

Comparative study of Al and V co-doped ZnO thin films on quartz, polyethylene terephthalate, and polycarbonate substrates

Chisato Tateyama¹, Hiroshi Chiba^{1,2}, Tomoyuki Kawashima¹, and Katsuyoshi Washio¹

¹ Graduate School of Engineering, Tohoku University
6-6-05 Aza-Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan
Tel: +81-22-795-7123, E-mail: c.tateyama@ecei.tohoku.ac.jp

² Japan 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

Electrical and optical properties of aluminum (Al) and vanadium (V) co-doped ZnO (AVZO) films deposited on quartz and flexible polymer substrates were investigated. AVZO films exhibited nearly the same resistivity as V-doped ZnO (VZO) films regardless of the substrates and higher ZnO(002) diffraction intensities than VZO films particularly on quartz and polycarbonate substrates. Average optical transmittance (T_{ave}) at a wavelength between 450 and 800 nm increased about 10% by Al co-doping into VZO films. The improvement in T_{ave} was attributed to compensation of lattice defects by Al incorporation and surface texture with deep valleys.

1. Introduction

Zinc oxide (ZnO) is a promising material for several applications such as solar cells and flat panel displays due to its optical and electrical properties [1]. Recently, the ZnO films deposited on transparent and flexible polymer substrates have attracted attention [2]. However, concerning melting point of polymer substrates, the ZnO film has to be deposited at low temperature below 200°C. We have previously reported that vanadium (V)-doped ZnO (VZO) films on a polycarbonate (PC) substrate exhibited low resistivity similar to that on a quartz substrate [3], but optical transmittance decreased due to the formation of lattice defects by V doping [4]. We have also reported that average optical transmittance (T_{ave}) at a wavelength between 450 and 800 nm increased 70% with a low resistivity of 0.42 Ωcm for aluminum (Al) and V co-doped ZnO (AVZO) films deposited on a quartz substrate at 150°C [5]. In this study, AVZO films were deposited on polyethylene terephthalate (PET) and PC substrates by RF magnetron sputtering, and their electrical, optical, and crystallographic properties were investigated.

2. Experiment

50-nm-thick VZO and AVZO films were deposited on the quartz, PET, and PC substrates by RF magnetron sputtering. Al and V concentrations were fixed at 0.6 and 1.4 at.%, respectively. The sputtering gas was Ar (1.0 Pa). Radio frequency power and deposition temperature were 150 W and 150°C, respectively. Resistivity was evaluated by four-point probe measurement. Optical transmittance was

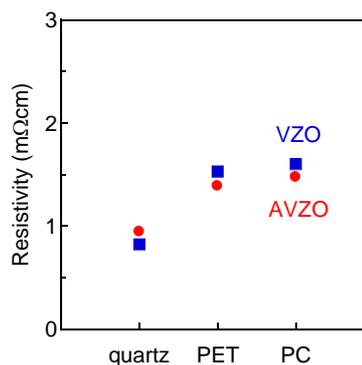


Fig. 1. Resistivities of VZO and AVZO films.

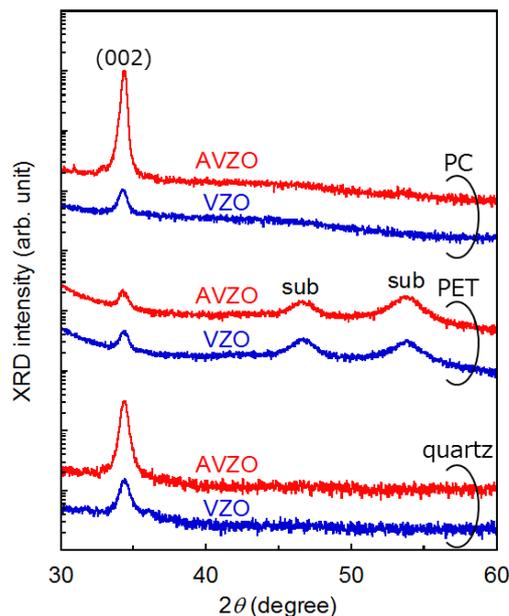


Fig. 2. XRD patterns of VZO and AVZO films.

measured by spectroscopic ellipsometry. The c-axis crystalline orientation was analyzed by an out-of-plane X-ray diffraction (XRD) measurement. The surface morphology was observed by an atomic force microscope (AFM).

3. Results and discussion

The resistivities of VZO and AVZO films are shown in Fig. 1. The resistivities of VZO films on the quartz, PET, and PC substrates were 0.8 mΩcm, 1.5 mΩcm, and 1.6

mΩcm, respectively. The resistivities of AVZO films were nearly the same to those of VZO films. Films on the polymer substrates exhibited slightly higher resistivities than those on quartz.

The XRD patterns are shown in Fig. 2. In the case of the films on the quartz and PC substrates, ZnO(002) diffraction intensities of AVZO films were higher than those of VZO films. From this result, Al incorporation was effective to compensate the defects which were generated by the V doping [4]. However, in the case on PET, the ZnO(002) diffraction intensity of AVZO film hardly changed. This is probably because the film crystallinity was affected by the orientation of PET substrate.

The optical transmittance spectra are shown in Fig. 3. Respective T_{ave} of VZO films were 59% on the quartz, 72% on PET, and 67% on PC. On the other hand, respective T_{ave} of AVZO films were 70% on the quartz, 80% on PET, and 75% on PC. Al co-doping contributed to improve transmittance about 10%. Since the defects like oxygen vacancies (V_O) and zinc vacancies (V_{Zn}) act as an absorption center of visible to near-infrared light [6,7], it can be considered that Al might compensate those defects.

The AFM images and the root mean square (RMS) roughness are shown in Fig. 4. Straight wrinkle-like patterns were observed on PC substrate. This is considered due to the difference in thermal expansion coefficient between ZnO and PC [3]. The films on PET and quartz exhibited a granular texture. The films on PET have large grain size of more than a few hundreds of nanometers with comparatively deep valleys. This surface texture probably made a gradual change of the refractive index between air and the film, and effectively decreased reflectance compared to the films on the quartz or PC [8]. On the other hand, the small difference in resistivity suggests that these differences in the surface morphology had little effect on resistivity.

4. Conclusions

Electrical, optical, and crystallographic properties of the AVZO films on the quartz, PET, and PC substrates were investigated. Despite the large difference in surface morphology, resistivity was nearly the same regardless of the substrates. The ZnO(002) diffraction intensities of AVZO films on the quartz and PC substrates were higher than those of VZO films. T_{ave} also increased about 10% by Al co-doping into VZO films on all substrates. This is considered as a result of the compensation of the lattice defects like V_{Zn} by the Al incorporation. Films on PET exhibited higher T_{ave} than the other films due to the surface texture with deep valleys which contributed to a gradual change in the refractive index between air and the film.

Acknowledgements

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

References

[1] C.F. Klingshim et al., Zinc Oxide: From Fundamental Proper-

ties Towards Novel Applications, Springer Berlin Heidelberg, (2010).

[2] A.N. Banerjee et al., *Thin Solid Films*, **496** (2006) 112.

[3] T. Suzuki et al., *Thin Solid Films*, **605** (2016) 53.

[4] T. Kawashima et al., *Mat. Sci. Semicond. Proc.*, In Press (2017) doi:10.1016/j.mssp.2016.10.052.

[5] C. Tateyama et al., The 64th JSAP Spring Meeting, Yokohama (2017) 15a-502-1.

[6] H.L. Guo et al., *Nanoscale*, **7** (2015) 7216.

[7] M.K. Kavitha et al., *Phys. Chem. Chem. Phys.*, **16** (2014) 25093.

[8] R. Dewan et al., *Bioinspir. Biomim.*, **7** (2012) 016003.

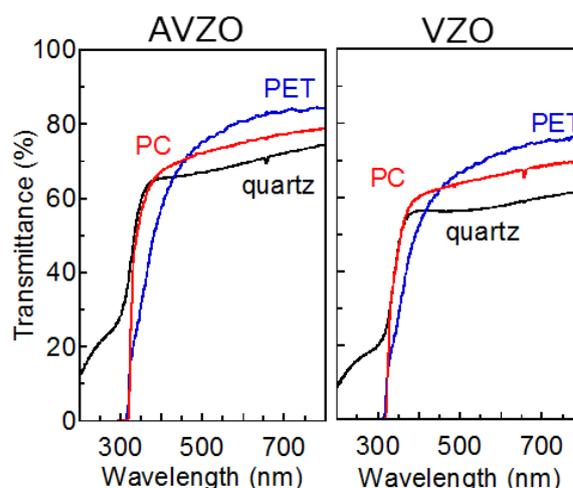


Fig. 3. Optical transmittance spectra of VZO and AVZO films.

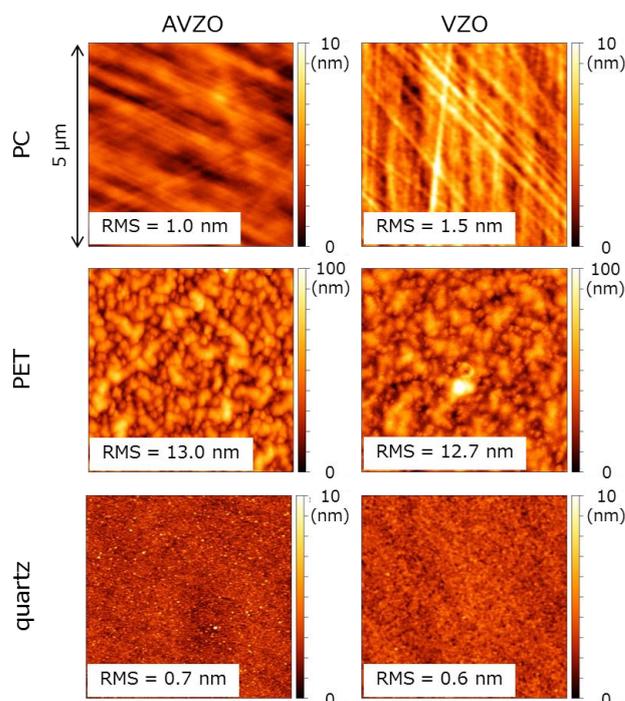


Fig. 4. AFM images of VZO and AVZO films.