski, A.; Welzel, T.; Ellmer, K. The impact of negative 
 oxygen ion bombardment on electronic and structural properties of 
magnetron sputtered ZnO-Al films. Appl. Phys. Lett. 2013, 102, 
No. 242106.