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 atmosphere, while resistivity of ZnO film increased remarkably due to the compensation of oxygen vacancies in O₂ heat treatments over 400 °C. Optical transmittance of 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 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 as-grown VZO film changed to those similar to

vanadium pentoxide after heat treatments over 500 °C.

Keywords: RF magnetron sputtering

ZnO

Vanadium

Heat treatment

Thermal stability

Resistivity

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 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 have been shown to become unstable at 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 500nm. 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 minutes 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 are shown in **Fig. 1**. Resistivity of as-grown ZnO and VZO films were 0.1 Ωcm and 0.5m Ωcm , respectively. Okuda et al. reported that low resistivity of about 5×10^{-4} Ωcm 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} Ωcm .

In the case of N₂ heat treatment, the resistivity of 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 450 °C and rose

sharply at $T_A = 500\text{ }^{\circ}\text{C}$. Here, it is notable that resistivity of ZnO and VZO films after N_2 heat treatment at 500 and 550 $^{\circ}\text{C}$ was nearly equal. This means that the number of free carriers bringing conductivity was almost the same and V^{3+} ions should disappear in VZO film following N_2 heat treatment at 500 $^{\circ}\text{C}$.

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 $^{\circ}\text{C}$. Comparing with N_2 heat treatment, this indicates that compensation of oxygen vacancies (V_O) occurred by O_2 heat treatment [15]. Resistivity of ZnO film became saturated at T_A of over 450 $^{\circ}\text{C}$ due to the full compensation of V_O . On the other hand, resistivity of VZO film kept unchanged up to T_A of 450 $^{\circ}\text{C}$ in contrast to ZnO film and increased at 500 $^{\circ}\text{C}$. Here, we notice again that the resistivity of VZO film after O_2 heat treatment at 500 $^{\circ}\text{C}$ was nearly equal to that of ZnO and VZO films after N_2 heat treatment at 500 $^{\circ}\text{C}$. This means that the increase in resistivity of VZO films after N_2 and O_2 heat treatments at 500 $^{\circ}\text{C}$ 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 VZO film measured by XRF after any heat treatments. Furthermore, as a result of thermal stability up to T_A of 450 $^{\circ}\text{C}$, it should be considered that doping of V disturbed the compensation of oxygen vacancies.

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 $^{\circ}\text{C}$ are shown in **Fig. 2**. Dependence of optical transmittance at a

wavelength of 500 nm on T_A are 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 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 VZO film increased with T_A and raised 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 VZO 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 attributed to improve transparency in 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 (10-11) plane was weak and there was no peak from (11-22) plane in 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 [0001] direction when heat treated in N_2 or O_2 atmospheres. In the case of N_2 heat treatment, the c-axis lattice 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 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 was 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 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 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 $10^3 \Omega\text{cm}$ (V_2O_3 : $10^{-4} \Omega\text{cm}$) 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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Figure Captions

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

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.

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.

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.

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