

Thermal solid-phase crystallization of amorphous V-doped ZnO film stacked on highly oriented ZnO

Kenta Shito¹, Hiroshi Chiba^{1,2}, Tomoyuki Kawashima¹, and Katsuyoshi Washio¹

¹Graduate School of Engineering, Tohoku University

6-6-05, Aza-Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

Tel: +81-22-795-7122, Fax: +81-22-263-9396, E-mail: k.shitou@ecei.tohoku.ac.jp

²Japan Society for the Promotion of Science Research Fellowships for Young Scientists,

Koji-machi Business Center Building, 5-3-1 Koji-machi, Chiyoda-ku, Tokyo, 102-0083, Japan

Abstract

In this study, effects of an insertion of highly oriented ZnO (ho-ZnO) layer between a vanadium-doped ZnO (VZO) film and a sapphire substrate, and thermal solid-phase crystallization (SPC) of the stacked VZO/ho-ZnO film were investigated. Crystal orientation of as-deposited interfacial VZO film on an a-face sapphire substrate was improved by the ho-ZnO insertion, whereas that on a c-face sapphire substrate wasn't improved. ZnO(100) and ZnO(002) full width at half maximum (FWHM) of the calcined VZO film on the a-face sapphire decreased from 2° to 0.6° and 0.9° to 0.7°, respectively, due to the insertion of the ho-ZnO.

1. Introduction

ZnO has attractive properties such as transparency to visible light and large exciton binding energy [1-3]. Although a highly oriented crystalline ZnO (ho-ZnO) is necessary to obtain these advantages, direct growth of thick ho-ZnO film on lattice-mismatched substrate is still difficult because of the 2D-3D transition of growth mode due to the strain relaxation [4]. In our previous studies, we investigated thermal solid-phase crystallization (SPC) of a pseudo-amorphous vanadium-doped ZnO (pa-VZO) film on a c-face sapphire substrate [5,6]. The pa-VZO film has a thin oriented seed layer at an interface of the substrate, and this oriented seed layer determined the crystallinity of whole VZO film after SPC. In the present study, effects of an insertion of the thin ho-ZnO film, which is still in 2D growth mode, between the pa-VZO film and the a- or c-face sapphire substrate on the film crystallinity after SPC were investigated.

2. Film preparation

The VZO/ZnO stacked film was deposited by RF magnetron sputtering (Ar atmosphere: 1.0 Pa, RF power: 150 W). The ho-ZnO film was deposited at 450°C with a fixed thickness of 5 nm, whereas the pa-VZO (V concentration: 4 at.%) film was deposited at room temperature with various thickness from 5 to 200 nm. The stacked film was calcined by lamp heating for 5 min at 800°C in N₂ atmosphere.

3. Results and discussions

Crystallinity of as-deposited films

The XRD ϕ -scan patterns from ZnO(100) for the as-deposited films are shown in Fig. 1. Thickness of the VZO layer (t_{VZO}) was 5 nm. VZO/Al₂O₃(0001) only exhibited diffraction peaks from the normal domain (ZnO[100]//Al₂O₃[110]) while diffraction peaks from the rotation domain also appeared when ho-ZnO was inserted. On the other hand, both VZO/Al₂O₃(11-20) and VZO/ZnO/Al₂O₃(11-20) exhibited diffraction peaks only from a single domain. Furthermore, the VZO/ZnO film exhibited much more intense and sharper peak than that of the VZO film. This result suggests that the crystal orientation of

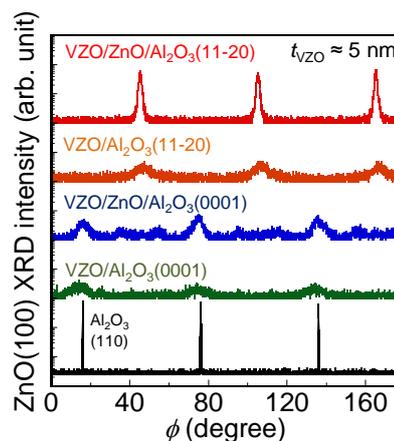


Fig. 1. The XRD ϕ -scan patterns from ZnO(100) for as-deposited VZO and VZO/ZnO films.

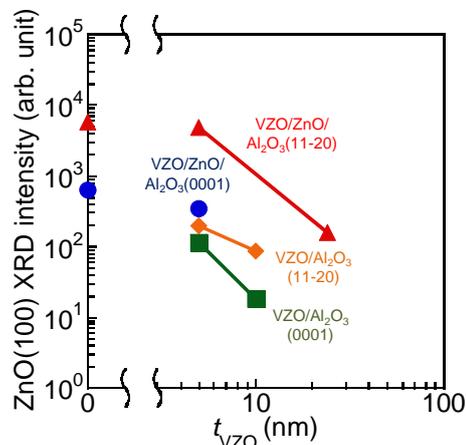


Fig. 2. The dependences of ZnO(100) intensity on t_{VZO} for as-deposited films.

the seed layer of VZO was effectively improved on the a-face sapphire substrate by the ho-ZnO insertion. The dependences of ZnO(100) XRD intensity on t_{VZO} for the as-deposited films are shown in Fig. 2. XRD intensity of all films decreased as t_{VZO} increased, and no diffraction peak was observed at t_{VZO} above 25 nm for VZO/ZnO/Al₂O₃(11-20), 5 nm for VZO/ZnO/Al₂O₃(0001), and 10 nm for the others. This indicates that surface of VZO is pseudo-amorphous regardless of substrates and the ho-ZnO insertion when t_{VZO} is larger than 25 nm. The ZnO(002) XRD rocking curves (RC) for the as-deposited VZO and VZO/ZnO films are shown in Fig. 3. All films exhibited similar full width at half maximum (FWHM) of about 0.09° regardless of the ho-ZnO insertion. However, on the a-face sapphire substrate, the diffraction intensity of the VZO/ZnO film is much higher than that of the VZO film. This result suggests that the ho-ZnO insertion is effective to improve the crystal orientation of VZO on the a-face sapphire substrate, whereas it isn't effective for the films on the c-face sapphire substrate.

Crystallinity of calcined films

The dependences of FWHM of ZnO(100) ϕ -scan peaks and ZnO(002) RC on t_{VZO} for the calcined films are shown in Fig. 4 and Fig. 5, respectively. Both FWHM tends to decrease with increasing t_{VZO} up to about 100 nm. Any diffraction peaks from the rotation domain were not observed in the ϕ -scan patterns. Regarding the ZnO(100) FWHM, VZO/Al₂O₃(0001) exhibited FWHM of about 1 – 2° regardless of the ho-ZnO insertion. On the other hand, FWHM of the 100-nm-thick VZO/Al₂O₃(11-20) film largely decreased from 2° to 0.6° by the ho-ZnO insertion. This is attributed to the improvement in crystal orientation of the seed layer. Differences of the ZnO(002) FWHM became smaller than those of the ZnO(100) FWHM. Minimum FWHM of about 0.7° were given at t_{VZO} above 100 nm for the films except VZO/Al₂O₃(0001), which has weakly orientated seed layer. These results indicate that the ho-ZnO insertion is particularly effective for the VZO/ZnO film on the a-face sapphire substrate to attain high crystallinity after SPC.

4. Conclusions

SPC of the pa-VZO/ho-ZnO stacked films on the a- or c-face sapphire substrate was investigated. The initial orientation of VZO/Al₂O₃(11-20) was improved by the ho-ZnO insertion, whereas that of VZO/Al₂O₃(0001) wasn't improved. It was also found that the deposited VZO films were pseudo-amorphous regardless of substrates and the ho-ZnO insertion when t_{VZO} is larger than 25 nm. Broad XRD peaks were observed in VZO/ZnO/Al₂O₃(0001) after SPC, while VZO/ZnO/Al₂O₃(11-20) exhibited sharper peaks which is also better than VZO/Al₂O₃(11-20). This improvement in the crystallinity is attributed to the improvement of the crystal orientation of the initial seed layer via ho-ZnO insertion on the a-face sapphire substrate.

Acknowledgements

This study was partially supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant number 16J01620.

References

- [1] H. Kim, et al., *Appl. Phys. Lett.*, **76** (2010) 259.
- [2] K. Takanezawa, et al., *Jpn. J. Appl. Phys.*, **47** (2008) 8049.
- [3] Ü. Özgür, et al., *J. Appl. Phys.*, **98** (2005) 041301.
- [4] S.I. Park, et al., *Appl. Phys. Lett.*, **77** (2000) 349.
- [5] A. Watanabe, et al., *Thin Solid Films*, **605** (2016) 73.
- [6] A. Watanabe, et al., *J. Electron. Mater.*, **45** (2016) 2008.

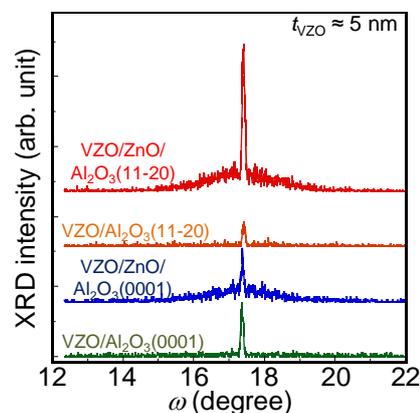


Fig. 3. ZnO (002) rocking curve for as-deposited VZO and VZO/ZnO films.

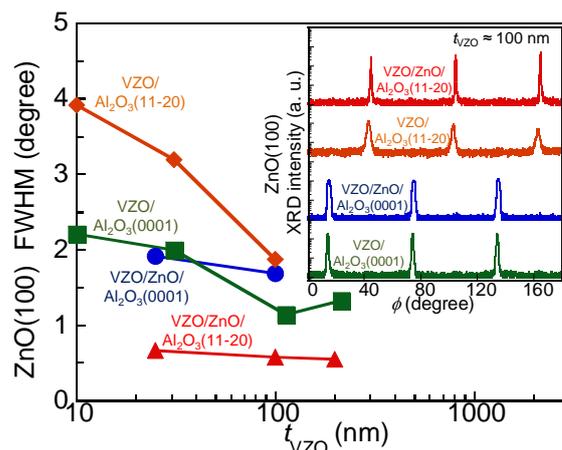


Fig. 4. The dependences of FWHM of ZnO(100) ϕ -scan peaks on t_{VZO} for calcined film. The inset shows the XRD ϕ -scan patterns from ZnO(100) at t_{VZO} of 100 nm.

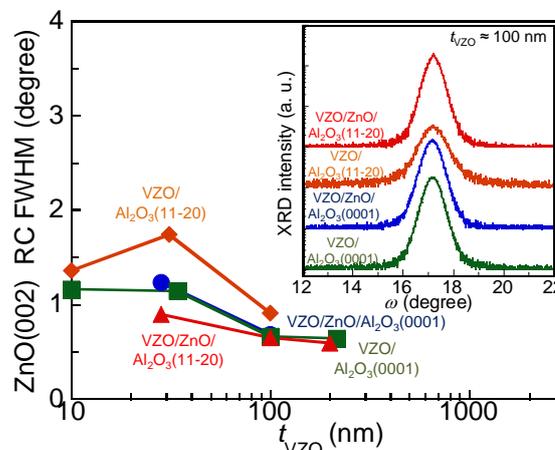


Fig. 5. The dependences of FWHM of ZnO(002) RC on t_{VZO} for calcined film. The inset shows ZnO(002) RC at t_{VZO} of 100 nm.