

## The characteristics of Al-doped ZnO films deposited with RF magnetron sputtering system in various H<sub>2</sub>/(Ar+H<sub>2</sub>) gas ratios

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The properties of Al-doped ZnO (AZO) films were investigated as a function of H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio using an AZO (2 wt% Al<sub>2</sub>O<sub>3</sub>) ceramic target in a radio frequency (RF) magnetron sputtering system. The deposition process was done at 200 °C and in 2 × 10<sup>-2</sup> Torr working pressure and with various ratios of H<sub>2</sub>/(Ar + H<sub>2</sub>) gas. During the AZO film deposition process, partial H<sub>2</sub> gas affected the AZO film characteristics. The electron resistivity (~9.21 × 10<sup>-4</sup> Ωcm) was lowest and mobility (~17.8 cm<sup>2</sup>/Vs) was highest in AZO films when the H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio was 2.5%. When the H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio was increased above 2.5%, the electron resistivity increased and mobility decreased with increasing H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio in AZO films. The carrier concentration increased with increasing H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio from 0% to 7.5%. This phenomenon was explained by reaction of hydrogen and oxygen and additional formation of oxygen vacancy. The average optical transmission in the visible light wavelength region over 90% and an orientation of the deposition was [002] orientation for AZO films grown with all H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios.

**Key words:** Al-doped ZnO film, RF magnetron sputtering, H<sub>2</sub> gas, TCO.

### Introduction

Transparent conductive oxide (TCO) films are being more widely used recently due to the rapid development of the optoelectronic industry, with applications such as liquid crystal displays, solar cells, and organic light emitting diodes (OLEDs). Sn-doped In<sub>2</sub>O<sub>3</sub> (ITO) has been mostly used as the TCO because of its excellent conductive and transparent properties in the visible light wavelength region. However, ITO contains In, which is a limited resource in the earth and very expensive. Therefore, it is highly desirable to substitute the ITO in a TCO film in optoelectronic devices with a more common and less expensive material that has high transparency in the visible light wavelength region.

AZO is often considered as a substitution material for the ITO film as the TCO electrode in optoelectronic devices [1, 2]. ZnO (the main portion of AZO) has several advantages, such as high transparent conduction in the visible light wavelength region, low cost, non-toxicity, and abundance in the earth. ZnO has a hexagonal wurtzite structure and a 3.37 eV direct wide energy band gap.

Although much research has been done over the last few decades, it is still difficult to grow an AZO film that has sufficient conductivity and stability. Based on

experimental results, AZO material is a n-type semiconductor with zinc interstitial (Zn<sub>i</sub>) or an oxygen vacancy (V<sub>o</sub>) donor [3], and optimum doped Al. Van de Walle has reported that hydrogen is also a donor source in ZnO material [4, 5]. The hydrogen ion is stable and serves as a shallow donor with a high carrier concentration in AZO films. Also the hydrogen atom can react with oxygen and extract it from the AZO films, resulting in an increase of the electron carrier density with increasing oxygen vacancy [6, 7]. It is necessary to investigate the effect of hydrogen gas during the deposition of AZO films.

AZO film has been deposited by various deposition techniques such as sputtering [8], chemical vapor deposition [9], spray pyrolysis [10] and pulsed laser deposition systems [11]. The sputtering approach is most commonly used because the system can readily deposit on a large surface area and is fast compared with other systems [12].

In this study, the AZO films deposited on a Corning glass substrate were investigated as a function of H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio in RF sputtering system. This work aims to investigate the structural, electrical and optical properties of AZO films deposited with various H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios using four methods: the Van der Pauw method at room temperature, X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV/Visible spectrophotometer.

### Experimental

AZO films were deposited on the Corning glass (#1737)

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**Table 1.** Process conditions of the RF magnetron sputtering system for AZO film deposition.

Deposition parameter	Value
R.F. power	100 W
Ar + H <sub>2</sub> gas	25 sccm
substrate temperature	200 °C
distance between target and substrate	5 cm
rotation speed	3 rpm
deposition time	60 min.
background pressure	$5 \times 10^{-6}$ Torr
working pressure	$2.0 \times 10^{-2}$ Torr

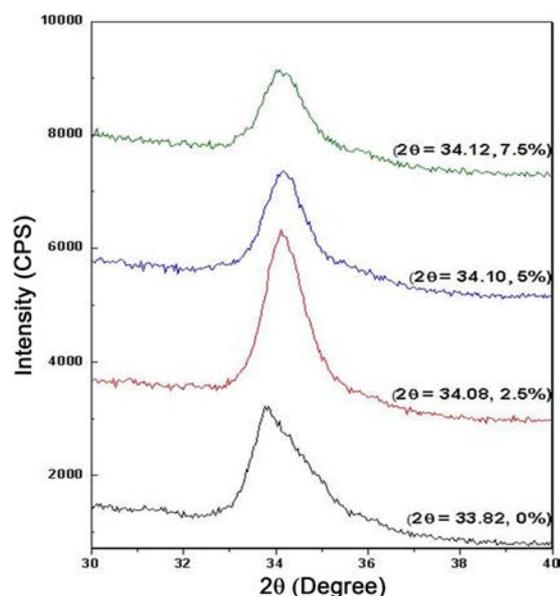
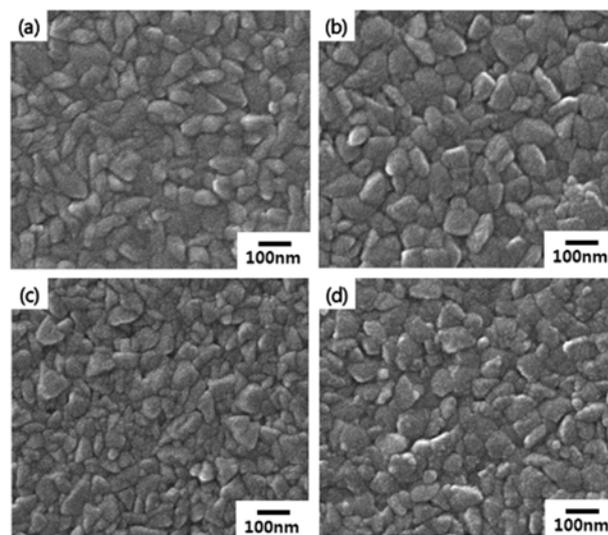
substrate at various H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios with RF magnetron sputtering system. Before the AZO film deposition process, the chamber was pumped down to  $5 \times 10^{-6}$  Torr base pressure using turbo-molecular and rotary pumps. The working pressure of AZO film deposition was maintained at  $2 \times 10^{-2}$  Torr by MFC control of H<sub>2</sub> and Ar gas. Before the deposition of AZO films, the Corning glass substrate was treated to sequential ultrasonic cleaning with acetone, ethanol and de-ionized water. Two inches of AZO (2 wt% Al doped ZnO, 99.99%) were used, and the process conditions appear in Table 1.

The thickness of deposited AZO thin film was about 200 nm. The tests of structural, electrical and optical properties were done at room temperature. The structural properties were investigated with XRD (PANalytical B.V., X'Pert-Pro) and SEM (SEM, FEI, Quanta 200) for crystalline orientation and surface appearance, respectively. The electrical property was measured for resistivity, carrier concentration and Hall mobility using the Van der Pauw method at room temperature (Ecopia, HMS-3000). The optical property was measured with a UV/Visible spectrophotometer in the 300-800 nm range (Perkin Elmer, Lambda-950).

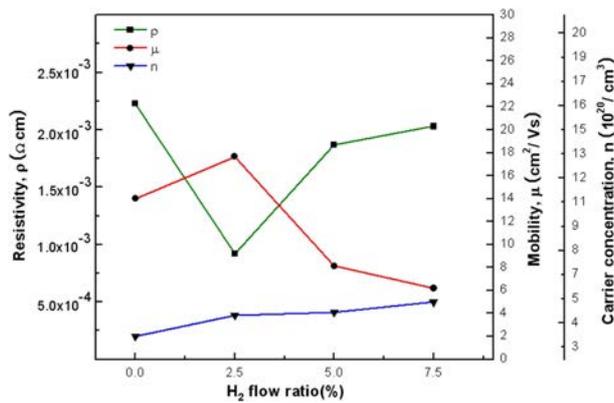
## Results and discussion

The properties of AZO films were investigated as a function of H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio in RF magnetron sputtering system. AZO films were deposited with the process conditions shown in Table 1.

AZO film is known to be deposited with a [002] preferential orientation of the c-axis perpendicular to the substrate [13]. The position of the (002) peak was investigated from XRD data as a function of the H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio. Fig. 1 shows the XRD pattern of AZO films deposited at various H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios. The (002) XRD peak was observed at around  $2\theta = 33.8^\circ$  on the AZO film grown without hydrogen gas. However the (002) XRD peak position shifted to the higher diffraction angle (2.5% H<sub>2</sub> gas:  $2\theta = 34.08^\circ$ , 5.0% H<sub>2</sub> gas:  $2\theta = 34.10^\circ$ , 7.5% H<sub>2</sub> gas:  $2\theta = 34.12^\circ$ ) with increasing H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio as shown in the

**Fig. 1.** XRD patterns of AZO films at 0, 2.5, 5.0 and 7.5 % H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios.**Fig. 2.** SEM micrographs of AZO film surface at (a) 0, (b) 2.5, (c) 5.0 and (d) 7.5% H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratios.

picture. This result was due to the fact that it's possible for oxygen to be bound to hydrogen atoms and be extracted from the AZO films during the deposition process, resulting in the shrinkage of AZO with hydrogen. The (002) XRD peak intensity of full width of the half maximum (FWHM) increased with increasing H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio with ratio above 2.5%. This relation of increasing FWHM with increasing H<sub>2</sub>/(Ar + H<sub>2</sub>) gas ratio with ratio above 2.5% indicates a degraded or amorphous crystal. It is possible to increase the grain size with a small addition of hydrogen during the process, but above a critical amount of hydrogen resulted in degradation or amorphous crystal. An appropriate amount of doping was known to improve the texture of the growing ZnO film [14].



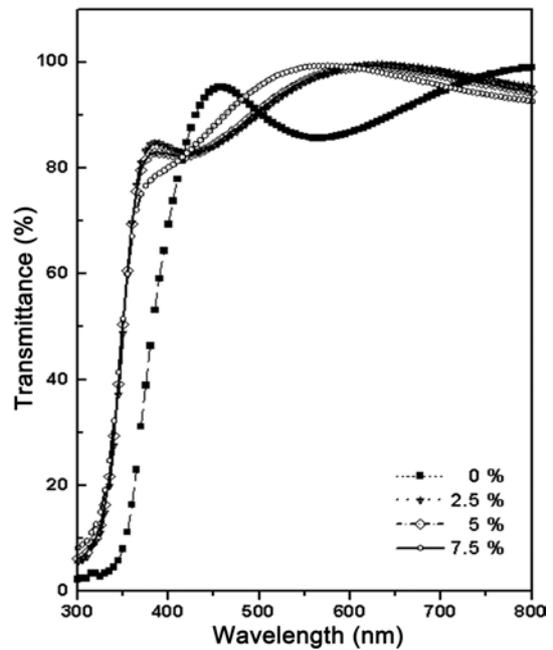
**Fig. 3.** Resistivity, electron carrier density and mobility of AZO films at 0, 2.5, 5.0 and 7.5%  $H_2/(Ar + H_2)$  gas ratios.

The SEM surface morphology of AZO thin films was almost similar with 0%, 2%, 5% and 7.5%  $H_2/(Ar + H_2)$  gas ratios as shown in Fig 2. However, the grain size of AZO film grown with 2.5%  $H_2/(Ar + H_2)$  gas ratio was the largest observed among them, and the surface morphology of AZO films grown with 7.5%  $H_2/(Ar + H_2)$  gas ratio appeared to be degraded or amorphous crystal.

Fig. 3 shows the resistivity, Hall mobility and carrier concentration of the AZO films as a function of  $H_2/(Ar + H_2)$  gas ratio. In the case of AZO films deposited in various  $H_2/(Ar + H_2)$  gas ratios, observations indicated n-type semiconductor. The resistivity was  $\sim 1.87 \times 10^{-3} \Omega\text{cm}$  (electron mobility:  $\sim 14 \text{ cm}^2/\text{Vs}$ , carrier concentration:  $\sim 3.4 \times 10^{20}/\text{cm}^3$ ) without  $H_2$  gas and decreased to  $\sim 9.21 \times 10^{-4} \Omega\text{cm}$  (electron mobility:  $\sim 17.8 \text{ cm}^2/\text{Vs}$ , carrier concentration:  $\sim 4.4 \times 10^{20}/\text{cm}^3$ ) with 2.5%  $H_2/(Ar + H_2)$  gas ratio. The electron carrier concentration slowly increased and mobility drastically decreased with increasing  $H_2/(Ar + H_2)$  gas ratio with ratio above 2.5%, respectively. And the resistivity increased again with increasing  $H_2/(Ar + H_2)$  gas ratio with ratio above 2.5%. The carrier concentration increased with increasing  $H_2/(Ar + H_2)$  gas ratio from 0% to 7.5%.

We have expected the minimum resistivity of AZO film to occur when the  $H_2/(Ar + H_2)$  gas ratio is 2.5% due to the optimum electron mobility and electron concentration compared to those of other  $H_2/(Ar + H_2)$  gas ratios. As description of XRD pattern in Fig. 1, crystalline lattice decreased with increasing hydrogen gas. This might be due to additional formation of oxygen vacancy caused by the reaction of hydrogen and oxygen, causing the extraction of oxygen from the AZO films, resulting in an increase in the electron carrier concentration. The grain grows without any hindrance from 0% to 2.5%  $H_2/(Ar + H_2)$  gas ratio, resulting in an increase in electron mobility. It seemed that hydrogen accelerated the growth of AZO grain until a certain critical amount as shown in Fig. 2(b).

The drastic decrease of the electron mobility with ratio above 2.5%  $H_2/(Ar + H_2)$  gas ratio might be



**Fig. 4.** Optical transmittance spectra of AZO films at 0, 2.5, 5.0 and 7.5%  $H_2/(Ar + H_2)$  gas ratios.

attributed to the increase in the ionized impurity and the decrease in the average crystalline size. When the amount of hydrogen added during the process was more than the critical amount, the AZO film quality deteriorated with the increase in hydrogen gas in the AZO film as shown in Fig. 2(d).

Fig. 4 shows the optical transmittance of AZO films deposited at various  $H_2/(Ar + H_2)$  gas ratios. Average transmittance of these samples in the visible light wavelength region was over 90%. The transmittance of the AZO films deposited with hydrogen gas was higher than that for the AZO film deposited without hydrogen gas at the wavelength less than  $\sim 420 \text{ nm}$  and the wavelength range from  $\sim 490 \text{ nm}$  to  $\sim 740 \text{ nm}$ . This phenomenon was reversed from  $\sim 420 \text{ nm}$  to  $\sim 490 \text{ nm}$  wavelength and above  $\sim 740 \text{ nm}$  wavelength region. The absorption edge of AZO films grown under the  $H_2 + Ar$  gas shifted to the short wavelength region, which was due to the Fermi level moving into the conduction band with the increase of the carrier concentration [15].

## Conclusions

Low resistivity and high transparent AZO film was deposited successfully by RF magnetron sputtering system using an AZO (2 wt%) target in 2.5%  $H_2/(Ar + H_2)$  gas ratio. The resistivity and mobility were measured at  $\sim 9.21 \times 10^{-4} \Omega\text{cm}$  and  $\sim 17.8 \text{ cm}^2/\text{Vs}$ , respectively. When the  $H_2/(Ar + H_2)$  gas ratio was increased by more than 2.5%, the resistivity increased and mobility decreased with increasing  $H_2/(Ar + H_2)$  gas ratio in the AZO film. The carrier concentration increased with increasing  $H_2/$

(Ar + H<sub>2</sub>) gas ratio from 0% to 7.5%. All of the AZO films were deposited in the preferred c-axis [002] direction. The average optical transmission in the visible light wavelength region was over 90%.

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