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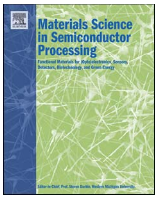

Study on thermal solid-phase crystallization of amorphous ZnO thin films stacked on vanadium-doped ZnO films

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ABSTRACT

Thermal solid-phase crystallization (SPC) of an amorphous ZnO film stacked on a vanadium-doped ZnO (VZO) film was investigated. ZnO films were deposited on 30-nm-thick amorphous VZO films on c-face sapphire substrates at room temperature by RF magnetron sputtering. Stacked film was subsequently calcined at 800 °C in a nitrogen atmosphere. ZnO film grew in an amorphous state up to about 150-nm thick on the amorphous VZO film, but self-orientation occurred in a thicker layer. Any secondary phase such as Zn_2VO_4 was not formed in the case of total film thickness (t_{total}) ≥100 nm. V concentration decreased by thermal diffusion of V through the ZnO layer from the VZO film, and thereby the formation of secondary phase was effectively avoided. The amorphous ZnO layer was crystallized from highly-aligned initial thin layer of VZO film when t_{total} ≤200 nm and crystal orientation of the stacked film was superior to single VZO film. However, the c-axis orientation was deteriorated drastically at t_{total} ≈400 nm due to SPC affected by the tilted regions existed in the as-deposited ZnO film. Therefore, it is suggested that careful selection of ZnO film thickness is necessary to obtain the high-quality ZnO films in this method.

1. Introduction

Zinc oxide (ZnO) is a fascinating material for optoelectronic devices such as ultraviolet light-emitting diodes, laser diodes, and solar cells [1–3] because of its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) [4,5]. However, the heteroepitaxial growth of high-quality ZnO thin films on lattice-mismatched substrates like sapphire and silicon has been difficult, so it was hard to bring out unique features of ZnO. Various buffer layers have been investigated to obtain high-quality ZnO films [6–8], and solid-phase crystallization (SPC) from an amorphous phase has been extensively studied as an effective method for fabricating the high-quality films [9,10]. SPC of ZnO film has not been much reported because it was difficult to fabricate an amorphous ZnO film. However, the amorphization of ZnO film was recently achieved by nitrogen doping, and its SPC by calcination on a-plane sapphire [$Al_2O_3(110)$] and quartz substrates were reported [11–13]. It was further demonstrated that the SPC-ZnO thin film has a possibility to be applied as a buffer layer to grow high-quality ZnO films.

In our previous studies, a vanadium-doped ZnO (VZO) thin film with low resistivity and good visible-light transmittance by controlling V concentration was obtained [14]. Furthermore, it was found that vanadium (V) atoms are likely to act to retard the nucleation of ZnO [15] and a pseudo-amorphous VZO film with initial thin oriented layer was able to fabricate at room temperature (RT) under the condition of V concentration of about 4 at% on a c-face sapphire [$Al_2O_3(001)$] substrate [16]. Thereby, a SPC-VZO film has a possibility to become a highly-oriented conductive ZnO film. This is an attractive advantage in comparison to the similar approaches like nitrogen-mediated SPC. Although the amorphous layer started to crystallize from the initial oriented layer by calcination, secondary phase such as Zn_2VO_4 was formed due to the high V concentration and it deteriorated crystal quality of VZO. Here is a dilemma [17].

In this study, SPC of the amorphous ZnO film stacked on amorphous VZO film was investigated in order to suppress the formation of secondary phase by decreasing the V concentration in the whole film through the thermal diffusion of V atoms. ZnO layer up to about 150-nm thick was able to grow in amorphous state on 30-nm-thick amorphous VZO film, but tilted regions started to grow when the ZnO thickness became over about 150 nm. This caused the deterioration of crystal quality at total film thickness (t_{total}) ≈400 nm, although secondary phase was not formed in calcined ZnO/VZO film at t_{total} over

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about 100 nm.

2. Preparation of stacked ZnO/VZO film and evaluations

The stacked ZnO/VZO film was deposited on c-face sapphire substrates at RT by RF magnetron sputtering (Ar atmosphere: 1.0 Pa, RF power: 150 W). The target-to-substrate distance was fixed at 60 mm. A ZnO ceramic target (99.99% purity) was used with V chips (99.9% purity) placed on an erosion area. The V concentration of VZO was controlled to be about 4 at% by the number of V chips, and was estimated by X-ray fluorescence analysis (XRF, Rigaku RIX2100) using Rh radiation. ZnO film thickness in ZnO/VZO film (t_{ZnO}) varied from 20 to 370 nm whereas VZO film thickness was fixed to 30 nm. Film thickness was measured by a step profiler (Kosaka Laboratory Ltd. ST4000 M).

The stacked films were calcined by lamp heating for 5 min at 800 °C in a nitrogen atmosphere (99.9995% purity) for SPC. The crystal orientation was evaluated by X-ray diffraction (XRD, Rigaku SmartLab) using Cu radiation. The X-ray source was operated at a power of 40 kV×30 mA. The surface morphology was measured by atomic force microscopy (AFM, Asylum Research Cypher ES). The depth profile was measured by secondary ion mass spectrometry (SIMS, CAMECA IMS-7 f) with O^+ as the primary ion and a beam current of 20 or 50 nA. Neutralizer was not used in order to avoid the influence on signals of observation atoms from films.

3. Experimental results and discussions

3.1. Amorphization of ZnO film on VZO film

The in-plane XRD ϕ-scan patterns from ZnO(100) for as-deposited VZO and ZnO/VZO films, referring to that from Al_2O_3(110), are shown in Fig. 1. The ω was 0.3° and the X-ray penetration depth is accordingly considered to be from several nm to several tens of nm. The XRD patterns are superimposed by being shifted along y-axis. ZnO(100) six-fold symmetry consisted of the normal domains, which have an aligning relationship of ZnO[100]//Al_2O_3[110] and represent the lattice mismatch of about 18%, was observed from 2-nm-thick VZO film, while no diffraction peak was seen from 30-nm-thick VZO film. As previously reported, 4-at% VZO highly aligned to the c-axis direction only at the initial stage of deposition and becomes amorphous thereafter [16]. ZnO films deposited on the 30-nm-thick amorphous VZO film have no ZnO(100) diffraction peak.

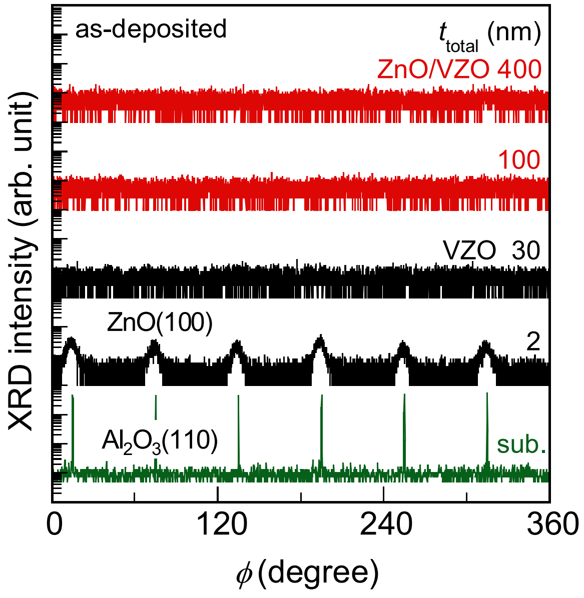

Fig. 1. In-plane XRD ϕ-scan patterns from ZnO(100) for as-deposited VZO and ZnO/VZO films with various t_{total}.

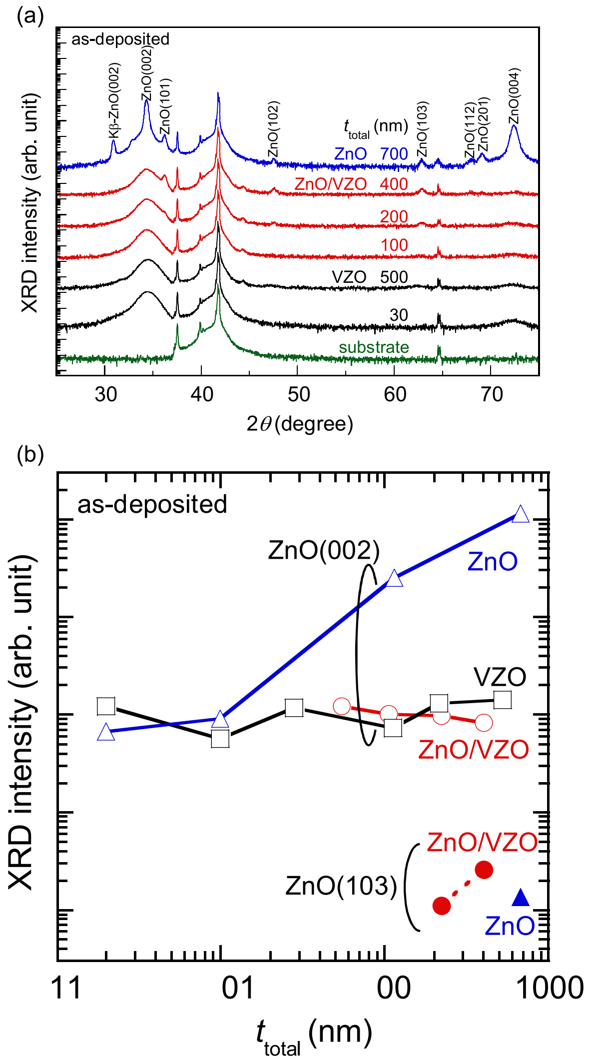

Fig. 2. (a) Out-of-plane XRD 2θ-ω-scan patterns for as-deposited ZnO, VZO, and ZnO/VZO films with various t_{total}. (b) Dependence of ZnO(002) and (103) XRD intensity on t_{total}.

The out-of-plane XRD 2θ-ω-scan patterns for as-deposited ZnO, VZO, and ZnO/VZO films, referring to that from Al_2O_3 substrate, are shown in Fig. 2(a). The diffraction peaks at 2θ=37.5°, 39.9°, 40.2°, 41.7°, and 64.5° are attributed to the Kβ-, W-Lα1-, W-Lα2-, Kα-Al_2O_3(006), and Kα-Al_2O_3(009), respectively. The dependences of ZnO(002) XRD intensity on t_{total} are shown in Fig. 2(b). The ZnO(002) XRD intensity of single ZnO films increased with thickness, and the diffractions from tilted planes such as ZnO(101), (102), (103), (112), and (201) were observed from 700-nm-thick film. The ZnO(002) XRD intensity of single VZO films was almost constant and any diffraction from tilted planes was not observed. This is because ultrathin-initial layer of VZO films is mainly textured along c-axis direction. The ZnO(002) XRD intensity of stacked ZnO/VZO films was almost same as that of single VZO films, however the diffractions from ZnO(101), (102), and (103) were observed when t_{total} was ≥200 nm. This might mean that the ZnO films deposited on amorphous VZO film grew in the pseudo-amorphous state when t_{ZnO} was smaller than about 150 nm but the self-orientation occurred in a thicker ZnO layer.

3.2. Solid-phase crystallization of stacked ZnO/VZO film

The dependences of full width at half maximum (FWHM) of the