



# Effect of vanadium doping on amorphization of ZnO thin films on c-plane sapphire substrate



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## ARTICLE INFO

### Article history:

Received 28 April 2015

Received in revised form 1 October 2015

Accepted 1 October 2015

Available online 9 October 2015

### Keywords:

Zinc oxide

Vanadium

Buffer layer

Amorphization

RF magnetron sputtering

## ABSTRACT

The effect of vanadium (V) doping on amorphization of zinc oxide (ZnO) thin films deposited on c-plane sapphire substrate at room temperature by RF magnetron sputtering was investigated. From the in-plane X-ray diffraction measurements, the diffraction intensity from 30° rotated domains observed in the ZnO film weakened with increasing V concentration. Faint diffractions from both the 30° rotated and normal domains were seen in the V-doped ZnO (VZO) film of 1.7-at.% V, and relatively strong diffractions only from the normal domain were observed at 2.1-at.% V while the 30° rotated domains diminished. There were only weak normal domains for VZO over 2.4-at.% V. Concerning the c-axis orientation, the broad (0002) diffraction peaks were observed in all VZO films, and the peak was the widest for the 3.8-at.% VZO film. From the dependence of crystallinity on thickness for the highly-doped VZO (V: 3.8 at.%) films, the c-axis orientation deteriorated with increasing film thickness and no diffraction signal was seen for the VZO films over 35-nm thick. This means that the VZO film aligned by the c-plane sapphire grew only at the initial stage, but an accumulation of disordered layers worsened the crystallinity with thickening the film. From the above-mentioned results, even in the ZnO film in which the grains tend to align to the c-axis orientation preferentially, the doping of transition metals, like V in this study, plays an effective reaction to form the pseudo-amorphous thin film. It is considered that this phenomenon is attributed to the feature of transition metal in which the transition metal atoms can take a state of various valence or coordination numbers.

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## 1. Introduction

ZnO is one of the most fascinating oxide semiconductors with unique features such as wide direct band gap (3.37 eV), large exciton binding energy (60 meV) and transparency in visible lights [1,2]. To apply the ZnO films to a variety of electronic devices, both the fabrication of high-quality epitaxial ZnO films reducing residual electrons and the control of conductivity (n- or p-type) by impurity doping have been required. However, even undoped ZnO films show usually n-type conductivity, so it is difficult to fabricate high-quality epitaxial ZnO films on the large lattice-mismatched substrates. Therefore, to obtain high-quality ZnO films, some kinds of buffer layers have been studied [3–5]. Recently, the method utilizing the solid-phase crystallization (SPC) from the amorphous phase has been demonstrated by using nitrogen mediation [6–8]. The ZnO films were crystallized in the solid phase by annealing of amorphous ZnON films deposited by RF magnetron sputtering on a-plane sapphire [Al<sub>2</sub>O<sub>3</sub>(11–20)] substrate. By

using SPC-ZnO thin film as the buffer layer, high-quality ZnO films have been obtained [9].

Transparent vanadium (V)-doped ZnO (VZO) films have some attractive features; for example, low resistivity [10], ferromagnetism [11–14] and intense piezoelectricity [15,16]. Recently, we have demonstrated unique phenomena in VZO films deposited on c-plane sapphire [Al<sub>2</sub>O<sub>3</sub>(0001)] substrate. That is, V atoms tend to retard the nucleation of the ZnO film, and the surface and grain size of VZO films subsequently became smooth and small, respectively [17]. Therefore, the incorporation of V atoms is considered to disorder the crystal structure and has a possibility to form amorphous films. That is, highly-doped VZO films could be utilized as the amorphous films for the source of SPC. Furthermore, a good SPC process is expected from the following reason. That is, the vanadium pentoxide V<sub>2</sub>O<sub>5</sub> precipitates from the amorphous vanadium oxide at relatively low temperature of about 500 °C [18], so V atoms might have a chance to form the precursor for SPC and to assist in providing the single-crystal ZnO buffer layer. In this paper, the effect of V doping on amorphization of ZnO thin films deposited on c-plane sapphire substrate by RF magnetron sputtering was investigated. As a result, pseudo-amorphous VZO films were fabricated by the high doping of V atoms.

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## 2. Preparation of VZO films and evaluations

VZO films were deposited on c-plane sapphire substrates at room temperature (RT) by RF magnetron sputtering using a ceramic ZnO target (99.99% purity) with V chips (99.9% purity). The sputtering gas was Ar (1.0 Pa) and the RF power was 150 W. The distance from the target to the substrate was set at 60 mm. The VZO films are in the range from 2- to 100-nm thick. The film thickness was measured by step profiler (ST4000 M; Kosaka Laboratory Ltd.). The V concentration was estimated by X-ray fluorescence analyses (XRF, Rigaku RIX2100) with an Rh target. The electrical properties were measured by van der Pauw method and were almost the same as the previous study [10]. The crystalline orientation was evaluated by X-ray diffraction (XRD, Rigaku SmartLab). The surface morphology was observed by atomic force microscopy (AFM, Asylum Research Cypher ES).

## 3. Results and discussions

### 3.1. V concentration dependence of crystallinity

The 10-nm-thick VZO films were deposited from 0- to 3.8-at.% V. The XRD  $\phi$ -scan patterns from ZnO(10–10) and the dependence of the (10–10) diffraction intensity on the V concentration are shown in Fig. 1(a) and (b), respectively. The diffraction intensity from 30° rotated domains observed in VZO films weakened with increasing V concentration and almost disappeared at 2.1-at.% V, similar to the result as reported in ref. [17]. Here, the 30° rotated domains are unfavorable to be formed due to the large mismatch of about 32%. However, because the substrate

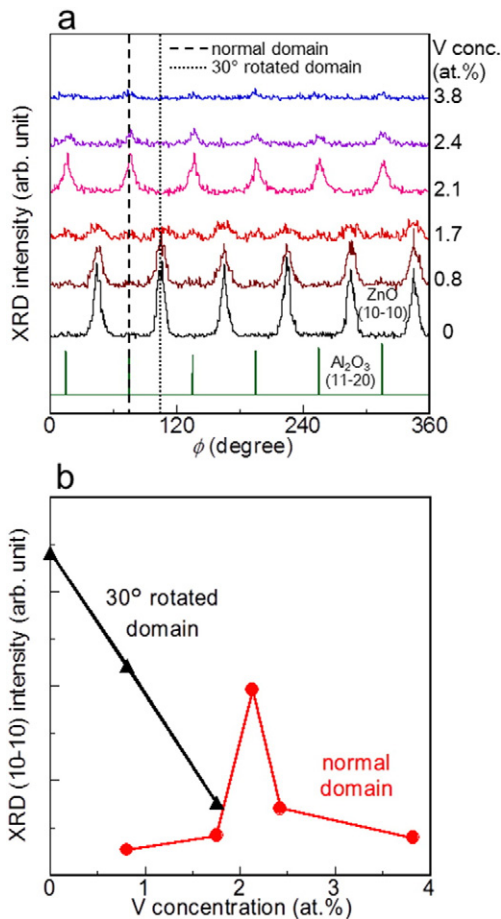


Fig. 1. (a) XRD  $\phi$ -scan patterns from ZnO(10–10) and Al<sub>2</sub>O<sub>3</sub>(11–20). (b) Dependence of ZnO(10–10) diffraction intensity on V concentration for 10-nm-thick ZnO and VZO films with various V concentrations.

temperature was low, the adhered atoms nucleated at the unsuitable site and the metastable ZnO(10–10) domains parallel to Al<sub>2</sub>O<sub>3</sub>(10–10) were formed. On the other hand, normal domains appeared at about 0.8-at.% V and its diffraction intensity increased up to 2.1-at.% V. This means that V atoms enabled to form the stable normal domains even at low temperature, because it was considered that V acted to block the metastable Zn nucleation. For the higher-doped VZO films, the diffraction decreased drastically and weak diffractions from the normal domain were observed. This dependence of crystallinity on V concentration is different from the result shown in ref. [17]. That is, almost constant diffractions from normal domains were observed when the VZO films were deposited at 200 °C. For this reason of difference, it is supposed to be caused by the formation of V clusters at RT due to the high-doping of V.

The dependence of the diffraction intensity from ZnO(0002) at  $2\theta$  of around 34.4°, on the V concentration is shown in Fig. 2. The XRD  $\theta$ - $2\theta$ -scan patterns are shown in the insets. The diffraction peaks at  $2\theta$  of around 37.7° are attributed to the sapphire(11–20) substrate. The ZnO(0002) diffraction peaks were observed regardless of V concentration, but they were similarly weak and broad. Furthermore, they became the divergent shape with increasing V concentration. These results indicate that the VZO films were aligned to the c-axis direction by the inherent property of hexagonal crystal structure, even at high V doping.

The AFM images (1  $\mu\text{m}^2$  area) and root-mean-square (RMS) surface roughness of the ZnO and VZO films deposited at various V concentrations are shown in Fig. 3. There were no dependence of grain size and no change in surface morphology on V concentration. Concerning the RMS surface roughness, the surfaces of the VZO films were rougher than that of ZnO film (ZnO: 0.38 nm, VZO: over 0.62 nm). In our previous investigation, the grain size became small and the RMS surface roughness decreased with increasing V concentration in the case of VZO films deposited at 200 °C [17]. Therefore, in the case of low-temperature deposition at RT, it is supposed that V atoms acting like the inhibitor for ZnO nucleation tend to gather and roughen the surface.

### 3.2. Film thickness dependence of crystallinity

The ZnO and VZO (3.8 at.%) films from 2- to 100-nm thick were deposited. The XRD  $\phi$ -scan patterns from ZnO(10–10) of the VZO films and the dependence of the diffraction intensity on the film thickness are shown in Fig. 4(a) and (b). The (10–10) diffraction intensity from the VZO films weakened with increasing film thicknesses and no diffraction signal was seen over 35-nm thick. It found that the films at the initial stage of the growth aligned strongly to the c-axis direction according to the c-plane sapphire substrate even at the high doping of V. However, by the V doping effect of retarding nucleation, the c-axis orientation deteriorated rapidly when the thickness of VZO film became

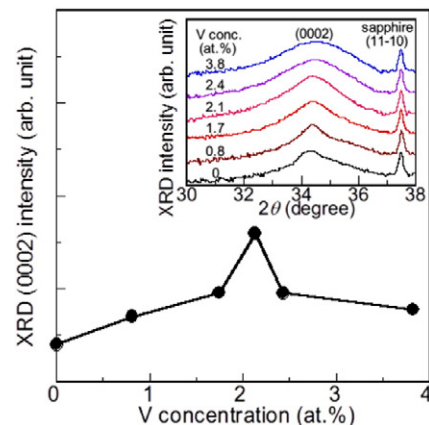


Fig. 2. Dependence of ZnO(0002) diffraction intensity from 10-nm-thick films on V concentration. The inset shows the XRD  $\theta$ - $2\theta$ -scan patterns.

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