A comparative study of substrate effects on the orientation-selective growth of epitaxial Mg$_{0.4}$Zn$_{0.6}$O thin films by pulsed laser deposition

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Abstract. Selective growth of single-oriented epitaxial Mg$_{0.4}$Zn$_{0.6}$O (MZO) films on LaAlO$_3$ (LAO) (001) and Al$_2$O$_3$ (0001) substrates were obtained by the pulsed laser deposition method. It was found that the orientation of the MZO films was determined at the initial deposition stage by the substrates orientation only. Highly (001)-oriented MZO films could be stabilized on the LAO (001) substrates, while (111)-oriented MZO films were shown on the Al$_2$O$_3$ (0001) substrates. X-ray diffractometer and transmission electron microscope characterizations exhibit excellent epitaxial relationships of (001) and (111) orientation of films on LAO and Al$_2$O$_3$ substrates, respectively. Under the present deposition conditions, the surfaces of MZO films with different single orientation were smooth and featureless.

1. Introduction

Oxide semiconductors have attracted considerable scientific and technological attention in last few years. The rich choice of oxides and their dopants provides a wealth of potentially useful electrical properties [1-3]. ZnO is a wide bandgap semiconductor and an ideal material for realizing room temperature excitonic devices [4, 5]. Recently, as an alternative to the group III nitride material system, the wide bandgap wurtzite ZnO ($E_{\text{gap}} \sim 3.37$ eV) [6, 7], cubic MgO ($E_{\text{gap}} \sim 7.50$ eV) [8] and their ternary alloy Mg$_x$Zn$_{1-x}$O are of substantial interest. The success in the wide band gap engineering of Mg$_x$Zn$_{1-x}$O to short wavelengths paves the way for heterostructure device applications, which may eventually compete with the group III nitrides [9-11]. Pulsed laser deposition method has revealed that pure ZnO wurtzite phase can be maintained at high MgO content of 33% [12]. For MgO content above 33% cubic phase segregation occurs and both cubic MgO and hexagonal ZnO coexist. At higher MgO content, only cubic phase is observed. Ohtomo et al [13] and others [14, 15] have grown high-quality, single-phase Mg$_x$Zn$_{1-x}$O thin films with Mg concentrations up to 33 at.% using PLD. All the above-mentioned Mg$_x$Zn$_{1-x}$O thin films possess hexagonal structure. Choopun et al [12] and Narayan et al [16] reported the growth of cubic Mg$_x$Zn$_{1-x}$O thin films grown by PLD with Mg composition x in the range of 0.50-0.86 and 0.82-1.00, respectively. However, the cubic MgO and hexagonal ZnO show phase separation after rapid thermal annealing.
In this study, we report the different orientation growth of Mg$_{0.4}$Zn$_{0.6}$O (MZO) films on cubic LaAlO$_3$ (LAO) (001) substrates and hexagonal Al$_2$O$_3$ (0001) substrates. MZO films grown from ablating MZO target have mixed phases in this stage. Its formation of (001) or (111) orientation could be induced by using LAO (001) or Al$_2$O$_3$ (0001) substrates with different crystal orientation. To the author’s knowledge, Mg$_x$Zn$_{1-x}$O mixed phase is reported for the first time by the real experiment technique. This provides templates to grow ZnO related compounds on different structure substrates with different orientations. It is particularly useful if one wants to study the phase transition in Mg$_x$Zn$_{1-x}$O series of films. The ZnO doping compounds may lead to devices with performance that supersedes those offered by group-III nitrides.

2. Experimental detail
Deposition of MZO films was carried out by PLD (KrF excimer laser, $\lambda$=248 nm, Lambda Physik, Complex 205, duration=10 Hz, laser energy=250 mJ) of a MZO ceramic target in a stainless steel chamber with base pressure of about 2 $\times$ 10$^{-5}$ torr. The target was prepared by sintering a pellet of ZnO (99.95% purity) and MgO (98% purity) powders with the conventional solid state reaction. Grinding, pressing, and sintering were repeated three times during the target preparation and the sintering temperature was progressively increased from 1100°C to 1400°C. Cubic LAO (001) substrates and hexagonal Al$_2$O$_3$ (0001) substrates cleaned by acetone were used and positioned parallel to and at a distance of about 45 mm from the target. The temperature was kept at 650°C during the depositions. After deposition, the films were annealed and then naturally cooled to room temperature. The deposition time for all samples was 30 min, resulting in films of about 350-500 nm thickness. The orientation and crystalline quality of films were measured by the $\theta$-2$\theta$ and $\omega$ scans of X-ray diffraction (XRD) with Cu-K$\alpha$ radiation and transmission electron microscope (TEM), which is carried out using a JEOL JEM-2011 transmission electron microscope operated at 200 kV. The morphology of the film surface was examined by scanning electron microscopy (SEM).

3. Results and discussion
The MZO target used for film deposition in this study is mixed-phase compound, as shown of its XRD pattern in figure 1. Apart from reflections that could be indexed according to the hexagonal ZnO phase, some reflections from the cubic MgO phase appeared. To create a reduced atmosphere for the growth of stoichiometric MZO compound, we used a multiphase target and the vacuum atmosphere (2 $\times$ 10$^{-5}$ torr) to deposit MZO films by the PLD technique.

Figure 1. XRD pattern of the air-sintered target from the mixture of stoichiometrical MZO composition.
Figure 2, 3 and 4 show XRD patterns including θ-2θ, ω and φ scans of a typical MZO film deposited at 650°C on LAO (001) and Al$_2$O$_3$ (0001) substrates. No impurity phases were recorded for the as-deposited films on different substrates although the target is not single phase. In figure 2(a) with 2θ range of 20° - 100°, we observed the peaks corresponding to (002) and (004) planes of MZO, (001), (002) and (003) planes of LAO. The 2θ peak of MZO (002) plane which equals to 42.6° with a full width at half maximum (FWHM) of 1.116° is coincided with the LAO substrate (002) CuK$_β$ peak with the FWHM equals to 0.297°. Some weak peaks due to the CuK$_β$ radiation were also indexed. This suggests that MZO film grows epitaxially on LAO substrate with preferred (001) orientation. Lattice parameter for MZO is determined to be 4.24Å. The inset shows close up view at 2 theta near 94°. The MZO (004) and LAO (004) CuK$_β$ diffractions are clearly discernable. In figure 2(b), strong reflections from MZO (111) and (222) diffraction planes appeared, we also observed the peaks corresponding to (0006) and (00012) planes of sapphire. It is shown that MZO grows epitaxially on sapphire with preferred (111) orientation. The Al$_2$O$_3$ substrate (0006) CuK$_β$ peak and (00012) CuK$_β$ peak were also indexed.

![Figure 2. XRD 2-theta scans of the (a) MZO/LAO(001) film (pressure: $3 \times 10^{-5}$ torr; temperature: 650 ° C). The inset shows the close up view of 2 theta at near 94° and (b) MZO/Al2O3(0001) film.](image-url)
Figure 3 show the XRD rocking curves on the MZO(004)/LAO(001) reflection and MZO (222)/Al₂O₃ (0001) reflection. The full width at half maximum (FWHM) of the curves are 1.0488° and 0.5441°, respectively, indicating good crystalline quality of the films. Note that the FWHM of the rocking curves on the LAO (003) reflection and Al₂O₃ (00012) reflection are 0.297° and 0.207°, respectively.

![Rocking curves on the (a) MZO(004)/LAO(001) diffraction plane and (b) MZO(222)/Al₂O₃(0001) diffraction plane.](image)

Figure 4(a) and (b) show x-ray φ scans on the MZO (220) and LAO (220) reflections and MZO (002) and Al₂O₃ (1002) reflections, respectively. It is clear from the clean four-fold symmetry diffraction profiles that a heteroepitaxial cubic MZO film has been grown on the LAO (001) substrate. There is however a 45° twist between the (0 01) MZO and (001) LAO planes. The LAO CuKβ(220) four-fold symmetry diffraction peaks are also detected when performing the φ scan of MZO film because MZO (220) and LAO CuKβ (220) planes possess quite similar 2 theta values. The epitaxy relationship between the MZO film and LAO substrate is (100) MZO||(100)LAO (out-of-plane) and (011) MZO||(010)LAO (in-plane). The heteroepitaxial MZO film is also obtained on Al₂O₃ (0001) substrate. It is noticed that the peaks are separated by 60° due to a six-fold symmetry in the diffraction profiles of MZO (002), while the peaks are separated by 120° due to a three-fold symmetry in the diffraction profiles of MZO (004) and LAO (001).
profiles of Al$_2$O$_3$ (1002). Also there is a 30° twist between the (002) MZO and (0001) Al$_2$O$_3$ planes. The epitaxy relationship is concluded to be (111)$_{\text{MZO}}$|| (0001)$_{\text{Al}_2\text{O}_3}$ (out-of-plane) and (002)$_{\text{MZO}}$|| (1002)$_{\text{Al}_2\text{O}_3}$ (in-plane). Detailed epitaxy relationship should be studied further with TEM images.

In order to get more precise information about the nature of the MZO/LAO and MZO/Al$_2$O$_3$ interfaces and the crystalline quality of the MZO films on both substrates we performed transmission electron microscopic investigation on this heterostructure. The bright-field cross-section TEM micrographs from the MZO/LAO(001) film and MZO/Al$_2$O$_3$(0001) film are shown in figure 5(a) and (c). For the film deposited on LAO substrate, crystal grains are alloy-like grown. Apparently the film at near the interface has higher density of defects than the film at near the surface. It is also seen that
there are regular dark patches in the LAO substrate along the interface boundary. All these are clear evidences of lattice mismatch induced straining on the film and substrate. For the film deposited on sapphire, typical columnar crystal grains fabricated by PLD vertical to the substrate could be obtained and the top of the column is very flat. The corresponding selected area electron diffraction (SAED) patterns of these two films at region near the film/substrate interface are shown in figure 5(b) and (d). These patterns contain diffraction spots corresponding to the epitaxial MZO films with LAO and sapphire substrates, respectively. The results confirm the epitaxial relationships obtained from X-ray diffraction.

Figure 5. Cross-section TEM micrographs of (a) MZO/LAO(001) film and (c) MZO/Al2O3(0001) film and corresponding SAED patterns at region near the film/substrate interface of (b) MZO/LAO(001) film and (d) MZO/Al2O3(0001) film.

SEM photographs of cross section of these two kinds of oriented films on LAO and sapphire substrates are shown in figure 6. The surfaces of the MZO films grown at the vacuum atmosphere are reasonably smooth, and the surfaces of these orientated films remained featureless at magnifications up to 50000. In particular, there were no large droplets or particulates that are common in PLD deposited films. The cross-section morphology reveals sharp boundary and layer thickness is about 350-500 nm. Also, from the pictures, we know that the MZO/LAO film has a larger average roughness than that of the MZO/Al2O3 film. Substrate factor is the only reason to interpret this phenomenon.
Figure 6. Scanning electron micrograph of cross section of the (a) MZO/LAO(001) film and (b) MZO/Al₂O₃(0001) film.

4. Conclusion
Single-oriented epitaxial cubic MZO films were prepared on LAO (001) and Al₂O₃ (0001) substrates by the PLD technique. All films were smooth and no large of droplets. The film on the LAO substrate has a larger average roughness than that of the film on the Al₂O₃ substrate. It was found that the orientation selection is controlled at the initial stage of deposition and the growth orientation is solely determined by the substrates orientation. Heteroepitaxial relationship of (100)ₘₙₐₜₐ₉ || (100)ₖₜₐₘₜₔₜ (out-of-plane) and (011)ₘₙₐₜₐ₉ || (010)ₖₜₐₘₜₔₜ (in-plane) can be realized on LAO substrate. (111)ₘₙₐₜₐ₉ || (0001)ₖₜₐₘₜₔₜ (out-of-plane) and (002)ₘₙₐₜₐ₉ || (1002)ₖₜₐₘₜₔₜ (in-plane) relationship could be induced by using of Al₂O₃ (0001) substrate. The cross-section morphology reveals layer thickness of about 350-500 nm.

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