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Epitaxial growth of high quality cubic MgZnO films on MgO substrate

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ABSTRACT

Epitaxial growth of cubic $Mg_{0.33}Zn_{0.67}O$ films on MgO (1 0 0) substrate by metalorganic chemical vapor deposition (MOCVD) was reported. X-ray diffraction (XRD) ω-scans and ϕ-scans demonstrate the films exhibit single (2 0 0) orientation and highly uniform in-plane orientation with four-fold symmetry. The epitaxial relationship between the layer and substrate is MgZnO (1 0 0)//MgO (1 0 0). Smooth surface with the rms roughness of 1.8 nm in 5×5 μm area is obtained. Atomic force microscopy (AFM) reveals formation of islands attributed to the strain in the epitaxial MgZnO films. These results demonstrate the high quality single crystal $Mg_{0.33}Zn_{0.67}O$ films and their potential in high-performance deep ultraviolet optoelectronic devices.

1. Introduction

ZnO and its ternary MgZnO have been received as important wide band gap semiconductor materials for their applications in ultraviolet optoelectronic devices such as LEDs, LDs and photodetectors due to their large exciton binding energy (60 meV for ZnO and 85 meV for MgO) [1–5]. With the Mg composition increasing, the MgZnO alloy transforms from hexagonal ZnO structure to cubic MgO structure, with the band gap covering a wide energy range (3.3–7.8 eV) [6]. Compared with the hexagonal MgZnO, decreased phonon scattering, and hence higher ballistic electron velocities, is expected in cubic MgZnO due to its higher structure symmetry. This enables the cubic MgZnO a potential candidate in deep ultraviolet (<300 nm) optoelectronic device applications. Many authors have reported the cubic MgZnO based photodetectors work in deep ultraviolet, especially, solar blind region [7–9].

Most of the cubic MgZnO films currently reported were grown on sapphire and Si substrate [10–12]. In previous reports, we prepared the $Mg_{0.5}Zn_{0.5}O$ films on sapphire at a relatively low temperature of 450 °C by MOCVD [8]. However, due to the large lattice mismatch and thermal mismatch between the MgZnO layers and substrates, rough surface morphology with (1 1 1) or (1 0 0) facets was always obtained as demonstrated by experiments and the crystal quality of the cubic MgZnO films was limited. Rough surface leads to high density of surface traps in the devices, which is unfavorable for the improvement of the device performance and achievement of photodetector arrays. Yang et al. [13] reported the hetero-epitaxy of cubic MgZnO films on $SrTiO_3$/Si template with high quality by the pulse laser deposition (PLD) technique. The capability to produce superior material quality by epitaxial growth on homogeneous substrate has been accepted widely. However, there are few reports on the growth of cubic MgZnO films on MgO substrate [14].

In this letter, high quality single crystal cubic $Mg_{0.33}Zn_{0.67}O$ films were epitaxially grown on MgO (1 0 0) substrate by MOCVD. XRD results demonstrate the single (2 0 0) orientation and uniform in-plane orientation of the films. A smooth surface is obtained from AFM results.

2. Experimental procedure

The MgZnO films were deposited on polished MgO (1 0 0) substrate in a LP-MOCVD system. Dimethyl dicyclopentadienyl magnesium (MCp2Mg), diethyl zinc (DEZn) and high pure oxygen (O_2) (99.999%) were employed as the precursors. High purity (99.999%) nitrogen was used as a carrier gas to lead the precursors into the growth chamber. The deposition temperature was kept at 450 °C and the chamber pressure at 150 Torr during the growth process. The growth procedure is consisting of two steps. Firstly, a thin MgZnO buffer layer was deposited on MgO substrate with the

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Zn and Mg molar flow rate controlled at 2.4 and 18 μmol/min, respectively, for 15 min and the thickness was about 10 nm from the SEM section images. Secondly, the Zn and Mg molar flow rate was controlled at 3 and 18 μmol/min, respectively, with other conditions unchanged. The total thickness of thin film is about 400 nm. The schematic figure of the films' structure is shown in Fig. 1.

The transmission spectrum of the MgZnO films was recorded using a Shimadzu UV-3101PC scanning spectrophotometer. The composition of the MgZnO thin films was measured by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250). The structure characterization was carried out in D/max-RA X-ray diffraction (XRD) (Rigaku) with Cu Kα 0.154 nm line as the radiation source and double crystal Bruker D8 GADDS X-ray diffractometer with area detector. The surface morphology was investigated by atomic force microscopy (AFM).

3. Results and discussion

The composition in the MgZnO films was determined to be $Mg_{0.33}Zn_{0.67}O$ from the XPS results. The crystal structure and quality of the MgZnO films was analyzed by XRD and X-ray rocking curve (XRC) measurements. In Fig. 2, the diffraction peak at 42.48° is corresponding to the (2 0 0) orientation of the MgZnO films, besides the diffraction peak at 43.04° for MgO (2 0 0) substrate. No other peaks were detected from the spectrum. This indicates the single orientation of the cubic MgZnO films. The full width at half maximum (FWHM) of the MgZnO (2 0 0) diffraction peak is 0.13° from the Gaussion fit of the curve. The narrow width indicates the high crystal quality of the MgZnO films. The double crystal rocking curve of MgZnO (2 0 0) and MgO (2 0 0) was also performed and was shown in the inset of Fig. 2. Due to the thickness contrast of the layers and substrate, the MgZnO (2 0 0) diffraction intensity is rather low compared with that for the MgO substrate. The symmetric Gaussion curve for MgZnO (2 0 0) peak indicates the high quality of the films.

To determine the in-plane orientation of the MgZnO films and its lattice correlation with the substrate, double-crystal XRD ϕ-scans of MgZnO and MgO (2 2 0) reflections were carried out at χ=45° (which is the angle between the (1 0 0) and (1 1 0) planes in a cubic system) from 0° to 360°. The (2 2 0) peaks' position for MgZnO and MgO was at 61.7° and 62.3°, respectively. As seen in Fig. 3, four sharp (2 2 0) diffraction peaks can be seen clearly with 90° apart for both MgZnO and MgO. This indicates the four-fold symmetry for the MgZnO films with (2 0 0) orientation in the cubic system. The FWHM of (2 2 0) diffraction peak is 0.40° for the MgZnO layers, which indicates the highly uniform in-plane orientation in MgZnO films. This value is comparable with that for the MgO substrate (0.22°). The above results indicate that the achievement of high quality single crystal cubic MgZnO films. In addition, it can be seen that the angular positions of the ϕ-scan (2 2 0) peaks due to the films and the substrate overlapping one another. This confirms the MgZnO and MgO follow cube-on-cube alignment with the epitaxial relationship of MgZnO (1 0 0)//MgO (1 0 0). This is the first report on the epitaxial growth of MgZnO films on MgO substrate by the MOCVD technique.

The Zn content in the grown MgZnO films (67%) is much higher than that of the Hullavarad's report ($Mg_{0.9}Zn_{0.1}O$ films by PLD) [14]. This may be attributed to the low growth temperature (450 °C). In early reports, high Zn content $Mg_{0.48}Zn_{0.52}O$ films have been achieved on the sapphire substrate [9]. The low substrate temperature can reduce the diffusion rate of the atoms

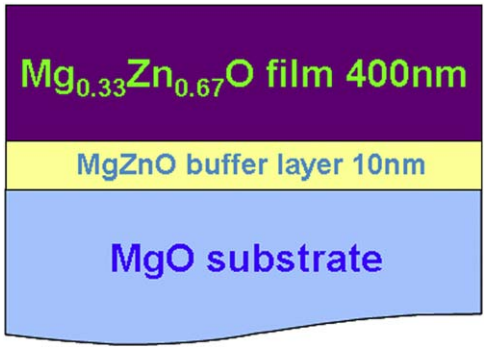

Fig. 1. The schematic structure of the $Mg_{0.33}Zn_{0.67}O$ films grown on MgO substrate.

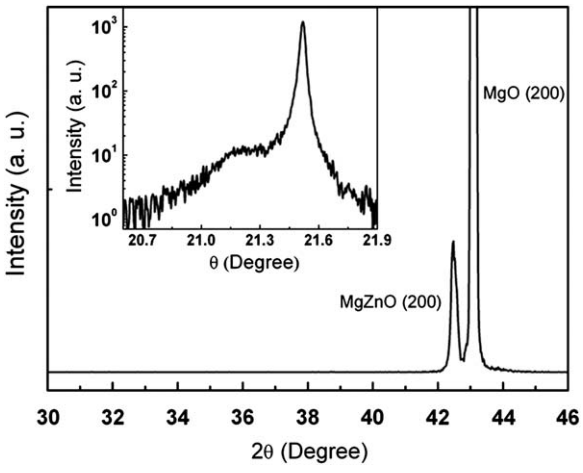

Fig. 2. XRD spectrum for the MgZnO films on MgO substrate. The inset is a rocking curve of (2 0 0) reflection ω-scans.

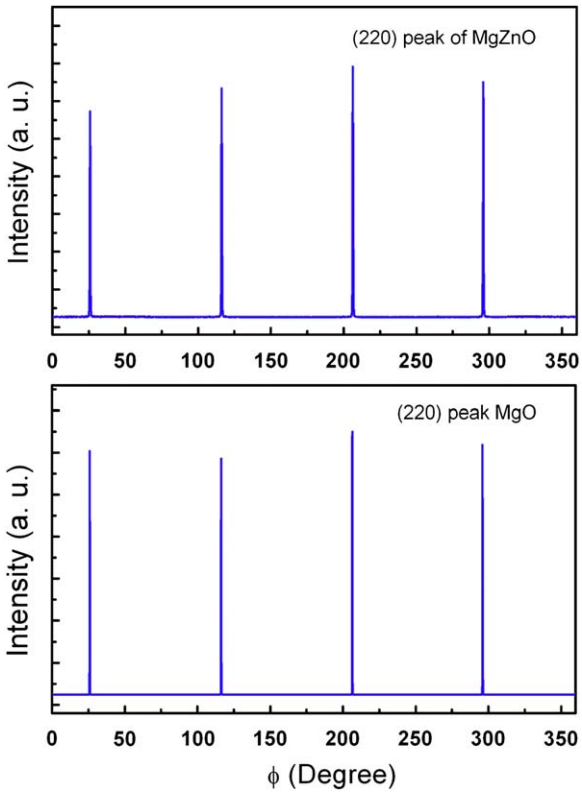

Fig. 3. XRD ϕ-scans of (2 2 0) reflections for MgZnO layers and MgO substrate.

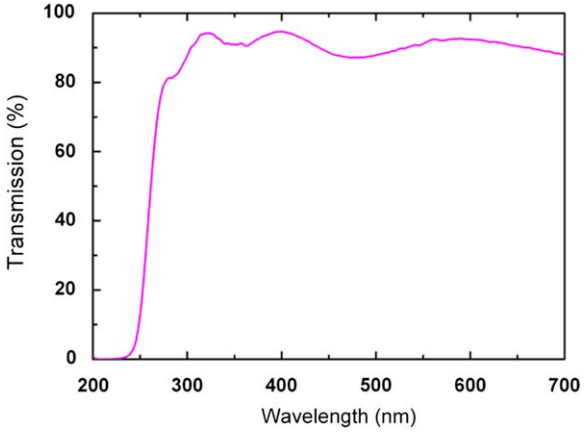

Fig. 4. Transmission spectrum of the $Mg_{0.33}Zn_{0.67}O$ films.

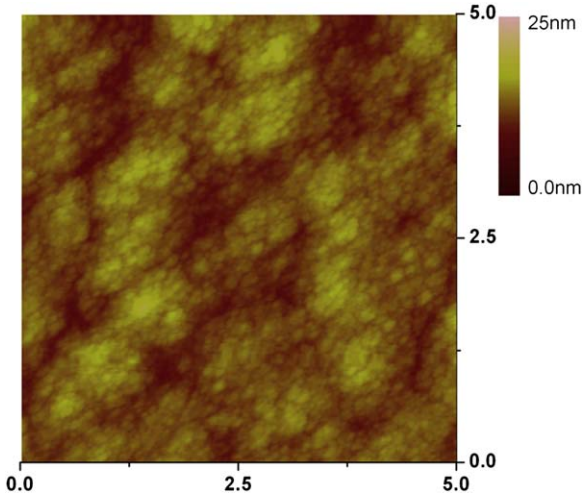

Fig. 5. AFM image of the $Mg_{0.33}Zn_{0.67}O$ films in 5×5 μm area.

on the substrate surface during the growth, and the metastable phase MgZnO films with high Zn content can be obtained.

The transmission spectrum of the MgZnO films is shown in Fig. 4. From the spectrum, the absorption edge of the cubic MgZnO films located at around 250 nm corresponds to the optical band gap energy of ~4.96 eV. The transmission rate at visible range and UVA region (320–400 nm) is higher than 80%, which indicates the good optical quality of the films. This indicates the as grown MgZnO films are potential in solar blind photodetectors.

The surface morphology of the MgZnO films was examined by SEM and AFM. The films show highly smooth surface from SEM results (not shown). As seen in Fig. 5, the rms roughness of the films' surface is 1.8 nm in 5×5 μm area, which demonstrates the high crystal quality of the films. The situation is different from the (1 1 1) orientated MgZnO films on *c*-sapphire substrate, which shows large cubes with (1 0 0) facet on the surface. In addition, large islands are distributed randomly with a scale of 500 nm in average. From the XRD results, lattice mismatch between the MgO substrate and $Mg_{0.33}Zn_{0.67}O$ films is existed (1.3%) and it would bring strain into the epitaxial films. Lattice mismatch strain commonly leads to Stranski–Krastanov (SK) growth, during which adatoms are initially deposited in the form of a two-dimensional (2D) pseudomorphic layer, and elastic strain energy that increases with the layer thickness is finally relieved by the formation of islands [15,16]. It is believed the formation of the islands is attributed to the lattice strain exist in the MgZnO films.

4. Conclusions

In conclusion, the cubic $Mg_{0.33}Zn_{0.67}O$ films were epitaxially grown on MgO (1 0 0) substrate by MOCVD. The films exhibit single (2 0 0) orientation from XRD results. XRD ϕ-scans indicate the highly uniform in-plane orientation and four-fold symmetry in MgZnO films. The epitaxial relationship between the layer and substrate is MgZnO (1 0 0)//MgO (1 0 0). Smooth surface with the rms roughness of 1.8 nm in 5×5 μm area is obtained. The absorption edge of the cubic MgZnO films is located at around 250 nm. AFM reveals formation of islands attributed to the strain in the epitaxial MgZnO films. These results demonstrate the high quality single crystal $Mg_{0.33}Zn_{0.67}O$ films on MgO substrate and their potential in deep ultraviolet optoelectronic devices.

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