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Epitaxial growth of superlattice $YbGaO_3(ZnO)_5$ and $InGaO_3(ZnO)_5$ films by the combination of sputtering and reactive solid phase epitaxy

Hou-Guang Chen *, Yung-Shiang Lin

Department of Materials Science and Engineering, I-Shou University, Kaohsiung 840, Taiwan

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ABSTRACT

This article describes the epitaxial growth of superlattice $YbGaO_3(ZnO)_5$ (YGZO) and $InGaO_3(ZnO)_5$ (IGZO) thin films, which feature nanoscale multilayered structures, on (111) plane yttria-stabilized zirconia (YSZ) substrates through a combination of sputtering and reactive solid phase epitaxy processes. Our fabrication process involved thin ZnO epilayers deposited through sputtering onto the YSZ substrates, and then $YbGaO_3(ZnO)_5$ or $InGaO_3(ZnO)_5$ thin films deposited at room temperature on ZnO epi-layers, followed by high-temperature annealing (1200 °C) of the bilayer structures. To suppress vaporization of ZnO from the films, high-temperature annealing was performed in a box made of ceramic ZnO. We used X-ray diffraction and transmission electron microscopy (TEM) to analyze the thin films annealed under various conditions. The microstructural evolution in the film formed during reactive solid phase epitaxy process was explored by TEM observations. Single-crystalline YGZO and IGZO thin films without varying composition could be synthesized through a suitable annealing process in the ceramic ZnO box.

1. Introduction

Homologous oxides having the general formula $RAO_3(MO)_m$ (R = Sc, Yb, Lu, In; A = Ga, Al, Fe, In; M = Zn, Mg; m = integer) are attracting increasing attention because their crystal structures feature alternating stacks of RO_2^- layers and $AO(MO)_m^+$ blocks, forming periodic layered structures along the [0001] direction. The space group of these $RAO_3(MO)_m$ systems is assigned as $R\bar{3}m$ (for odd values of m) or $P6_3/mmc$ (for even values of m), with the width of the $AO(MO)_m^+$ block being directly dependent on the value of m [1]. Such self-organized nanoscale layered structures, which can exhibit spatial confinement of charged carriers [2], can be regarded as superlattices or quantum wells; they can possess fascinating optoelectronic, electrical, thermoelectric, and spintronic properties [3–6]. The growth of single-crystalline $RAO_3(MO)_m$ oxide thin films is, however, essential for us to understand the fundamental physical phenomena exhibited by these compounds. Indeed, the growth and characterization of various $RAO_3(MO)_m$ epilayers have been studied by several groups [3,6,7]. Ohashi et al. employed self-buffer-epitaxy to form $In_2O_3(ZnO)_5$ thin films; highly crystalline $In_2O_3(ZnO)_5$ epilayers were obtained after post-annealing treatment [6]. Hosono et al. reported that high-quality epitaxial $InGaO_3(ZnO)_5$ thin films, exhibiting superior electrical properties, could be prepared through a combination of pulsed laser deposition (PLD) and reactive solid phase epitaxy (R-SPE) techniques [8]. Recently, Seo et al. demonstrated single-crystalline $InGaO_3(ZnO)_m$ thin films with periodic superlattice structure adequate to the transparent thermoelectric application [3,4].

In this study, we attempted to synthesize two types of single-crystalline homologous oxide films with chemical formula of $YbGaO_3(ZnO)_5$ (YGZO) and $InGaO_3(ZnO)_5$ (IGZO) through a combination of sputtering deposition and R-SPE processing. In comparison with PLD systems, sputtering deposition is relatively cost-effective and allows large-area deposition. Herein, a modified R-SPE process to suppress evaporation of the constituent elements having high vapor pressure during high-temperature thermal treatment was devised. We then used X-ray diffraction (XRD) and transmission electron microscopy (TEM) to study the growth mechanism of the epitaxial YGZO and IGZO thin films prepared through R-SPE processing.

2. Experimental procedure

Both YGZO and IGZO thin films were fabricated by combining radio-frequency sputtering deposition and R-SPE treatment on (111) plane yttria-stabilized zirconia (YSZ) substrates. The $YbGaO_3(ZnO)_5$ and $InGaO_3(ZnO)_5$ ceramic targets were prepared from Yb_2O_3, In_2O_3, Ga_2O_3, and ZnO powders. The mixed powder was dry-pressed and then sintered at 1350 °C for 12 h to obtain $YbGaO_3(ZnO)_5$ (JCPDS No. 40-1351) and $InGaO_3(ZnO)_5$ (JCPDS No. 40-0255) ceramic disks, which were examined using powder XRD [Fig. 1(a–b)]. Upon the

* Corresponding author. Tel.: +886 7 6577711x3113; fax: +886 7 6578444.
E-mail address: houguang@isu.edu.tw (H.-G. Chen).

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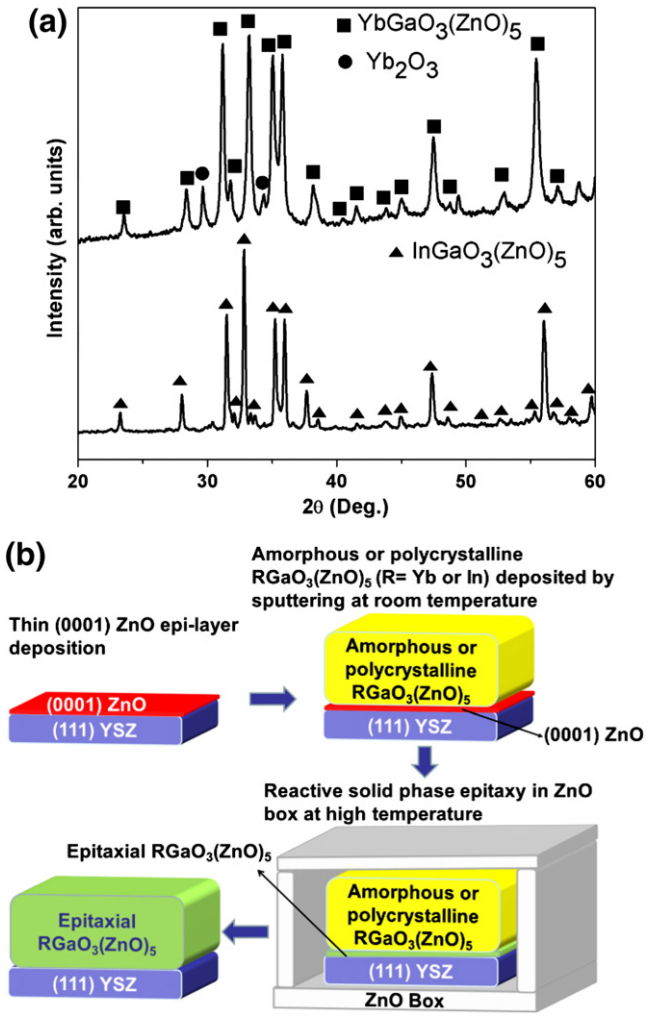

Fig. 1. (a) Powder XRD pattern of the $YbGaO_3(ZnO)_5$ and $InGaO_3(ZnO)_5$ ceramic target, revealing a small amount of the Yb_2O_3 phase in $YbGaO_3(ZnO)_5$ target. (b) Schematic representation of the $RAO_3(ZnO)_5$ (R = Yb and In) epitaxial films formed using the modified R-SPE process.

powder XRD pattern, the $YbGaO_3(ZnO)_5$ target contained a small amount of the Yb_2O_3 phase. Prior to R-SPE processing, a thin ZnO epitaxial layer (thickness: ca. 20 nm) was sputtered on the YSZ substrate at 500 °C for use as a seed layer for the solid phase epitaxy reaction. Next, an amorphous or polycrystalline YGZO or IGZO thin film was deposited at room temperature on the epitaxial ZnO seed layer, respectively. Finally, R-SPE was performed through post-annealing at 1200 °C for various durations. To compensate for the evaporation of zinc from the deposited film, the bilayer samples were introduced into a box made of ceramic ZnO during high-temperature R-SPE treatment. The formation of YGZO or IGZO films through this modified R-SPE process is illustrated schematically in Fig. 1(b).

Crystalline characteristics of YGZO or IGZO epitaxial films were investigated by X-ray diffraction (XRD, Philips X'Pert diffractometer with a Cu K_α radiation source). The diffractometer was equipped with a mirror and a two-bounce Ge(220) channel-cut monochromator. Phase identification was done by XRD in a Bragg–Brentano geometry ($2\theta/\omega$-scan). The mosaicity of the film was evaluated by symmetric on-axis X-ray diffraction rocking curve (XRC) measurements (ω-scan). Cross-sectional transmission electron microscopy (XTEM) was performed using a Philips Tecnai 20 microscope operated at 200 kV. The XTEM specimen was prepared by focused ion beam technique (FIB, SII NanoTech. SMI 3050). Optical transmission spectra were obtained by a JASCO V-670 double beam UV–vis–NIR spectrometer.

3. Results and discussion

Fig. 2(a) presents XRD $2\theta/\omega$-scan data for YGZO and IGZO thin films formed on YSZ substrates under various R-SPE conditions. In the XRD $2\theta/\omega$-scan spectrum generated from YGZO thin film annealed at 1200 °C for 30 min (sample A), we detect intense 000*l* reflections for $YbGaO_3(ZnO)_5$ along with YSZ (111) diffraction, indicating that the YGZO thin films featured a *c*-axis-preferred orientation. In addition, an unknown peak at a value of 2θ of 35.6°, labeled with an asterisk, appeared in the spectrum of sample A. This unknown peak might have been contributed by the $(10\underline{\bar{1}}\underline{1})$ plane, herein the fourth index which is a two-digit number is underlined, of $YbGaO_3(ZnO)_5$ ($2\theta = 35.7°$) or another $YbGaO_3(ZnO)_m$ phase having a different value of *m*. This unknown peak cannot be indexed simply based on JCPDS cards, because the diffraction peaks of $YbGaO_3(ZnO)_m$ systems having various values of *m* are quite complex and have many similar peak positions. Remarkably, the XRD pattern of the YGZO film annealed at 1200 °C for 60 min (sample B) featured more-intense diffraction peaks corresponding to 000*l* reflections with a constant separation of $\Delta(2\theta)$ of approximately 4.7°. Such

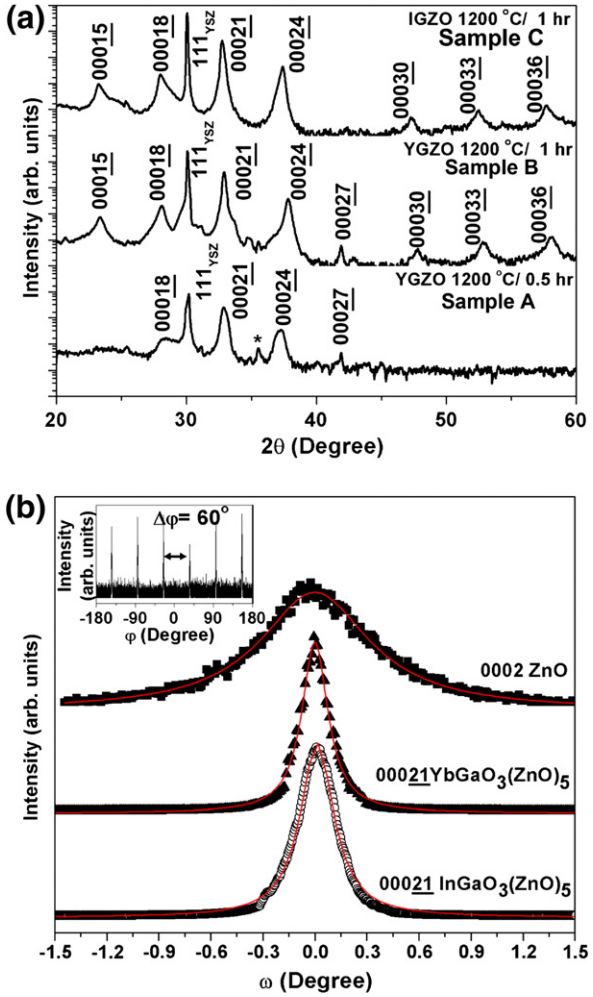

Fig. 2. (a) XRD $2\theta/\omega$-scan patterns of YGZO and IGZO films formed on YSZ substrates under various R-SPE conditions. (b) Symmetric on-axis XRC profiles for the 0002$\underline{1}$ reflection of the YGZO (sample B) and IGZO (sample C) films, and the ZnO 0002 XRC for an epitaxial ZnO film deposited on the YSZ substrate. Insets show the corresponding XRD φ-scan spectrum of ZnO $11\bar{2}2$ reflection.