

# Optical and electrical properties of (Al, V) co-doped ZnO films prepared by RF magnetron sputtering

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ZnO transparent conducting thin films co-doped with Al and V were prepared on quartz substrates by radio frequency (RF) magnetron sputtering. All thin films were shown to be *c*-axis oriented, exhibiting only a (002) diffraction peak. The (002) diffraction peaks move to high angle direction and the *c*-axis lattice constant decreased with increasing Al concentration. The optical transmittance in the visible region was higher than 80 %. The optical band gap of Al and V co-doped ZnO (AVZO) thin films was broadened with increasing Al concentration. The electrical properties of AVZO films were systematically analyzed. The results indicate that Al is incorporated is more effective in improving electrical properties of AVZO films. In addition, AVZO films have ferromagnetic properties and it is expected to be considered as a promising material for spintronics.

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**Keywords:** Semiconductors, Electrical properties, Optical properties

## 1. Introduction

Zinc oxide (ZnO) has been exploited for many applications, such as transparent conducting oxides, blue-violet, light-emitting diodes (LEDs), piezoelectric devices, and solar cells [1-3]. In recent years, much effort has been invested in producing diluted magnetic semiconductors (DMS) on ZnO basis for possible application in magneto- and spin-electronics [4,5]. A lot of evidences of magnetic behavior have been reported for ZnO doped with TM like Mn, Co, V, Cu and Fe, indicating significant influence of the TM ions on the ZnO- based DMS [6-9]. Theoretical calculations predicted that doping V may induce FM in semiconducting oxides [10], some work studied ferromagnetism under room temperature in V-doped ZnO [11]. The V-doped ZnO system exhibits multifunctional properties which makes it an interesting material for technological applications [12]. In single-doped ZnO, Al doped ZnO (AZO) thin films has attracted most of the researchers' attention, the transparent conducting films, AZO, with high electrical conductivity and high transparency in the visible light region have been extensively applied in electrical and optical applications such as solar cells, flat panel displays, anode contact for organic light-emitting diodes, and electro-optical devices [13].

Single elements, are the most commonly used doping agents in ZnO films, the optical and magnetic properties were studied and were very sensitive essentially to the concentration of the doping element, its nature, the

synthesis route, etc. However the optimal chemical and physical properties of current ZnO thin film have not been reached, co-doping of two elements in ZnO films are being explored to achieve this goal, such as Al and F, Al and Sn, Al and N, Al and Er, Cr and V, Ni and Cu, Co and Ni, Cr and Co, Al and Ga [14-16].

Up to now, few studies have been reported on Al and V co-doped ZnO (AVZO) films [17]. Detailed studies of the optical, electrical and magnetic properties of rf-sputtering grown co-doped ZnO films are still necessary. In this work, ZnO thin films doped with double impurities (Al,V) was studied. The effects of the Al doping concentration on the structural, optical, electrical and magnetic properties of AVZO thin films were investigated.

## 2. Experimental details

The AVZO films were dynamically deposited on quartz substrates by using RF magnetron sputtering. The targets were prepared by the conventional ceramic technology, whereby appropriate amounts of ZnO, Al<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> (99.9% purity) powders were mixed and sintered at 600 °C for 10 h to obtain ceramic targets with nominal composition of Zn<sub>0.97-x</sub>V<sub>0.03</sub>Al<sub>x</sub>O (*x*=0.01, 0.03 and 0.05). The diameter of the target is 5.0 cm. The base pressure in the chamber was <math>5 \times 10^{-4}</math> Pa and the working pressure was maintained at 0.4 Pa with a high purity Ar gas regulated by a mass flow controller. The RF sputtering power was fixed at 120 W and the substrate temperature was maintained

constant at 500 °C. The films were slowly cooled down to room temperature at the same oxygen pressure as during the deposition.

X-ray diffraction was employed to determine the phase structure of the film, performed on a D/max-Rigaku XRD diffraction spectrometer with a Cu K $\alpha$  line of 1.5417 Å and a monochromator at 50 kV and 300 mA. Field emission scanning electron microscope (FESEM JSM-6700F) was used to observe the surface morphology of samples. The optical transmittance of the films was characterized by UV-visible spectrophotometer (SP752PC). The electrical properties were measured at a room temperature by a Hall measurement system (Lakeshore's 7704 Hall system) using the standard four-probe technique. Magnetic hysteresis loops were measured by a Lake Shore 7407 vibrating sample magnetometer (VSM) with a maximum field of 10 kOe.

### 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the AVZO films grown on quartz substrate with different doping concentration. All the diffraction peaks can be indexed to a wurtzite structure of ZnO which belongs to space group ( $P63mc$ ). No diffraction peaks from any other chemical species such as yttrium oxides were detected within the sensitivity of XRD. The (002) plane diffraction peak suggests that the films have a  $c$ -axis orientation growth. By comparing the (002) peak position of the samples with different Al concentrations, it is seen that the diffraction peaks of AVZO films gradually move to high angle direction with increasing Al concentration. This demonstrates that the lattice constant of ZnO changes on incorporation of Al atoms. So  $c$ -axis lattice constant is calculated by using the Bragg's law. Fig. 1(b) shows the variation of the lattice constant and diffraction angle of the (002) peak as a function of Al content in the sample. The decrease in lattice constant of  $c$ -axis with increasing Al concentration confirms the Al substitution in Zn sites as the smaller ionic radius (0.53 Å) of Al ion compared to (0.74 Å) of Zn ion [18].

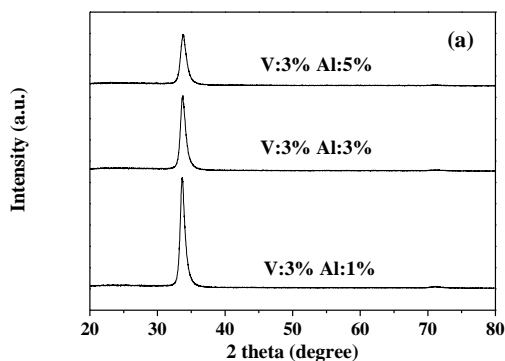


Fig. 1. (a) XRD patterns of the AVZO films grown on quartz substrate with different doping concentration.

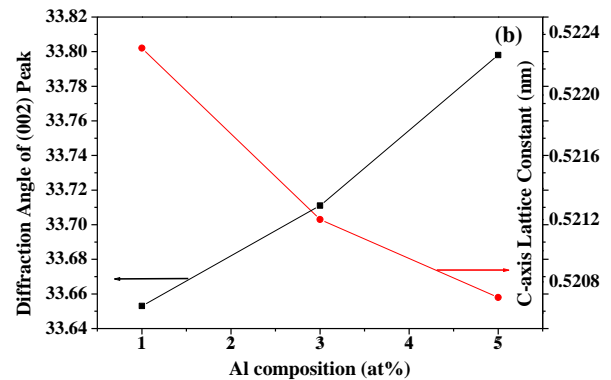


Fig. 1. (b) The variation of the lattice constant and diffraction angle of (002) peak as a function of Al content in the sample.

High transmittance at the visible-light wavelength is a key factor for the semiconducting material in a transparent device, such as the ZnO thin-film transistor. The optical transmittance of AVZO film on the quartz substrates is shown in Fig. 2(a). It can be seen that the AVZO film shows transmittance higher than about 82 % in the visible light range. The value of the optical band gap can be calculated using the fundamental absorption, which corresponds to electron excitation from the valance band to conduction band. The absorption coefficient ( $\alpha$ ) is calculated using the equation:  $\alpha = \frac{\ln 1/T}{d}$  where T is transmittance and  $d$  is film thickness. The absorption coefficient ( $\alpha$ ) and the incident photon energy ( $h\nu$ ) is related by the following equation [19-20]:  $(\alpha h\nu)^2 = A(h\nu - E_g)$  where  $h\nu$ , A and  $E_g$  are photon energy, constant and optical band gap, respectively. The direct energy gap  $E_g$  is obtained by extrapolations of the linear portion of the plots of  $(\alpha h\nu)^2$  versus  $h\nu$  [21], as shown in Fig. 2(b). A blue shift of the optical band edge was observed with increasing the Al concentration. The band gap energy was obtained by the extrapolations of the linear regions of the optical absorption edges. Fig. 3 shows the variation of band gap increased from 3.28 to 3.54 eV with increasing Al concentration from 1 % to 5 %. A linear fit to the bandgap energy versus Al concentration gives, where is the band gap energy of AVZO, is the Al concentration of AVZO thin films. The correlation between the blue shift of the absorption edge and the increased conductivity with Al doping can be attributed to the Bustein-Moss increase of the band gap with increasing carrier concentration in semiconductors [22]. The increase in  $E_g$  for AVZO thin films is possibly due to the existence of Al ions in the AVZO film structure [23].

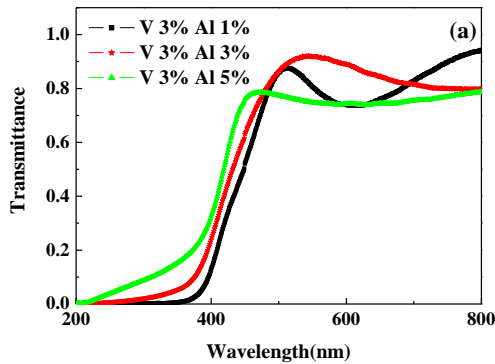


Fig. 2.(a) The optical transmittance of AVZnO film on the quartz substrates.

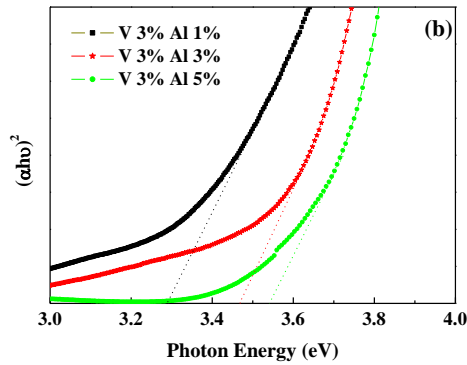


Fig. 2.(b) The plots of  $(\alpha h\nu)^2$  versus  $h\nu$  of the AVZO thin films.

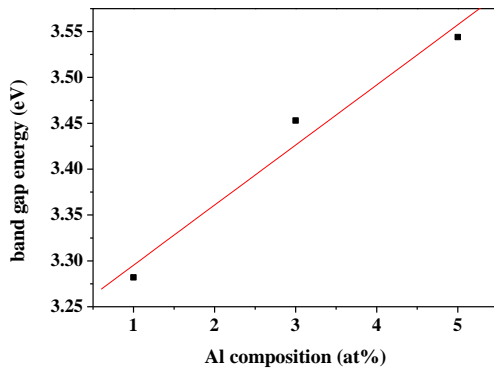


Fig. 3. The variation of band gap increased from 3.28 to 3.54 eV with increasing Al concentration from 1% to 5%.

To investigate the magnetic properties of the AVZO thin films, magnetization hysteresis measurements were performed at room temperature. The diamagnetic behavior of the sample holder was calibrated without thin film specimens, because the dilute magnetic semiconductors exhibit weaker magnetization. Fig. 4 shows the magnetization versus magnetic field ( $M-H$ ) curves for  $Zn_{0.94}V_{0.03}Al_{0.03}O$  films. The film exhibits well definite magnetization hysteresis. According to its saturation magnetization intensity, the magnetic behavior

at room temperature can be classified to dilute ferromagnetism. The ferromagnetism in the transition metals, AVZO thin films can be assumed due to the exchange coupling between localized d spins of the transition metals ions mediated by free delocalized carriers [24-25], and it is expected to be considered as a promising material for spintronics.

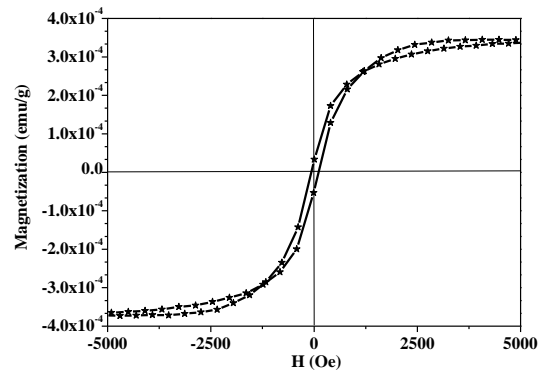


Fig. 4. The magnetization versus magnetic field ( $M-H$ ) curves for  $Zn_{0.94}V_{0.03}Al_{0.03}O$  films.

The electrical properties of AVZO films are shown in Fig. 5. Fig. 5(a) shows electrical resistivity in the AVZO films at room temperature. The resistivity of AVZO thin films decreased with increasing of Al doping concentration. The decreasing of the resistivity may attribute to the increase of Al donor concentration by substitution of  $Zn^{2+}$  sites with  $Al^{3+}$  ions in the ZnO lattices [26]. The carrier concentration and carrier mobility of the AVZO thin films are shown in Fig. 5(b) and (c). As shown in the Fig. 5 (b), the carrier concentration of AVZO thin films increased with increasing of Al doping concentration. Generally, it is known that the  $n$ -type conductivity in ZnO is due to the presence of Zn interstitials and oxygen vacancies. These defects in ZnO are easily ionized and electrons produced by ionized defects contribute to electrical conductivity. In this work, there are two reasons for increased in carrier concentration of the AVZO thin films. On one hand, the defects play an important role in AVZO thin films' electrical conductivity and act as donors in the crystal. On the other hand,  $Al^{3+}$  replaced  $Zn^{2+}$  resulted in higher electrical conductivity than pure ZnO. This phenomenon caused the increase of the carrier concentration. The carrier mobility of AVZO thin films increased with increasing of Al doping concentration in Fig. 5(c). The carrier mobility also showed the same tendency as with the carrier concentration. The decreasing of carrier mobility may be due to the decline of crystallinity which increased the number of scattering electrons in the grain boundary [26-27].

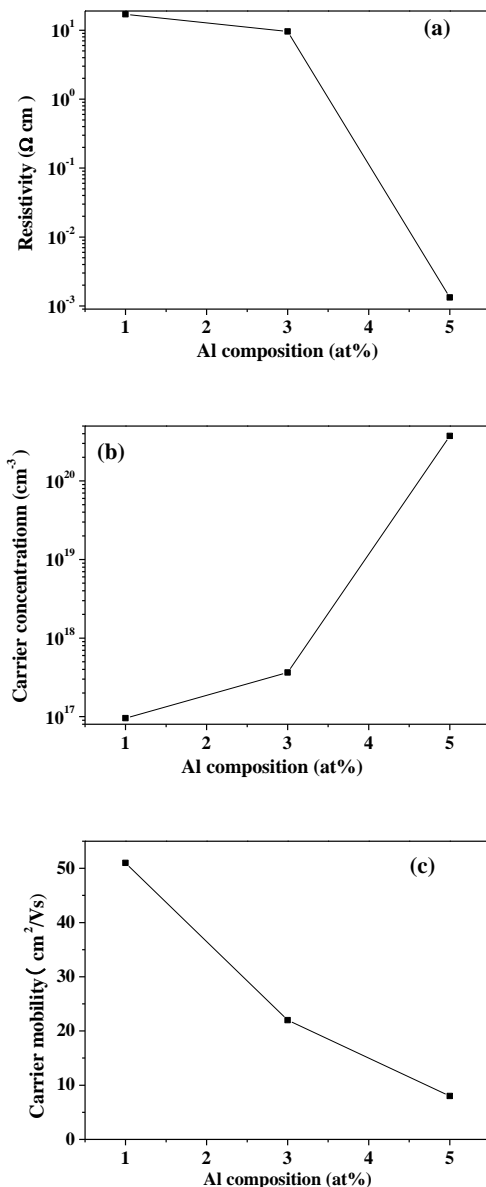


Fig. 5. The electrical properties of plots of the carrier concentration and resistivity of AVZO thin films with different Al contents. (a) Resistivity in the AVZO films at room temperature, (b) and (c) Plots of the carrier concentration and carrier mobility of AVZO films with different Al contents.

#### 4. Conclusions

In this letter, high quality AVZO thin films with good crystalline were fabricated on quartz substrates. The crystalline structures of AVZO films were systematically investigated by varying the Al compositions. The XRD patterns show that AVZO thin films have a preferential orientation along the (002) plane. The optical and electrical properties of AVZO films were characterized as increasing of the Al concentration in the films. The results show that the optical band gap broadened with Al

incorporation of AVZO thin films. In addition, the electrical resistivity of the films decreased with increasing Al concentration. AVZO thin films have ferromagnetic properties and high optical transmittance in the visible range. We believe that the capability of preparing AVZO films with high conductivity, high transparency and dilute ferromagnetism would significantly promote the development of AVZO transparent electrodes on different substrates for electronic, optical devices and spintronics.

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