Aluminum and vanadium co-doping effects on the optical and electrical properties of oriented ZnO films

Takeru Okada, Chisato Tateyama, Kotaro Hoshino Tomoyuki Kawashima and Katsuyoshi Washio
Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, 6-6-05Aramaki Aza Aoba, Aoba-ku, Sendai 980-8579, Japan
E-mail: takeru.okada@tohoku.ac.jp

Keywords: ZnO, co-doping, conductive oxides, transparent oxides

Abstract
The fabrication of bifunctional zinc-oxide thin films remains a challenge. Here, we investigate the effects of aluminum-vanadium co-doping on the electrical conductivity and the optical transparency of zinc oxide films. We find that by co-doping, aluminum enhances film transparency via zinc-vacancy-defect substitution, while vanadium enhances electrical conductivity. The roles of two dopants and defects are interesting information that is useful to applications of transparent conductive oxides.

Introduction
Transparent conductive oxides (TCOs) have potential for wide applications in display, light-emitting-diodes, and touch panels. However, the rarity of popular TCOs such as indium tin oxide (ITO) requires the search for alternative materials [1–4]. To this end, zinc oxides (ZnO) is a promising candidate because it is transparent, conductive, nontoxic, and cheap [5–8]. Further, as a direct wide-band-gap semiconductor at room temperature with a large exciton binding energy of 60 meV, ZnO has gained much attention in a various applications such as sensors, solar cell, display, light-emitting-diode, sensor, photocatalysis, and flexible devises [9–14]. Furthermore, highly oriented ZnO (without forming tilted orientation) expands the possibility of applications, such as micro-electro-mechanical-system or transducers of photoacoustic tomography probes [15].

Doping is known as useful method to modify electrical properties of ZnO. Vanadium doping is known to enhance ZnO electrical conductivity by promotion of high-valent cation doping. The carrier density of vanadium doped ZnO (VZO) are incorporated into substitutional zinc site. Since vanadium has high affinity to oxygen compared with zinc, the doping of vanadium induces the formation of oxygen vacancy defects. These oxygen vacancy defects cause n-type conductivity and reduction of optical transmittance [16–19]. Aluminum-doped ZnO (AZO) also has conductivity and optical transparency and considered as a candidate because of its low cost and wide availability [20–25]. However, the electrical conductivity of the ZnO film begins to decrease at higher concentration of aluminum due to increase in the solubility limit of dopant quantity [26]. For further improving the properties, co-doping of metal elements is considered as a solutions [27]. Aluminum and vanadium co-doped ZnO has optical transparency and electrical conductivity [28, 29], however, investigations of crystal orientation and dopant concentrations on the properties are remained issue. Here, we investigate the effects of aluminum and vanadium co-doping on the properties of ZnO. Because we expect aluminum atoms to migrate to and substitute light-absorbing defects, we aim to determine whether aluminum doping can produce an aluminum-vanadium co-doped ZnO (AVZO) that is both transparent and conductive.

Experiment
A radio frequency (RF) sputtering system was used for film deposition; the crystallographic, electrical, and optical properties have been investigated from viewpoint of dopant concentration and deposition temperature. All film depositions were performed by a RF magnetron sputtering system (EIKO, ES-350SU). Quartz was used
as a substrate. The base pressure was kept below $10^{-6}$ Pa. Argon gas was used for plasma generation and its pressure was fixed to 1.0 Pa during film deposition. The applied RF power was 150 W. The film deposition temperature was varied from room temperature to 200 °C. The distance between the target (ceramic ZnO, 99.99%) and the substrate was set to 110 mm.

Both the vanadium doping and the aluminum doping were performed by co-sputtering of the metal chips onto an erosion area of the target. The doping concentration was controlled by changing the number of metal chips on the target. The dopant concentrations were measured by x-ray fluorescence spectroscopy (RIGAKU RIX2100) using rhodium radiation. Variation of the atomic concentration measurement is within 0.1%. The film thicknesses were measured by stylus profiler (Kosaka Laboratory Ltd ST 4000-M). The film crystallinity measurements were done by x-ray diffraction (XRD, RIGAKU SmartLab) using Cu K$_\alpha$ radiation (operation power of XRD was 40 kV $\times$ 30 mA). The film thickness was set to 500 nm on quartz substrate. The Hall-effect measurements were done using self-made device under 0.4 T of magnetic field using indium electrodes. The electrical and optical properties were measured by four-probe method (ITSUBISHI CHEMICAL ANALYTECH Loresta AX MCP-T370) and ellipsometry (J.A. Woollam Co. M-2000), respectively.

**Results and discussion**

First, the roles of dopants are discussed in terms of defect geometry. Native point defects in ZnO films consist of vacancy, interstitial, and antisite defects [19]. Zinc vacancy defects introduce partially occupied state in the band gap, and therefore act as acceptors. Oxygen vacancies in ZnO films have low formation energy and are always present in low concentrations under equilibrium condition. This situation is changed when vanadium is doped [30]. In our case, the roles of the oxygen vacancy should be considered.

We do not consider the interstitial defects in this paper for the following reason. There are two types of interstitial defects: zinc and oxygen interstitials. Zinc interstitials are further categorized into two: tetrahedral and octahedral. The tetrahedral interstitial is unstable and has one zinc and one oxygen as nearest-neighbor atoms along the c-axis, affecting geometrical orientation. The octahedral is in the interstitial channel along the c-axis. These two zinc interstitials reduce the electrical conductivity in ZnO and increase carrier concentration, however, excess zinc is required for defect formation. Co-sputtering of ZnO and metallic zinc is a method to obtain the zinc interstitial contained film [31]. Oxygen interstitials forms under excess oxygen condition, and the formation energy of oxygen interstitials are high in equilibrium.

Antisite defects, where an oxygen atom wrongly occupies a site on the zinc sublattice or vice versa, has a high formation energy under equilibrium condition, which make them unlikely to form under our experimental conditions. Therefore, the defects to discuss here are focusing upon the vacancies: oxygen and zinc vacancy.

Next, the effects of aluminum and vanadium co-doping on ZnO crystallization are discussed. To investigate a substitution effect by vanadium and aluminum doping, the AVZO crystallinity is probed by XRD for different aluminum-dopant concentrations, at the fixed vanadium-dopant concentration of 1.5 at%.

Figure 1(a) shows the resulting XRD peaks at around 34° originating from the ZnO (002) diffraction. As indicated by the peak-intensity increase between the black and red curves in figure 1(a), aluminum doping at concentrations as low as 0.4 at% enhances AVZO crystallinity. The AVZO crystallinity is further enhanced by an increase in aluminum concentration from 0.4 to 0.6 at% (red and blue curves in figure 1(a)). No further crystallinity enhancement is observed when the aluminum concentration is increased to 1.3 at% (blue and green curves in figure 1(a)).

Moreover, figure 1(b) shows the ZnO (002) diffraction-peak angle shifts with increasing aluminum concentrations from $\approx$ 34.3° up. This angle shift indicates an elongation along the c-axis, suggesting the substitution of zinc-vacancy defects by aluminum atoms [32]. Figure 1(b) also indicates that the diffraction peak angle shift is saturated when 0.6 at% of aluminum is co-doped with 1.5 at% vanadium. The combined results from figures 1(a) and (b) are evidence supporting the presence of a co-doping effect.

Next, the effects of vanadium and aluminum co-doping on the properties are discussed. Figure 2(a) shows vanadium concentration dependence on the electrical resistivity and optical transmittance at the fixed aluminum doping concentration. In this paper, the average transmittance is the average of wavelength range from 450 to 800 nm. Low resistivity of approximately 0.4 m$\Omega$cm is observed at the vanadium concentration of 1.4 at%, while optical transmittance indicates monotonically decrease.

A different trend is observed in figure 2(b). This figure shows the transparency is recovered by aluminum doping and is maintained from 0.5 to 1.4 at%. The local minimum of the resistivity is observed at 0.6 at% of aluminum. Vanadium has high oxygen affinity compared with zinc, thus the doping of vanadium induces oxygen vacancy defect, resulting in the reduction of the optical transparency [33]. From here on, the investigation focuses on the effects of dopant addition by comparing AZO, VZO, and AVZO. The concentration of aluminum in AZO and vanadium in VZO are fixed at 0.6 and 1.5 at%, respectively. The dopants of AVZO is...
0.6 at% of aluminum and 1.5 at% of vanadium. When a cation (aluminum or vanadium) is doped in the ZnO, the resistivity begins to increase beyond a certain cationic dopant concentration, which is attributed to the solubility limit. Cation-cation co-doping, AVZO in this paper, is effective in increase the solubility of the total dopants beyond the individual solubility limit of the cation elements [28]. This physical view agrees with the resistivity changes in figure 2.

Figures 3(a) to (c) compare the effects of deposition temperature on the electrical properties of these films. The carrier density measurements against deposition temperature in figure 3(a), although with significant variations, shows a general decrease in density with the increasing deposition temperature. Similarly, the electrical resistivity measurements also show a variation, with a slight decreasing trend with the increasing deposition temperature as shown in figure 3(c) (for AVZO, the electrical resistivity is measured to be less than 0.5 mΩcm at 150 °C). In contrast, the mobility measurements show an increasing trend with the increasing temperature (figure 3(b)). This observation is explained by the fact that, since a higher temperature suppresses defect formation, a higher deposition temperature also reduces carrier scattering at these defect sites, thus enhancing the mobility. From figure 3, we deduce that the optimum deposition temperature window for obtaining high transmittance and low resistivity AVZO ranges between 150 °C and 175 °C.

Next, the effects of dopants on film visible-light transmittance are discussed. Figure 4(a) compares the optical transmission of AZO, VZO, and AVZO. Without aluminum, the transmittance of VZO is measured to be ~40% in visible light region. This lower transmittance is caused by the light absorbing defects at zinc sites. These
defects are compensated by aluminum doping, resulting in increases in visible-light transparency by comparable extents of AVO and AVZO in figure 4(a).

The compensation of the vacancy defects by aluminum doping is effective in the absence of vanadium, resulting in AZO has highest transmittance which is significant below 150 °C. Both AZO and AVZO have comparative transmittance in the temperature range from 150 to 175 °C (figure 4(b)). The difference between AZO and AVZO below 150 °C is explained by oxygen vacancy defects. The oxygen vacancy defects in ZnO-based film induces large optical absorption. This result indicates that the doping of vanadium promotes the oxygen vacancy formation [30, 34, 35]. The oxygen vacancy defects in ZnO-based film induces large optical absorption. This result indicates that the doping of vanadium promotes the oxygen vacancy formation [30, 34, 35]. Oxygen vacancy formation by vanadium doping occurs preferentially over the compensation by aluminum at low temperature condition, and both reactions are comparative at higher condition.
While AZO and VZO in figure 4(a) show similar absorption edge, the edge of AVZO is shifted to shorter wavelengths, indicating that AVZO has high density of the carrier. This observation is further confirmed by figure 3(a), which shows an high carrier density similar to that of the optical band gap [36–38].

Next, the effects of deposition temperature on crystallinity are discussed. Figures 5(a) to (d) show the XRD patterns of AZO, VZO, AVZO, and ZnO, respectively. The deposition temperatures are room temperature, 150 °C, and 200 °C. The ZnO (002) diffraction peak for the doped films show increase in intensity at higher temperature, indicating the migration is enhanced at higher temperatures [39]. In addition, a second diffraction peak at ~36° is observed in AZO and VZO at higher temperature, originating from ZnO (101). This tilted orientation indicates that high temperature deposition of VZO results in bi-product formation, and the tilted orientation forms easily in the absence of vanadium [40].

Figure 5(e) shows correlation between XRD diffraction intensity and optical transmittance of AZO, VZO, and AVZO. This higher crystallinity of VZO compared with AZO is explained by the enhanced adatom surface migration caused by vanadium doping [41]. As is observed, the diffraction intensity of AVZO is much higher.

**Figure 4.** (a) Transmission spectra of AZO, VZO, and AVZO films. The deposition temperature is 150 °C. (c) Average transmittance of each films.
than other films. Both AZO and AVZO have similar optical transmittance at high deposition temperature (150 °C), however, the tilted orientation in AZO is unavoidable as shown in Figure 5. Therefore, the co-doping mainly affects crystal orientation.

Due to the high oxygen affinity, the vanadium dopant induces formation of oxygen vacancy, resulting in increasing of the conductivity and reduction of transmittance. Then, the oxygen vacancy defects are compensated by aluminum doping. The zinc vacancy is complementarily compensated by both aluminum and vanadium. Thus, this co-doping-enhanced crystallinity is explained by aluminum and vanadium acting as complementary substitution species at vacancy sites, improving crystallinity and properties.

**Conclusion**

This work investigated the crystallographic, electrical, and optical properties of aluminum and vanadium co-doped ZnO. We found that co-doping enhances crystallization of ZnO due to substitution of aluminum at zinc site. This effect is most pronounced when the co-doped ZnO films are grown at 150–175 °C. These results suggested a method for producing co-doped ZnO that has both visible light transparency and high conductivity. Our investigation yielded interesting information on the formation process of conductive oxide films, which can be applied to a wide range of fields.

**Acknowledgments**

This research is supported by The Murata Science Foundation.

**Data availability statement**

The data that support the findings of this study are available upon reasonable request from the authors.

**Contributions of each author**

Takeru Okada: Writing-original draft and Investigation
Chisato Tateyama, Kotaro Hoshino Tomoyuki Kawashima: Investigation, Katsuyoshi Washio: Writing-review & editing

ORCID iDs

Takeru Okada @ https://orcid.org/0000-0002-5397-0970

References

[1] Minami T 2005 Transparent conducting oxide semiconductors for transparent electrodes Semicond. Sci. Technol. 20 S35–44
[2] Goria C R, Emanetoglu N W, Liang S, Mayo W E, Lu Y, Wraback M and Shen H 1999 Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (011)2 sapphire by metalorganic chemical vapor deposition J. Appl. Phys. 85 2595–602
[3] Park C H, Zhang S B and Wei S H 2002 Origin of p-type doping difficulty in ZnO: The impurity perspective Phys. Rev. B 66 073202
[4] Stehr J E, Johansen K M, Bjørheim T S, Vines L, Svensson B G, Chen W M and Buyanova I A 2014 Zinc–vacancy–donor complex: a crucial compensating acceptor in ZnO Phys. Rev. Appl. 2 022101
[5] Wang Z L 2004 Zinc oxide nanostructures: growth, properties and applications J. Phys. Condens. Matter 16 R829–58
[6] Janotti A and Van de Walle C G 2009 Fundamentals of zinc oxide as a semiconductor Reports Prog. Phys. 72 126501
[7] Ozgür U, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J and Morokum H 2005 A comprehensive review of ZnO materials and devices J. Appl. Phys. 98 041301
[8] Pearton S and Ren F 2014 Advances in ZnO-based materials for light emitting diodes Curr. Opin. Chem. Eng. 3 51–5
[9] Kumar M, Bhatt V, Kim J, Abhyankar A C, Chung H J, Singh K J, Bin C Y, Yun Y J, Lim K S and Yun J H H 2021 Holey engineered 2D ZnO-nanosheets architecture for suppersensitive ppm level H2 gas detection at room temperature Sensors Actuators, B Chem. 326 128839
[10] Li L, Zhai T, Bando Y and Golberg D 2012 Recent progress of one-dimensional ZnO nanostructured solar cells Nano Energy 1 91–106
[11] Zhang D, Yang T, Ma J, Wang Q, Gao R and Ma H 2000 Preparation of transparent conducting ZnO:Al films on polymer substrates by r.f. magnetron sputtering Appl. Surf. Sci. 158 43–8
[12] Fernández S and Naranjo F B 2010 Optimization of aluminum-doped zinc oxide films deposited at low temperature by radio-frequency sputtering on flexible substrates for solar cell applications Sol. Energy Mater. Sol. Cells 94 157–63
[13] Small C E, Chen S, Subbiah J, Amb C M, Tsang S W, Lai T H, Reynolds J R and So F 2012 High-efficiency inverted dithienomethane-thiophenopyrrolobenzodipyrromethene-based polymer solar cells Nat. Photonics 6 115–20
[14] Yang T L, Zhang D H, Ma J, Ma H L and Chen Y 1998 Transparent conducting ZnO:Al films deposited on organic substrates deposited by r.f. magnetron-sputtering Thin Solid Films 326 60–2
[15] Yang Y C, Song C, Wang X H, Zeng F and Pan F 2008 Giant piezoelectric d33 coefficient in ferroelectric vanadium doped ZnO films Appl. Phys. Lett. 92 012907
[16] Okada S, Matsuo T, Chiba H, Mori T and Washio K 2014 Transparent and near-infrared transparent ZnO:Al thin films grown by radio frequency magnetron sputtering Thin Solid Films 557 197–202
[17] Look D C, Hemskey J W and Sizelove J R 1999 Residual native shallow donor in ZnO Phys. Rev. Lett. 82 2552–5
[18] Hofmann D M, Pfisterer D, Sann J, Meyer B K, Tenz-Zaera R, Munoz-Sanjose V, Frank T and Penal G 2007 Properties of the oxygen vacancy in ZnO Appl. Phys. A 88 147–51
[19] Janotti A and Van De Walle C G 2007 Native point defects in ZnO Phys. Rev. B — Condens. Matter Matter. Phys. 76 1–22
[20] Fernández S, Martínez-Steel E, Gandía J J and Naranjo F 2009 Radio frequency sputtering deposition of high-quality conductive and transparent ZnO:Al films on polymer substrates for thin film solar cells applications Thin Solid Films 517 3152–6
[21] Nakrele A, Benramdane N, Bouzidi A, Kebbab Z, Medles M and Mathieu C 2016 Site location of Al-dopant in ZnO lattice by exploiting the structural and optical characterisation of ZnO:Al thin films Results Phys. 6 133–40
[22] Saini S et al 2019 Porosity-tuned thermal conductivity in thermoelectric Al-doped ZnO thin films grown by mist-chemical vapor deposition Thin Solid Films 685 180–5
[23] Tommy K N, Rafique R, Sharmin A, Bashar M S and Mahmood Z H 2018 Electrical, optical and structural properties of transparent conducting Al doped ZnO (AZO) deposited by sol-gel spin coating AIP Adv. 8 065307
[24] Urper O and Baydogan N 2020 Influence of structural changes on electrical properties of Al:ZnO films Mater. Lett. 258 126641
[25] Kuo S-Y, Chen W, Lai F, Cheng C, Kuo H, Wang S and Hsieh W 2006 Effects of doping concentration and annealing temperature on properties of highly-oriented Al-doped ZnO films J. Cryst. Growth 287 78–84
[26] Kumar K D A, Thomas R, Valanarasu S, Ganesh V, Shirk M, AliFayis S and Thirumalai J 2019 Analysis of Pr co-doped Al:ZnO thin films using feasible nebulizer spray technique for optoelectronic technology Appl. Phys. A 125 712
[27] Mallick A and Basak D 2017 Comparative investigation on cation- cation (Al-Sn) and cation- anion (Al-F) co-doping in RF sputtered ZnO thin films: Mechanistic approach Appl. Surf. Sci. 410 540–6
[28] Mallick A and Basak D 2018 Revisiting the electrical and optical transmission properties of co-doped ZnO thin films as n-type TCOs Prog. Mater. Sci. 96 86–110
[29] Suzuki S, Miyata T, Ishii M and Minami T 2003 Transparent conducting V-co-doped AZO thin films prepared by magnetron sputtering Thin Solid Films 434 14–9
[30] Kawashima T, Abe D and Washio K 2017 Investigation of a source of dominant donor in vanadium-doped ZnO films grown by reactive RF magnetron sputtering Mater. Sci. Semicond. Process. 70 213–8
[31] Singh C C and Panda E 2018 Zinc interstitial threshold in Al-doped ZnO film: effect on microstructure and optoelectronic properties J. Appl. Phys. 123 165106
[32] Kim K H, Park K C and Ma D Y 1997 Structural, electrical and optical properties of aluminum doped zinc oxide films prepared by radio frequency magnetron sputtering J. Appl. Phys. 81 7764–72
[33] Kanematsu T, Chiba H, Watanabe A, Usui S, Kawashima T and Washio K 2017 Effect of V doping on initial growth of ZnO film on c-face sapphire substrate Mater. Sci. Semicond. Process. 70 229–35
[34] Xia T, Wallmenmeyer P, Anderson A, Murovchick J, Liu L and Chen X 2014 Hydrogenated black ZnO nanoparticles with enhanced photocatalytic performance RSC Adv. 4 41654–8
[35] Guo H-L, Zhu Q, Wu X-L, Jiang Y-F, Xie X and Xu A-W 2015 Oxygen deficient ZnO$_{1-x}$ nanosheets with high visible light photocatalytic activity *Nanoscale* 7 7216–23

[36] Jin Z-C, Hamberg I and Granqvist C G 1988 Optical properties of sputter-deposited ZnO:Al thin films *J. Appl. Phys.* 64 5117–31

[37] Sernelius B E, Berggren K-F, Jin Z-C, Hamberg I and Granqvist C G 1988 Band-gap tailoring of ZnO by means of heavy Al doping *Phys. Rev. B* 37 10244–8

[38] Minami T, Nanto H and Takata S 1985 Optical properties of aluminum doped zinc oxide thin films prepared by RF magnetron sputtering *Jpn. J. Appl. Phys.* 24 L605–7

[39] Yamada T, Miyake A, Kishimoto S, Makino H, Yamamoto N and Yamamoto T 2007 Effects of substrate temperature on crystallinity and electrical properties of Ga-doped ZnO films prepared on glass substrate by ion-plating method using DC arc discharge *Surf. Coatings Technol.* 202 973–6

[40] Aryanto D, Marwoto P, Sudiro T, Wismogroho A S and Sugianto 2019 Growth of a $c$-axis-oriented Al-doped ZnO thin film on glass substrate using unbalanced DC magnetron sputtering *J. Phys. Conf. Ser.* 1191 012031

[41] Chiba H, Mori T, Kawashima T and Washio K 2015 Low-temperature heteroepitaxial growth of single-domain V-doped ZnO films on $c$-face sapphire *J. Electron. Mater.* 44 1351–6