Materials Research Bulletin 48 (2013) 1316–1320

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

Epitaxy of Zn_2TiO_4 (1 1 1) thin films on GaN (0 0 1)

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ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 8 November 2012
Accepted 12 November 2012
Available online 5 December 2012

Keywords:
A. Thin films
B. Sputtering
C. Electron microscopy
D. Electrical properties

ABSTRACT

High-permittivity spinel Zn_2TiO_4 thin films were grown on GaN (0 0 1) by rf-sputtering. Grazing-angle, powder, and pole-figure X-ray diffractometries (XRD) were performed to identify the crystallinity and the preferred orientation of the Zn_2TiO_4 films. Lattice image at the Zn_2TiO_4 (1 1 1)/GaN (0 0 1) interface was obtained by high-resolution transmission-electron microscopy (HR-TEM). An oxygen atmosphere in sputtering and post heat-treatment using rapid thermal annealing effectively enhanced the epitaxy. The epitaxial relationship was determined from the XRD and HR-TEM results: $(1\,1\,1)_{Zn_2TiO_4}||(0\,0\,1)_{GaN}$, $(2\,0\,\bar{2})_{Zn_2TiO_4}||(1\,1\,0)_{GaN}$, and $[2\,\bar{1}\,\bar{1}]_{Zn_2TiO_4}||[0\,\bar{1}\,1\,0]_{GaN}$. Finally, the relative permittivity, interfacial trap density and the flat-band voltage of the Zn_2TiO_4 based capacitor were ~18.9, 8.38×10^{11} eV^{-1} cm^{-2}, and 1.1 V, respectively, indicating the potential applications of the Zn_2TiO_4 thin film to the GaN-based metal-oxide-semiconductor capacitor.

1. Introduction

The pursuit of high-permittivity gate oxides for use in GaN-based metal-semiconductor field-effect-transistors (MES-FETs), hetero-junction FETs (HFETs), and high-electron-mobility transistors (HEMTs) has attracted great attention in the past few years [1,2]. However, several factors have limited the progress. For example, a poor Schottky contact is formed when metal comes into direct contact with the semiconductor directly, generating a leakage current. Metal-oxide-semiconductor FETs (MOS-FETs) and MOS-HFETs have reportedly been formed by introducing a thin oxide or nitride layer, such as AlN, Ga_2O_3, SiO_2, Si_3N_4, Al_2O_3, HfO_2, MgO, or Ta_2O_5 to overcome the leakage problem [3–9]. However, most studies of high-k layers for GaN-based MOS have focused on the deposition of few metal oxides [1–10], ignoring the fact that many ceramic materials have such advantages as high dielectric constant, high thermal stability, and low dielectric loss. Previously, we demonstrated epitaxial ilmenite $MgTiO_3$ as an excellent gate oxide for GaN-based MOS applications. The dielectric constant and interfacial trap density were ~17.8 and 6×10^{12} cm^{-2} eV^{-1}, respectively [11]. Similarly, spinel, which consists of face-centered cubic oxygen and cations that occupy octahedral or tetrahedral sites, can also grow epitaxially on GaN. The close-packed oxygen plane in spinel should have some epitaxial relationship with GaN (0 0 1) as it does at the ilmenite/GaN interface.

Zn_2TiO_4 is an inverse spinel that has been utilized in various applications, including sensors, pigment, catalyst, and microwave dielectrics [12,13]. This work investigates the epitaxy of zinc titanate (Zn_2TiO_4) and the use as a gate oxide of a GaN-based MOS capacitor. X-ray diffraction (XRD) and high-resolution transmission electron microscopy were used to determine the preferred orientation, crystallinity, and epitaxy relationship of the Zn_2TiO_4 films. Finally, the dielectric properties of the Zn_2TiO_4/GaN-based capacitor were investigated.

2. Experimental

High-purity ZnO (J.T. Baker) and TiO_2 (>99.9%; Showa Chemical Industry Co. Ltd.) powders were used as the starting materials in the preparation of an Zn_2TiO_4 target by solid-state sintering. The two powders were mixed, ball-milled for 24 h, sieved, and calcined at 1100 °C for 2 h. After the calcination, the ceramic was grounded and pressed into a 3 inch disc before it was sintered at 1150 °C for 4 h. The sintered compact had a density of >90%. The molar ratio of $ZnO/TiO_2 = 2/1$ was well-controlled, yielding a target of pure Zn_2TiO_4 in the absence of second phases.

Sputtering was conducted at an rf-power of 125 W and a working pressure of 2×10^{-3} torr following pre-sputtering for 15 min. Pure argon or mixed argon/oxygen (5 sccm/5 sccm) gases were separately introduced to the vacuum chamber for sputtering. All of the films were deposited at room temperature. The Zn_2TiO_4 thin film was ~30 nm-thick. The n-type GaN was grown on

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http://dx.doi.org/10.1016/j.materresbull.2012.11.066

(0 0 0 1) sapphire with a thickness of ~4 μm and a doping concentration of 1×10^{18} cm^{-3}. The films were post-annealed by either conventional furnace or rapid thermal annealing (RTA) in forming gas (5% H_2 + 95% N_2) and pure N_2, respectively. The structure and the orientation of the Zn_2TiO_4 thin films were characterized by X-ray diffractometry (XRD) using θ–2θ, Grazing angle (Siemens/D5000) and pole figure (Rigaku D/MAX2500) methods. An Al gate electrode was formed by thermal evaporation. High-resolution transmission-electron microscopy (HR-TEM, JEOL/JEM-2100) was used to obtain lattice image at the interface between GaN and Zn_2TiO_4. The electrical properties of the fabricated MOS capacitors were determined by measuring high-frequency capacitance–voltage (*C*–*V*) curves using an Agilent E4980A impedance analyzer.

3. Results and discussion

Fig. 1 plots the atomic stacking sequence and epitaxial relationship between Zn_2TiO_4 (1 1 1) and GaN (0 0 1). The plot is based on the fact that the oxygen in Zn_2TiO_4 (1 1 1) and Ga (or N) in GaN (0 0 1) have the same symmetry and small lattice mismatch (Fig. 1(b)). Therefore, the lattice constant of Zn_2TiO_4 is estimated to be 6% smaller than that of GaN (Fig. 1(a)). Fig. 2(a) shows the θ–2θ XRD patterns of the Zn_2TiO_4 films that were post-annealed at several temperatures by RTA (600–800 °C held for 3 min) and furnace annealing (800 °C, 1 h). The (1 1 1)-preferring orientation of the samples increased with RTA temperature. Moreover, samples that were treated by RTA had a stronger tendency to have a (1 1 1) texture than those treated in a furnace at the same

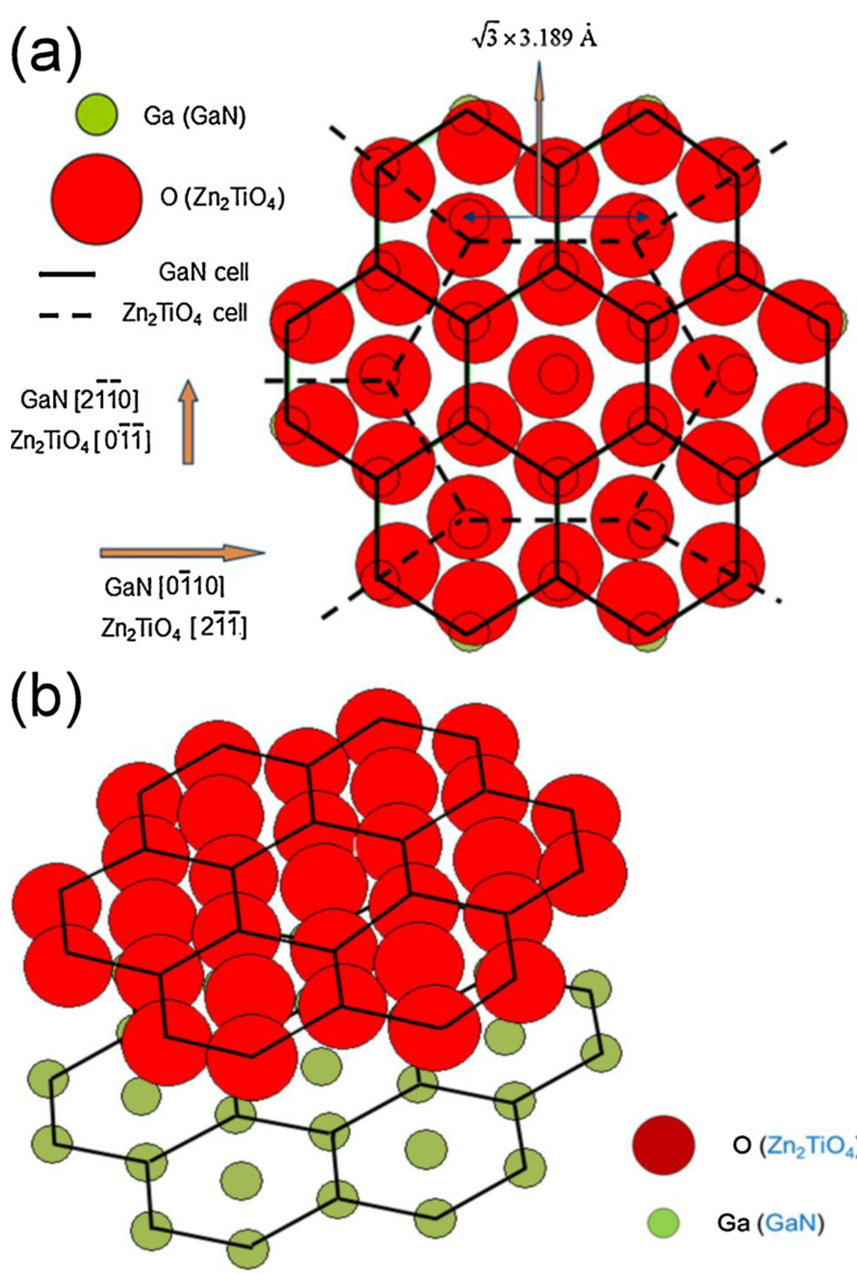

Fig. 1. Epitaxial relationship in Zn_2TiO_4 (1 1 1)/GaN (0 0 1) interface.