



Thermal stability of conductive and transparent V-doped ZnO thin films



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ABSTRACT

The thermal stability of electrical, optical and structural properties of vanadium-doped zinc oxide (VZO) thin films has been investigated after heat treatments up to 550 °C in N₂ and O₂ atmospheres. ZnO and VZO films were prepared by RF magnetron sputtering on quartz substrates at 200 °C. It was found that the resistivity of VZO films remains low at about $5 \times 10^{-4} \Omega \text{ cm}$ when heat treated at temperature up to 450 °C in both N₂ and O₂ atmospheres, while resistivity of the ZnO film increased remarkably due to the compensation of oxygen vacancies in O₂ heat treatments over 400 °C. Optical transmittance of the as-grown VZO film in the visible range (400–1100 nm) was 20–30% and improved up to about 80% when heat treated at temperature up to 500 °C in N₂ and O₂ atmospheres. Decreased c-axis lattice constant in the VZO film was larger in N₂ heat treatments than in O₂ heat treatments. Based on these experimental results, we made the hypothesis that V–O bonds similar to vanadium trioxide in the as-grown VZO film changed to those similar to vanadium pentoxide after heat treatments over 500 °C.

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1. Introduction

Transparent conductive electrodes play a major role in the fields of information and energy technologies [1]. ZnO thin films have been studied extensively as a component of flat-panel displays and solar cells. Doped ZnO thin films with low-resistivity and transparent properties comparable to indium tin oxide (ITO) have particularly been investigated [2,3]. However, resistivity of doped-ZnO films has been shown to become unstable at the relatively low temperature range of 300–400 °C [3–5].

Transition-metal doped ZnO films have a variety of attractive properties, such as ferromagnetic behavior and piezoelectricity [6–9]. Among them, low-resistivity vanadium-doped ZnO (VZO) films have a potential to extend further functionality [10,11]. However, the number of studies concerning thermal stability of VZO is limited [12,13]. Therefore, in this paper, thermal stability of VZO thin films in terms of electrical, optical and structural properties has been investigated for heat treatments up to 550 °C in N₂ and O₂ atmospheres.

2. Experiment

ZnO and VZO thin films were deposited on quartz substrates by RF magnetron sputtering. The gas used during the deposition was Ar (1.0 Pa). RF power and the substrate temperatures were 150 W and 200 °C, respectively. The deposition rate was 16–18 nm/min and the thickness of ZnO and VZO was about 500 nm. V was doped by co-

sputtering ceramic ZnO with V chips. V concentration of about 1.9 at.% was measured by X-ray fluorescence (XRF, Rigaku RIX2100 using Rh radiation). The ZnO and VZO thin films were heat-treated up to 550 °C for 5 min in N₂ or O₂ atmospheres (1000 Pa) to investigate their thermal stability. Heating and cooling rates were 60 °C/min and 100 °C/min, respectively, to avoid excessive stress in the films. Thermal stability was evaluated by the change in resistivity, optical transmittance, crystallinity, and surface morphology. Resistivity was measured by the Van-der-Pauw method and optical transmittance was measured using a spectrophotometer in the range of 300 to 1100 nm. The c-axis crystalline orientation was confirmed by out-of-plane X-ray diffraction (XRD, Rigaku SmartLab using CuK α radiation) measurements. The surface morphology was observed with atomic force microscopy (Park XE-100, in non-contact mode).

3. Results

3.1. Resistivity

Dependence of resistivity on heat treatment temperature (T_A) in N₂ or O₂ atmospheres for ZnO and VZO films is shown in Fig. 1. Resistivities of as-grown ZnO and VZO films were 0.1 $\Omega \text{ cm}$ and 0.5 m $\Omega \text{ cm}$, respectively. Okuda et al. reported that low resistivity of about $5 \times 10^{-4} \Omega \text{ cm}$ observed in VZO films was due to V dominant charge number of +3 [11]. That is, V atoms in VZO films have V–O bonds similar to vanadium trioxide (V₂O₃) resistivity of which is about $10^{-4} \Omega \text{ cm}$.

In the case of N₂ heat treatment, the resistivity of the ZnO film increased slightly over T_A of 450 °C and, in general, this has been thought to be due to the desorption of interstitial Zn atoms (Zn_i) [14]. On the other hand, the resistivity of VZO films remained low up to T_A of

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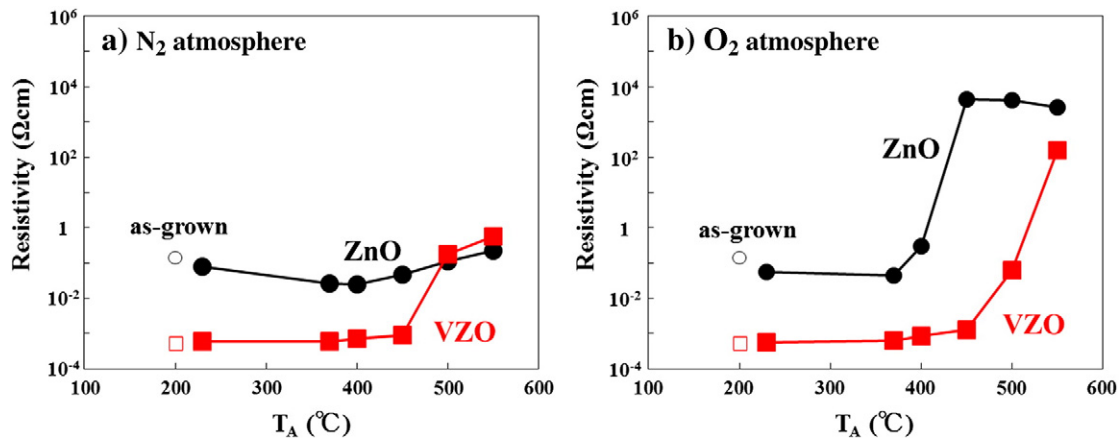


Fig. 1. Dependence of resistivity on T_A in (a) N_2 and (b) O_2 atmospheres for ZnO and VZO films.

450 °C and rose sharply at $T_A = 500$ °C. Here, it is notable that resistivity of ZnO and VZO films after N_2 heat treatment at 500 °C was nearly equal. This means that the number of free carriers bringing conductivity was almost the same and V^{3+} ions should disappear in the VZO film following N_2 heat treatment at 500 °C.

In the case of O_2 heat treatment, a remarkable increase (about 10^4 times) of resistivity was observed in ZnO films annealed between T_A of 400 and 450 °C. Comparing with N_2 heat treatment, this indicates that compensation of oxygen vacancies (V_O) occurred by O_2 heat treatment [15]. Resistivity of the ZnO film became saturated at T_A of over 450 °C due to the full compensation of V_O . On the other hand, resistivity of

the VZO film kept unchanged up to T_A of 450 °C in contrast to the ZnO film and increased at 500 °C. Here, we notice again that the resistivity of the VZO film after O_2 heat treatment at 500 °C was nearly equal to that of ZnO and VZO films after N_2 heat treatment at 500 °C. This means that the increase in resistivity of VZO films after N_2 and O_2 heat treatments at 500 °C occurred by the same phenomenon, i.e. the disappearance of V^{3+} ions. Here, it should be noted that there was no decrease in V concentration of the VZO film measured by XRF after any heat treatments. Furthermore, as a result of thermal stability up to T_A of 450 °C, it should be considered that doping of V disturbed the compensation of oxygen vacancies.

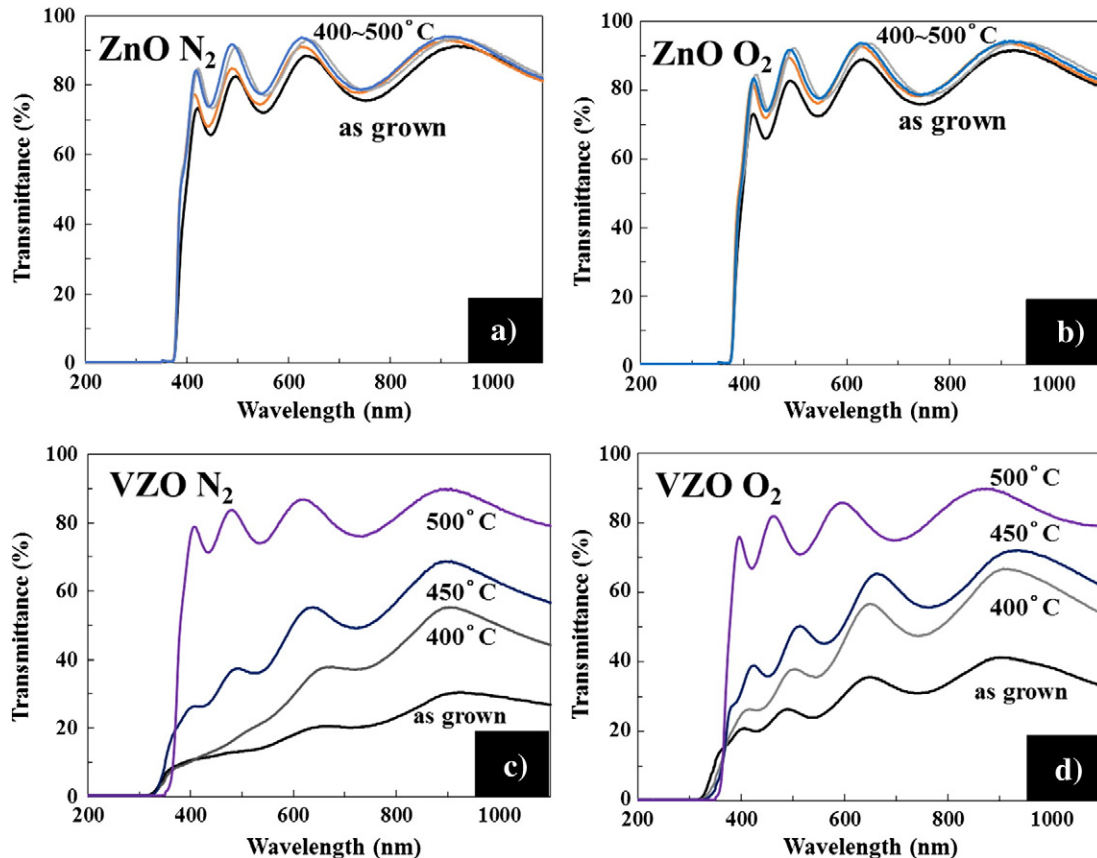


Fig. 2. Optical transmission spectra for as-grown and heat-treated ZnO films at T_A of 400, 450, 500 °C in (a) N_2 and (b) O_2 atmospheres, and as-grown and heat-treated VZO films at T_A of 400, 450, 500 °C in (c) N_2 and (d) O_2 atmospheres.

3.2. Transmittance

Optical transmission spectra in the wavelength range from 300 to 1100 nm for as-grown and heat-treated ZnO and VZO films of T_A up to 500 °C are shown in Fig. 2. Dependence of optical transmittance at a wavelength of 500 nm on T_A is shown in Fig. 3. Optical transmittance of the quartz substrate was about 90%. Optical transmittance for ZnO films was about 80% in the visible range (400 nm–1100 nm) and was stable when heat treated in both N_2 and O_2 atmospheres. This means that the desorption of Zn_i and the compensation of V_O did not affect the optical transmittance. On the other hand, for as-grown VZO, transmittance was 20–30%. Here, as described in Section 3.1, V ions with the charge number of +3 were incorporated into VZO films. So, it is considered that this decrease of transmittance of the VZO film is due to the formation of V–O bonds similar to V_2O_3 . Note that V_2O_3 is opaque. Transmittance of the VZO film increased with T_A and rose to about 80% at T_A of 500 °C in both N_2 and O_2 atmospheres. This T_A is equal to the temperature at which resistivity of ZnO films after N_2 and O_2 heat treatments increased. Furthermore, at T_A over 500 °C, transmittance of both ZnO and VZO films was almost equal. This means that the disappearance of V^{3+} ions is attributed to improve transparency in the VZO film.

3.3. Crystallinity

The XRD patterns of as-grown and heat-treated ZnO and VZO films at T_A up to 500 °C are shown in Fig. 4. The crystallinity is characterized by intensive diffraction peak from (0002) plane. Peaks from (10–11), (10–12), (10–13) and (11–22) planes other than the c-axis orientation were identified in ZnO films. Similar diffraction patterns have been observed after heat treatments in both N_2 and O_2 atmospheres and there was no significant change in crystallinity. Peaks from (10–11), (10–12) and (10–13) planes were also observed in VZO films and there was also no specific change after heat treatments in both N_2 and O_2 atmospheres. That is, it could be considered that the crystallinity was not changed much through heat treatments. Comparing with ZnO, the diffraction peak from the (10–11) plane was weak and there was no peak from the (11–22) plane in the VZO film, however, the heat treatments do not seem to affect the crystallinity of the VZO films, either.

The dependence of c-axis lattice constant on T_A , estimated from the diffraction angle of the (0002) plane peak, is shown in Fig. 5. Both ZnO and VZO films shrank along the [0001] direction when heat treated in N_2 or O_2 atmospheres. In the case of N_2 heat treatment, the c-axis lattice

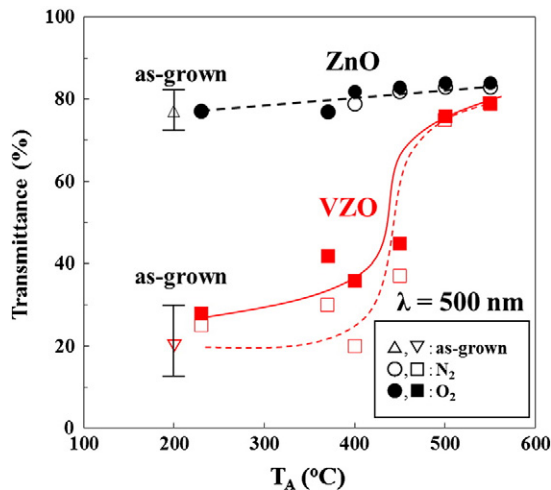


Fig. 3. Dependence of optical transmittance at wavelength of 500 nm on T_A in N_2 and O_2 atmospheres for ZnO and VZO films.

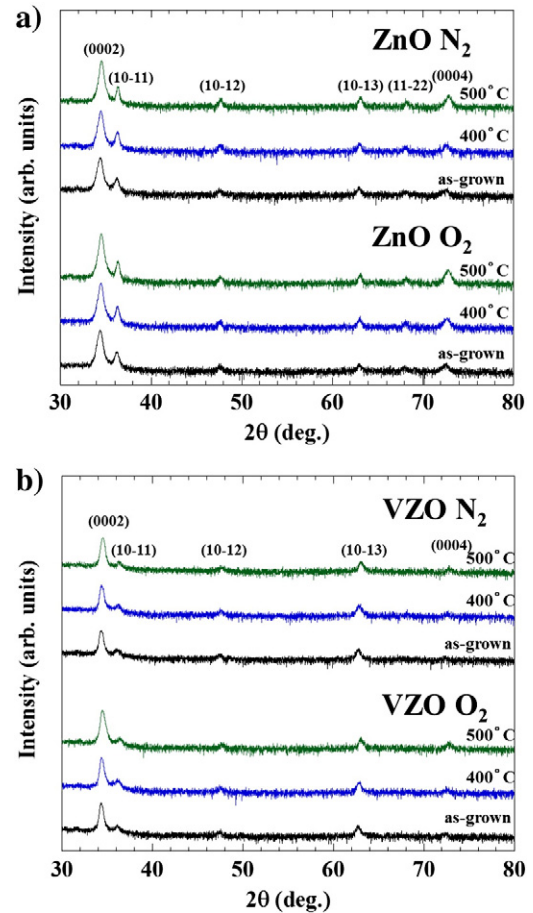


Fig. 4. XRD patterns of as-grown and heat-treated (a) ZnO and (b) VZO films at T_A of 400 and 500 °C in N_2 and O_2 atmospheres.

constant of ZnO films decreased linearly with increasing T_A over 350 °C and that of VZO films decreased with increasing T_A similar to ZnO films. However, the c-axis lattice constant of VZO films varied widely and became almost equal to that of ZnO films at T_A of 550 °C. This decrease of c-axis lattice constant is also attributed to the desorption of Zn_i . However, the larger shrinkage for VZO films than ZnO films cannot be explained only by the desorption of Zn_i . This is because the concentration of Zn_i in ZnO films is thought to be given by the substrate

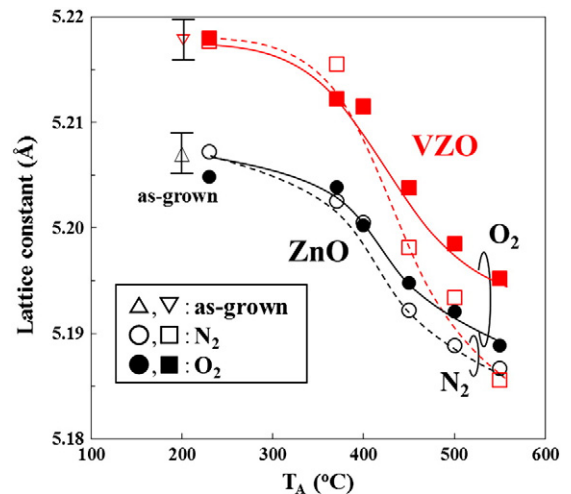


Fig. 5. Dependence of c-axis lattice constant for ZnO and VZO films on T_A in N_2 and O_2 atmospheres for ZnO and VZO films.

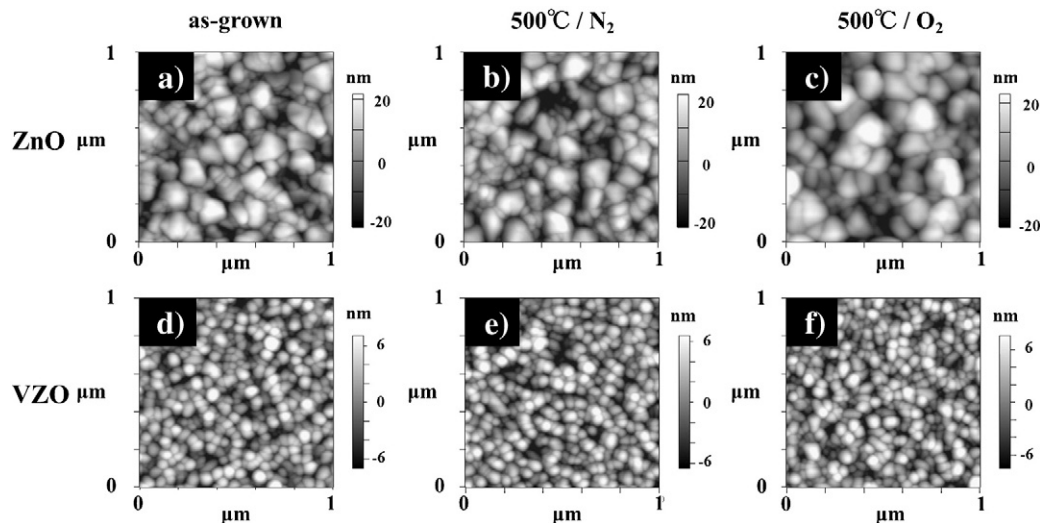


Fig. 6. Surface morphology of ZnO film for (a) as-grown, heat-treated at T_A of 500 °C in (b) N_2 , and (c) O_2 atmospheres, and VZO film for (d) as-grown, heat-treated at T_A 500 °C in (e) N_2 , and (f) O_2 atmospheres.

temperature [16], so the Zn_i concentration of VZO films was considered to be equal to that of ZnO films. The ionic radius of V^{5+} with a coordination number of 4 is about half that of V^{3+} with a coordination number of 6 and tetrahedrally coordinated V^{5+} is more stable in the hexagonal-system ZnO crystal structure. Here, we introduce the hypothesis that V–O bonds similar to V_2O_3 for as-grown VZO films changed to bonds similar to vanadium pentoxide (V_2O_5) after heat treatments. The disappearance of V^{3+} ions, that was derived from the results of changes in resistivity and optical transmittance by N_2 and O_2 heat treatments, is consistent with this hypothesis.

In the case of O_2 heat treatment, the c-axis lattice constant for both ZnO and VZO films also decreased with increasing T_A similar to the case of N_2 heat treatment. However, the shrinkage of the c-axis lattice constant in O_2 heat treatment was smaller than that in N_2 heat treatment. This means that the compensation of V_O caused by the supply of O atoms with the large ionic radius alleviated the shrinkage in the c-axis direction. This also follows that the shrinkage of the c-axis lattice constants of ZnO and VZO films changed by nearly the same dependence on T_A .

3.4. Surface morphology

The surface morphologies of ZnO and VZO films are shown in Fig. 6. The root-mean-square surface roughness of as-grown ZnO and VZO films was estimated at 10.5 nm and 3.3 nm, respectively. The grain size became small and the surface became smooth in VZO films caused by V doping. However, for both ZnO and VZO films, it was observed that the surface morphology and columnar structure were not changed much through heat treatments in both N_2 and O_2 atmospheres up to 500 °C. This corresponds with the evaluation result of crystallinity.

4. Discussion

We consider that the most characteristic difference in thermal stability between ZnO and VZO films comes mainly from the change of valence state of V ions by the heat treatment. That is, V–O bonds similar to V_2O_3 changed to those similar to V_2O_5 at T_A over 500 °C. The most remarkable result was that the low-resistive VZO film was kept stable up to T_A of 450 °C while the resistivity of ZnO increased drastically at T_A of 400 °C in O_2 heat treatment. This is considered to be a contribution of the obstruction of the V_O compensation by V doping. The change of V–O bonds similar to V_2O_3 to bonds similar to V_2O_5 as a result of heat treatment is the hypothesis at present. However, the changes of resistivity, transmittance, and the c-axis lattice constant by N_2 and O_2 heat

treatments can be explained consistently. This hypothesis is indirectly supported by the fact that V_2O_5 has relatively high-resistivity of about 10^2 to 10^3 Ω cm (V_2O_3 : 10^{-4} Ω cm) and its color is light orange (while V_2O_3 is: black). Of course, we consider that further physical analyses are necessary to verify this hypothesis and we would like to continue the study in this respect.

5. Conclusion

The thermal stability of electrical, optical and structural properties of VZO thin films was investigated after heat treatments up to 550 °C in N_2 and O_2 atmospheres. VZO films kept low resistivity after heat treatments up to 450 °C. Optical transmittance of VZO films improved up to about 80% at 500 °C. Decreased c-axis lattice constant in VZO films was larger in N_2 heat treatments than in O_2 heat treatments. We made a hypothesis that V–O bonds similar to vanadium trioxide in as-grown VZO film changed to those similar to vanadium pentoxide after heat treatments over 500 °C. This explained the changes of VZO properties after heat treatments consistently.

Acknowledgments

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