# Influence of Hydrogen on Al-doped ZnO Thin Films in the Process of Deposition and Annealing

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(Received May 13 2009, Accepted June 11 2009)

The Al-doped ZnO (AZO) films were deposited on a glass substrate by RF magnetron sputtering in pure Ar and Ar+$H_2$ gas ambient at temperature of 100°C and annealed in hydrogen ambient at the temperature range from 100 to 300 °C, respectively. It was found that either the addition of hydrogen to the sputtering gas or the annealing treatment effectively reduced the resistivity of the AZO films. When the AZO films were annealed at the temperature of 300 °C for 1hr in a hydrogen atmosphere, the resistivity decreased from $2.60\times10^{-3}$ Ωcm to $8.42\times10^{-4}$ Ωcm for the film deposited in pure Ar gas ambient. Under the same annealing conditions of temperature and hydrogen ambient, the resistivity of AZO films deposited in the Ar+$H_2$ gas mixture decreased from $8.22\times10^{-4}$ Ωcm to $4.25\times10^{-4}$ Ωcm. The lowest resistivity of $4.25\times10^{-4}$ Ωcm was obtained by adding hydrogen gas to the deposition and annealing process. X-ray diffraction (XRD) pattern of all films showed preferable growth orientation of (002) plane. The average transmittance is above 85 % and in the range of 400-1000 nm for all films.

*Keywords*: AZO, Hydrogen deposition, Hydrogen annealing

## 1. INTRODUCTION

Transparent conducting oxide (TCO) thin films are investigated for promoting efficiency of photovoltaic (PV) cells, flat-panel displays, and electrochromic windows[1]. An Al-doped ZnO (AZO) film is a promising alternative to ITO and is widely investigated for potential use as TCO that exhibits low costs, remarkable electrical conductivity, and chemical stability that the characteristics of ITO do not exhibit. Compared with ITO, AZO film is more useful in the fabrication of thin film solar cells[2].

When AZO thin films are used as an electric contact and window layer for thin film silicon solar cells, they should be required to have high transmission capabilities in a wavelength range of 400-1000 nm ($T \geq 80$ %) and low resistivity ($\rho \leq 10^{-3}$ Ωcm)[3]. It is difficult to obtain reproducible AZO thin films with these suitable properties at a low deposition temperature. However, a high deposition temperature may damage the substrates and devices. Recently, the introduction of $H_2$ gas to undoped ZnO films during film growth,[4-6] or post-heat treatment, [7-10] was performed to achieve the highly conductive films. The introduction of $H_2$ improves the electrical property of films at a low deposition temperature.

In this study, AZO thin films were deposited at the low temperature of 100 °C. The introduction of $H_2$ to the process of deposition and annealing treatment were carried out to modify the electrical properties of AZO thin films. The electrical, optical, and structural properties of films with respect to varying annealing temperature (100-300 °C) were examined. The experiment revealed that the AZO films with low resistivity can be obtained at the low growth temperature in Ar+$H_2$ ambient, without any obvious degradation in transmittance of AZO films compared with in Ar ambient.

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## 2. EXPERIMENT

AZO thin films were deposited on a glass substrate in Ar and Ar+$H_2$ respectively at the pressure of 20 mTorr and a temperature of 100 °C by RF magnetron sputtering using ZnO: $Al_2O_3$ (2 wt%) ceramic as a target. The $H_2$/ (Ar+$H_2$) percentage was maintained at 0.5 %. The substrates were ultrasonically cleaned sequentially in acetone, alcohol, de-ionized water with ending of nitrogen dry. Prior to film growth, the chamber was evacuated to $8\times10^{-6}$ Torr, and pre-sputtering time was 10 min. The RF power and deposition time were 150 W and 40 min, respectively. The as-deposited films were annealed in hydrogen atmosphere for 1 hr at various temperatures of 100-300 °C with pressure of 1 Torr. The influence of hydrogen on crystallinity of films was investigated by X-ray diffraction (XRD) and SEM Resistivity, mobility, and carrier concentration were measured by the Hall Effect in Van der Pauw configuration, and a spectrophotometer was used for measuring transmittances of the films in the wavelength range of 300-1100 nm.

## 3. RESULTS AND DISCUSSION

All the AZO films show the dominant two theta (002) diffraction peak with the crystal c-axis perpendicular to the substrate in XRD patterns. In Fig. 1, the (002) peak of AZO

 

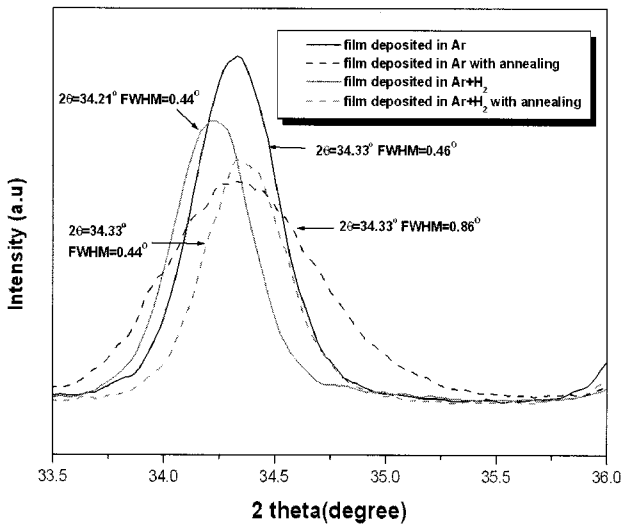


Fig. 1. XRD patterns of as-deposited and hydrogen annealed AZO films.

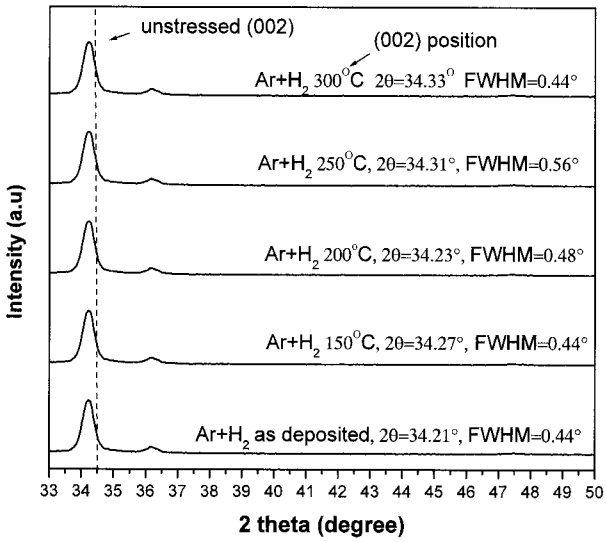


Fig. 2. XRD patterns of as-deposited and hydrogen annealed AZO films deposited in $Ar+H_2$

film deposited in Ar ambient is situated at 2θ=34.33 °, which is close to that of the standard ZnO crystal. The corresponding diffraction angle of the films prepared in $Ar+H_2$ is smaller than that in Ar, implying that the crystal c-axis of the film grown in the mixture of hydrogen was prolonged. This effect is due to hydrogen atoms situated in Zn-O bond center, making the lattice c-axis constant of films increase[11]. The full-width at half-maximum (FWHM) of the film deposited in Ar is increased after annealing at the temperature of 300 °C for 1 hr in hydrogen gas, implying that the average grain size is decreased according to the Scherrer formula. The FWHM of the film deposited in $Ar+H_2$ is unchanged. The position of the (002) diffraction peak of the film grown in $Ar+H_2$ increases after the same annealing temperature. The FWHM of the as-deposited film deposited in $Ar+H_2$ is smaller than that in Ar, implying that hydrogen is beneficial to large grain formation. Figure 2 shows the change of XRD patterns of

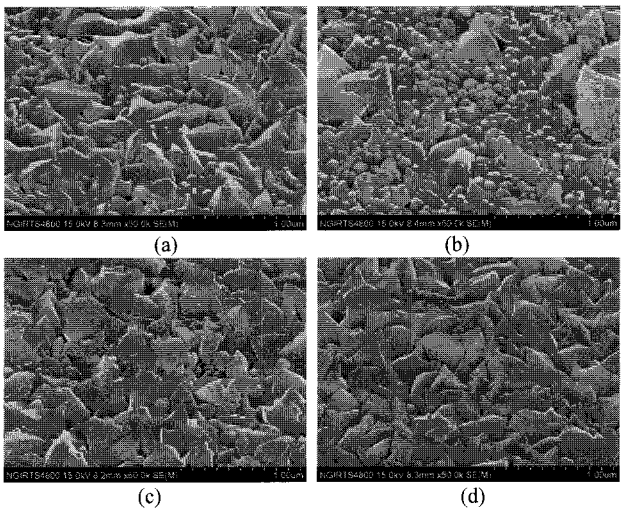


Fig. 3. Surface morphologies of as-deposited and hydrogen annealed AZO films. (a) The films deposited in Ar. (b) the films deposited in Ar with an annealing temperature of 300 °C. (c) The films deposited in $Ar+H_2$. (d) The films deposited in $Ar+H_2$ with an annealing temperature of 300 °C.

AZO films deposited in $Ar+H_2$ ambient. The position of the (002) peak shifts toward larger diffraction angles from 34.21 ° to 34.33 ° as the annealing temperature increases. It suggests the relaxation of residual tensile strain introduced in the films during the annealing process[8], indicating that as the annealing temperature increases the hydrogen escapes from grains more. From the values of FWHMs the average grain size is not evidently changed. Figure 3 shows the surface morphologies of as-deposited and hydrogen annealed films. After the annealing process, the morphology of the film deposited in $Ar+H_2$ becomes more compact and structured. The average grain size of the film grown in Ar decreases while that in $Ar+H_2$ does not change, which consists with the values of FWHMs shown in Fig. 1 and Fig. 2.

Figure 4 shows the influence of the annealing temperature on the electrical properties of AZO films. For the films deposited in Ar, the resistivity decreases from $2.60\times10^{-3}$ Ωcm for as-deposited film to $8.42\times10^{-4}$ Ωcm for 300 °C annealed film. The corresponding mobility increases from 5.4 $cm^2/V_s$ to 10 $cm^2/V_s$ and carrier concentration increases from $4.45\times10^{20}$ $cm^{-3}$ to $7.40\times10^{20}$ $cm^{-3}$. The reduction of resistivity is due to the increase of mobility and carrier concentration that is attributed to desorption of negatively charge oxygen species from the grain boundaries during the hydrogen annealing treatment[8]. For the films deposited in $Ar+H_2$, the resistivity of as-deposited films is measured to be $8.22\times10^{-4}$ Ωcm, which decreased 3 times in comparison to the films deposited in Ar. The reduction of resistivity also contributed to the increase of the mobility and carrier concentration, which is the same as the conclusion of Lee et.al.[12]. The decrease of the oxygen chemisorbed at grain boundaries induces the increases of the mobility and carrier concentration. Carrier concentration is also increased by the formation of oxygen vacancy and a small quantity of hydrogen atoms situates in Zn-O bond center[11]. The carrier concentration increases with the raising annealing temperature while the mobility decreases

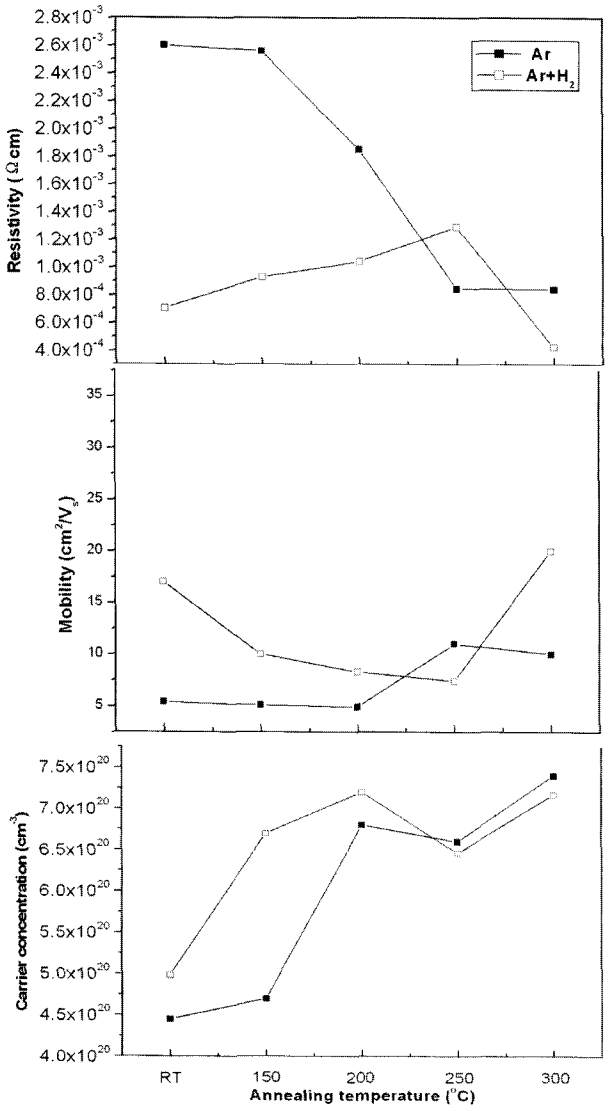


Fig. 4. Changes in electrical properties of the AZO films deposited in Ar and Ar+$H_2$ as a function of hydrogen annealing temperature.

as the annealing temperature increases to 250 °C and increases sharply at 300 °C. The boundary region can be described electrically in terms of two back-to-back Schottky barriers. These potential barriers created by charged states oppose the passage of carriers from a grain to the neighboring grains[13]. This is represented in the following:

$$Q_t = Nl_2 \quad (1)$$

Where $Q_t$ is the gap state density at grain boundaries, $N$ is the donor concentration in the bulk region, and $l_2$ is the depletion layer width. It is known that the carrier concentration $n$ in the bulk region is almost equal to the donor concentration $N$ for polycrystalline thin films. The barrier height $E_B$ should be given:

$$E_B = q^2Q_t^2/8\varepsilon N \quad (2)$$

Where $q$ is the electron charge and $\varepsilon$ is given by the product $\varepsilon_0\varepsilon_s$ which is the static dielectric constant of ZnO. The total mobility can be expressed as:

$$1/\mu = 1/\mu_{bulk} + 1/\mu_{gb} \quad (3)$$

$\mu_{bulk}$ is the mobility in the bulk of the crystal, and $\mu_{gb}$ is the mobility in the grain boundary. From the Eq. (1) and (2), the more the carrier concentration is then the higher the barrier height. There are absorbed $O^{-2}$ ions on the surface of ZnO nanocrystals during the film deposition[14,15]. In this experiment, the increasing carrier concentration leads to the increase of barrier height with the raising annealing temperature. Some $H_2$ that escaped from the grain is absorbed on grain boundary due to the low annealing temperature (under 250 °C). Those $H_2$ that absorbed on grain boundary make the barrier height increase. $\mu_{gb}$ is decreased by the increasing barrier height and the total mobility can be decreased by the Eq. (3), and the resistivity decreases accordingly. The mobility increases sharply as the annealing temperature reaches 300°C. It implies that the reaction of $ZnO+H_2=Zn_i + V_O + H_2O$ (g) will happen[7]. Therefore, the increase of oxygen vacancies and the interstitial zinc atoms enhanced the conductivity. However, the elimination of $H_2$ absorbed on the grain boundary reduces the barrier height because of a high annealing temperature, so the mobility is improved. The minimum resistivity of $4.25\times10^{-4}$ Ωcm was obtained. The AZO film with resistivity of $4.25\times10^{-4}$ Ωcm is suitable to be used as an electrical contact for silicon solar cells.

Transmittance of the as-deposited and the hydrogen-annealed AZO films are shown in Fig. 5. It can be seen that the average optical transmittance in the range of 400~1100 nm is 80 %~90 % for all the films. The optical energy band gaps of the films calculated from the absorption edges are larger compared to that of undoped ZnO (3.30 eV). The band gaps of the films deposited in Ar increase from 3.60 to 3.78 eV and those in Ar+$H_2$ mixture increase from 3.73 to 3.82 eV as the annealing temperature increases from 100 to 300 °C. This phenomenon is attributed to the Burstein-Moss effect that the optical band gap is widened with increasing carrier concentration due to the filling of the conduction band by the increase of electron carriers. The energy band gap broadening ($\Delta E_g$) can be expressed in the flowing:

$$\Delta E_g = \frac{h}{8m^*}\left(\frac{3}{\pi}\right)^{2/3} n_e^{2/3} \quad (4)$$

Where $h$ is Planck's constant, $m^*$ is the electron effective mass in the conduction band, and $n_e$ is carrier concentration. The higher the carrier concentration is then the higher band gap. Figure 5 shows the optical absorption edge of AZO films shift to the region of higher photon energy. The corresponding trends of the increase of optical band gaps are consistent with the trends of electron concentrations shown in Fig. 4. By comparing the optical band gap ranges of the films grown in Ar and Ar+$H_2$, we can obtain the implication that hydrogen is beneficial to widen the optical band gap of AZO films, which is useful to allow more short wavelength light to transmit through the films. The Blue shift of the absorption edges in transmittance spectra with an increasing annealing temperature supports the observed changes in the electrical properties(Fig. 5). The carrier

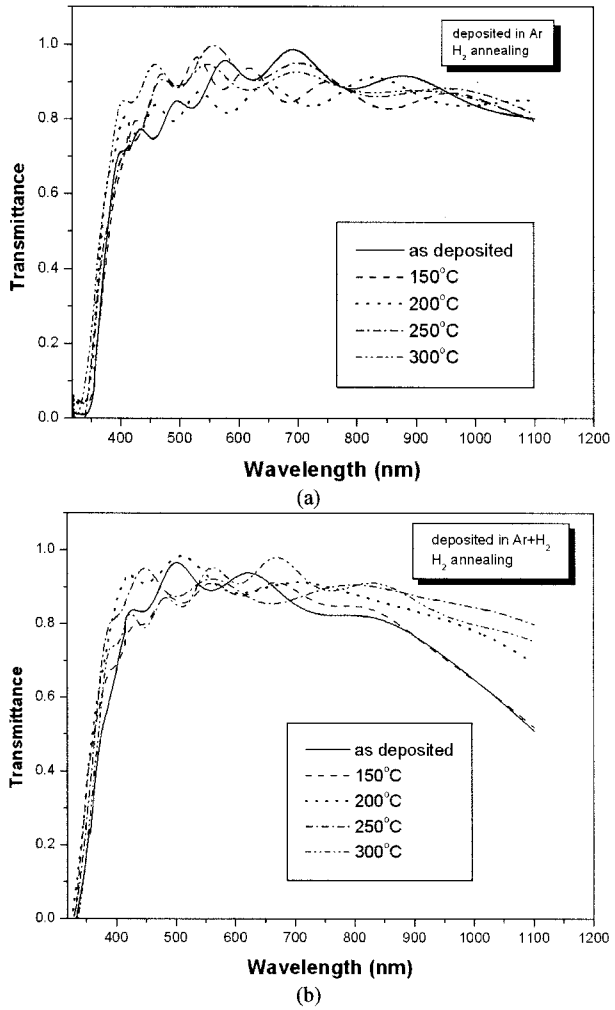


Fig. 5. The transmission spectra of the AZO films as-deposited and hydrogen-annealed for various annealing temperature.
(a) The films deposited in Ar. (b) The films deposited in Ar+$H_2$.

concentration of the film deposited in Ar also increases by the hydrogen annealing treatment. The results suggest that the electrical properties of the AZO films can be improved by controlling the temperature of annealing treatment in hydrogen ambient without changing in the transmittance of the films.

## 4. CONCLUSION

The crystallites of all the AZO films have a preferential growth orientation of (002) plane parallel to the substrate surface. After annealing in hydrogen gas, the grain size of the film deposited in Ar decreases and the microstructures of the film deposited in Ar+$H_2$ becomes more compact and shows a textured structure. For the films deposited in Ar+$H_2$, the resistivity of as-deposited films decreases 3 times compared to the films deposited in Ar. The hydrogen annealing process reduces the resistivity of the film grown in Ar to $8.42\times10^{-4}$ $\Omega$cm and the film grown in Ar+$H_2$ to $4.25\times10^{-4}$ $\Omega$cm. We obtained the lowest resistivity by adding hydrogen gas to the deposition and annealing process. Hydrogen gas was found effective for the whole process. The transmittance does not decrease by introducing $H_2$ to the deposition and annealing process. The technique can be used to produce transparent conductive windows for photovoltaic devices.

## ACNOWLEDGEMENTS

This research was supported by Wonkwang University in 2009.

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