Conductive and transparent V-doped ZnO thin films

grown by radio frequency magnetron sputtering

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Abstract

Transparent conductive films of vanadium (V)-doped zinc oxide (VZO) were deposited by radio frequency magnetron sputtering on quartz substrates using a ceramic ZnO target with V chips. The electric, optical and structural properties of VZO thin films (V concentration of 0-4 at.%) were investigated at various substrate temperatures (T_{SUB}) from 200 to 600 °C. The resistivity sharply decreased by V doping, and the resistivity reached a minimum of about $5 \times 10^{-4} \text{ } \Omega\text{cm}$ and $1 \times 10^{-3} \text{ } \Omega\text{cm}$ for $T_{\text{SUB}}=200 \text{ } ^\circ\text{C}$ and 600 °C, respectively. It was almost constant up to V concentration of 1.0-1.5 % and gradually increased at higher V concentration. The optical transmittance ($\lambda=500 \text{ nm}$) of VZO films (V=0.9-1.1 %) drastically degraded from about 80 % to 40 % for T_{SUB} of

below 225 °C while that of ZnO films was over 83% for T_{SUB} of over 200 °C. From the dependence of growth rate and the expansion of c-axis lattice constant in the VZO film, the V configuration was considered to be the charge number of 3.

Keywords: Transparent conducting oxide

ZnO

Transition Metal

Vanadium

Radio frequency magnetron sputtering

1. Introduction

Transparent conductive oxides (TCOs) have been considered as an essential material for many optoelectronic devices such as flat panel displays. Indium tin oxide (ITO) is currently the most widely-used material for transparent electrodes due to an advantage in terms of electrical and optical properties [1, 2]. However, a stable supply of ITO is difficult because of the cost and scarcity of indium. Therefore, impurity-doped zinc oxide (ZnO) has been extensively studied as an alternative to ITO in recent years [3, 4, 5, 6]. ZnO has a wide bandgap of about 3.3 eV at room temperature, and it is

transparent to visible light. Low resistivity on the order of $10^{-5} \Omega\text{cm}$ was obtained in the case of aluminum-doped ZnO [1, 7]. Doping of transition-metal ions [8], which has a potential to take a wide variety of both valence binding configurations and coordination numbers, enables to achieve low-resistivity and high- optical transmittance characteristics, ferromagnetic property, and piezoelectricity [9-16]. In this paper, the transition metal vanadium (V) was selected as the dopant, and the effects of the substrate temperature and V concentration on characteristics of V-doped ZnO thin films (VZO) were investigated.

2. Experiment

VZO thin films (500 nm thick) were deposited on quartz substrates by radio frequency magnetron sputtering. The gas used during the deposition was Ar (1.0 Pa). Sputtering conditions of radio frequency power and the substrate temperatures (T_{SUB}) were 150 W and 150-600 °C, respectively. V was doped by co-sputtering a ceramic ZnO with V chips. V concentration was measured by X-ray fluorescence (Rigaku RIX2100 using Rh radiation). The c-axis crystalline orientation was evaluated by out-of-plane X-ray diffraction (XRD, Rigaku SmartLab using $\text{CuK}\alpha$ radiation). The X-ray source was operated at a power of 40 kVx30 mA. The cross-sectional structures were observed

by transmission electron microscopy (TEM, Hitachi HF-2000 operated at 200 kV). All samples were prepared through thinning by using grinder and ion-milling. The surface morphology was observed by atomic force microscope (AFM, Park XE-100, using non-contact mode). Electrical properties were evaluated by four-point probe measurement (resistivity) and Hall effect measurement (resistivity, carrier density and mobility). Optical transmittance was measured by using a ultraviolet-near infrared ray spectrophotometer in the range from 300 to 1100 nm.

3. Results and Discussion

3.1 Deposition

V concentration was proportionally controlled by V chip count, as shown in Fig.

1. V concentration at $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$ was slightly higher than that at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ for the same V chip counts. The dependence of growth rate of ZnO and VZO ($V=0.9\sim 1.1\text{ at.}\%$) films on T_{SUB} is shown in Fig. 2 (a). The growth rate of ZnO and VZO decreased with increasing T_{SUB} , and the decrease ratio of VZO growth rate is higher than that of ZnO. The dependence of the growth rate on V concentration in VZO films for $T_{\text{SUB}}=200$ and $600\text{ }^{\circ}\text{C}$ is shown in Fig. 2 (b). The growth rate of VZO decreased with increasing V

concentration, and its decrease ratio was higher for $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$ though having large dispersion.

3.2 Crystalline structure

The XRD patterns of ZnO and VZO films are shown in Fig. 3. In the case of $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$ (Fig. 3 (a)), the diffraction peaks from (002), (101), (102), (103) and (004) planes were observed in ZnO films. The diffraction peaks from (002) and (004) planes became weak gradually with increasing V concentration in VZO films. This means the c-axis crystalline orientation was deteriorated by V doping. Furthermore, the diffraction peaks from (101) became also very weak in VZO films of over 1.5-at.% V concentration.

In the case of $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$ (Fig. 3 (b)), intense peaks from (002) and (004) planes were observed compared to $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$. This indicates that c-axis orientation improved at high T_{SUB} . The distinctive feature is observed for V doping of 0.74 and 1.06 at.%. That is, the peak from (101) was observed, the peaks from (002) and (004) plane weakened, and the peak from (100) plane disappeared. The dependence of XRD (002) diffraction intensity on V concentration for $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ is shown in Fig. 4. As described in the explanation of Fig. 3, an anomalous zone of V concentration

(shaded area) indicating peculiar dependence was confirmed. That is, the intensity for $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$ decreased and that for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ increased, contrary to the over-all tendency (depicted by broken lines). The reason why this anomalous dependence was observed is not clear at this point. Because, there's no common feature in the change of XRD patterns on V doping concentration between for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$.

In any case, there's an unstable transition region at about 1-at.% V concentration concerning the c-axis orientation. The dependence of c-axis lattice constant on V concentration at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ is shown in Fig. 5. The c-axis lattice constant was estimated from the (002) diffraction angle. The c-axis lattice constant of crystal ZnO grown by the hydrothermal method is $5.206\text{ }\text{\AA}$. In this study, ZnO expanded slightly at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and shrank at $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$ along the c-axis. There is a dispersion of about $0.015\text{ }\text{\AA}$ but no particular dependence is observed up to about 1-at.% V doping for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$. But besides that, the c-axis lattice constant of VZO increased proportional to V concentration. The cross-sectional TEM images of VZO ($V=1.7\text{ at.}\%$) and the selected area electron diffraction (SAED) patterns are shown in Fig. 6, for (a) $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and (b) $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$. As predicted in XRD measurements, columnar grains perpendicular to the quartz substrate surface are confirmed for both T_{SUB} . As shown in enlarged images of the VZO/quartz interface, the columnar structure

was seen immediately above the interface for $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$, while, a specific orientation was not observed near the interface for $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$. Therefore, the grain size of VZO is considered to be very small in the early stage of growth at $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$, and this deteriorates the c-axis orientation. As shown in the SAED diffraction pattern, the crystalline structure for $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$ is disorderly while it is a little orderly for $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$. The [0001] diffraction spot for $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$ was more intense than that of $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$. These indicate that VZO grown at the high temperature was improved in the c-axis orientation, as seen in ZnO growth [17].

3.3 Morphology

The surface roughness caused by the columnar structure was observed from TEM images (Fig. 6). The dependence of surface roughness on T_{SUB} for ZnO and VZO films ($V = 0.9 \sim 1.1\text{ at.}\%$) and AFM images are shown in Fig. 7. The surface roughness of ZnO at $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$ was very large of about 9 nm and that at $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$ reduced by half. On the other hand, the surface roughness of VZO increased slightly with T_{SUB} and it was in the range of 4-6 nm. The grain size of VZO was obviously smaller than that of ZnO. In the case of ZnO, the grain size at $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$ was slightly smaller than that at $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$. This induced the surface roughness to decrease. However, in the case of VZO, small circular grains at $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$ coalesced into snaky lines at $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$.

Therefore, this resulted in increase of surface roughness.

3.4. Resistivity and transmittance

The dependences of resistivity, carrier density, and Hall mobility on V concentration for VZO films grown at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ are shown in Fig. 8. The resistivity decreased sharply by V doping. It was almost constant up to V concentration of 1.0-1.5 at.% and increased gradually with increasing V concentration. The lowest resistivity was $5.0 \times 10^{-4}\text{ }\Omega\text{cm}$ and $1.2 \times 10^{-3}\text{ }\Omega\text{cm}$, for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$, respectively. The carrier density of VZO films was in the range of between 10^{20} and 10^{21} cm^{-3} by V doping and the averaged carrier density for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ was about twice that for $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$. The carrier density was almost constant for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ while it decreased with increasing V doping for $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$. The maximum Hall mobility for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ was about twice that for $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$ for V concentration of about 1 at.%. This is the main reason caused the difference of minimum resistivity. The Hall mobility for $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ decreased with increasing V concentration while it was almost constant for $T_{\text{SUB}}=600\text{ }^{\circ}\text{C}$. The dependences of resistivity, carrier density and Hall mobility on T_{SUB} for VZO films ($V=0.9\sim 1.1\text{ at.}\%$) are shown in Fig. 9. The resistivity increased with T_{SUB} over $400\text{ }^{\circ}\text{C}$. In contrast, the carrier density decreased

for T_{SUB} over 400 °C. The Hall mobility decreased with increasing T_{SUB} over 200 °C. As a result, the minimum resistivity was obtained for $T_{\text{SUB}}=200$ °C. The dependences of the resistivity and the optical transmittance at wavelength of 500 nm on T_{SUB} for both ZnO and VZO films ($V=0.9\sim 1.1$ at.%) were shown in Fig. 10. The resistivity of 6.3×10^{-4} Ωcm with the optical transmittance of 78 % was obtained at the substrate temperature of 250 °C. This is the most appropriate condition to apply VZO films as TCO films at this point. The optical transmittance of ZnO film was over 83 % for T_{SUB} of over 200 °C, however, that of VZO film was drastically degraded for T_{SUB} of below 225 °C. The transmittance spectrum of VZO films ($V=0.9\sim 1.1$ at.%) for $T_{\text{SUB}}=200, 225$ and 250 °C were shown in Fig. 11. Even though the change of T_{SUB} was only 25 °C, the optical transmittance for $T_{\text{SUB}}= 225$ °C is about half of that for $T_{\text{SUB}}=200$ °C.

4. Discussion

The ionization energy of Zn^{2+} is 17.96 eV, while those of V^{2+} and V^{3+} are 14.65 and 29.31 eV, respectively [18]. Therefore, to explain high V concentration at high T_{SUB} (Fig. 1) and the decrease of growth rate of VZO (Fig. 2), it should be considered that the charge number of V is probably +3. This is, the high ionization energy must be provided to dope V into ZnO. The decrease ratio of growth rate at high T_{SUB} in VZO is also

explained by this V configuration. The reason why V^{3+} ions incorporate into the wurtzite ZnO structure despite the coordination number of 6 is not clear. But, considering that the growth rate of VZO decreased with increasing V concentration, as shown in Fig. 2 (b), this speculation brings well coincidence of the observed phenomena. The above-mentioned V^{3+} incorporation is also supported by the expansion of c-axis lattice constant in VZO (Fig. 5). The ionic radius of V^{3+} is 0.64 Å and is about 10 % longer than that of Zn^{2+} (0.6 Å). In addition, resistivity of vanadium oxide V_2O_3 is about 10^{-4} Ωcm while that of V_2O_5 is about 10^2 to 10^3 Ωcm at room temperature [19, 20]. This supports the V charge number of +3 because the resistivity of VZO films is down to 10^{-3} Ωcm. Furthermore, the increment of carrier density is well accorded with V concentration. We've tried to obtain the verification of V charge number of 3. However, through Raman scattering, photoluminescence, and X-ray photoelectron spectroscopy, the evidence was not so strong that we could actually confirm it. This is because the amount of V is too small to get data. Therefore, the charge number of 3 remains a matter of speculation at this point. We'd like to make continuous efforts to provide further confirmation. That is, this means that V atoms located at the substitutional site are univalent. The reason why the carrier density and Hall mobility of VZO decreased with increasing V over 2 at.% is considered to be caused by the formation of V-V

clusters or V_xO_y oxides.

The reason why the drastic degradation of optical transmittance in VZO films between for $T_{SUB}=200$ and $225\text{ }^{\circ}\text{C}$ caused, is not clear. This is because it is well-known that the high carrier density causes to deteriorate the optical transmittance but the carrier density for $T_{SUB}=200$ and $225\text{ }^{\circ}\text{C}$ is nearly the same.

5. Conclusion

The characteristics of VZO films deposited by radio frequency magnetron sputtering on quartz substrates have been investigated. As a result, there were some kinds incomprehensible phenomena, but relatively low resistivity and good optical transmittance were obtained for VZO of about 1-at.% V concentration.

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Figure Caption

Fig. 1. Dependence of V concentration on V chip count in VZO films for $T_{\text{SUB}}=200$ and $600\text{ }^{\circ}\text{C}$.

Fig. 2. (a) Dependence of growth rate of ZnO and VZO ($V=0.9\sim 1.1\text{ at.}\%$) films on T_{SUB} .
(b) Dependence of growth rate on V concentration in VZO films for $T_{\text{SUB}}=200$ and $600\text{ }^{\circ}\text{C}$.

Fig. 3. XRD patterns of ZnO and VZO films at (a) $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and (b) $600\text{ }^{\circ}\text{C}$ with various V concentrations.

Fig. 4. Dependence of XRD (002) diffraction intensity of ZnO and VZO films at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ on V concentration.

Fig. 5. Dependence of c-axis lattice constant of ZnO and VZO films at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ on V concentration.

Fig. 6. Cross-sectional TEM images and selected area electron diffraction (SAED) patterns of VZO (V=1.7 at.%) films for (a) $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and (b) $600\text{ }^{\circ}\text{C}$.

Fig. 7. Dependence of surface roughness on T_{SUB} for ZnO and VZO films (V=0.9~1.1 at.%) with AFM images.

Fig. 8. Dependences of resistivity, carrier density, and Hall mobility on V concentration for VZO films grown at $T_{\text{SUB}}=200\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$

Fig. 9. Dependence of resistivity, carrier density and Hall mobility on T_{SUB} for VZO films (V=0.9~1.1 at.%).

Fig. 10. Resistivity and optical transmittance at wavelength of 500 nm on T_{SUB} for both ZnO and VZO films (V=0.9~1.1 at.%).

Fig. 11. Transmittance spectrum of VZO films (V=0.9~1.1 at.%) for $T_{\text{SUB}}=200, 225$ and $250\text{ }^{\circ}\text{C}$.

Fig.1 S. Okuda et al.

Fig.2 S. Okuda et al.

Fig. 2 (a)

Fig. 2 (b)

Fig.3 S. Okuda et al.

(a) $T_{\text{SUB}} = 200\text{ }^{\circ}\text{C}$

(b) $T_{\text{SUB}} = 600\text{ }^{\circ}\text{C}$

Fig.4 S. Okuda et al.

Fig.5 S. Okuda et al.

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Fig.8 S. Okuda et al.

Fig.9 S. Okuda et al.

Fig.10 S. Okuda et al.

Fig. 11 S. Okuda et al.