Influence of the gas flow of Argon and the distance between substrate and plasma on properties of Al-doped zinc oxide films

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Abstract. Al-doped ZnO (ZAO) films were deposited by DC magnetron sputtering using facing zinc oxide targets at room temperature and in argon atmosphere. The effects of the gas flow of Argon and the distance between substrate and plasma on the properties of the ZAO thin films were characterized by several techniques. By optimizing the craft of preparation, the electrical resistivity as low as 3.3×10⁻⁴ Ω·cm and the optical transmittance over 80% in the visible range were obtained for these thin ZAO films. Therefore, the ZAO thin films were suitable for the window layers of n-i-p thin film solar cells or transparent conductive films.

1. Introduction
The group III metal-doped ZnO materials, particularly the Al-doped ZnO (ZAO), have been studied with a focus on application to sensors, transparent electrode display, heat mirrors and transparent conducting oxide (TCO) coatings for solar cells [1–5]. ZnO:Al films have been prepared by several deposition techniques such as metal organic chemical vapor deposition, photo-MOCVD, reactive evaporation, spray pyrolysis, sol-gel process, dc and rf sputtering [6–16]. The latter method is the most widely used technique for preparing ZAO films. Facing targets magnetron sputtering was used because of their desirable features, such as higher deposition rate and film uniformity. Naturally, this technology was applied rarely and the investigation was not detailed. Therefore, it is meaningful to study the influence of the gas flow of Argon and the distance between substrate and plasma in order to obtain ZAO films with optimum properties using facing targets magnetron sputtering.

In this work, the ZAO films were grown by DC magnetron sputtering system using two facing Al-doped ZnO (with Al atom concentration of 2.5%) ceramic targets in an argon atmosphere at room temperature. We investigated the gas flow of Argon and the distance between substrate and plasma dependence of the properties of the ZAO thin films.

2. Experimental procedures
The ZAO films were deposited on 45mm×92mm×2mm soda–lime glass substrates by a magnetron sputtering system in which two targets were situated facing each other. Each target was sintered from zinc oxide (99.99%) and aluminum oxide (99.99%) mixture with aluminum content of 2.5 wt%. The substrate was placed outside the plasma to reduce the direct bombardment and thus to improve film
uniformity \cite{17, 18}. When the base pressure was $3 \times 10^{-3}$ Pa, Ar (99.999\%) was introduced into the chamber with a pressure of 0.6 Pa. The DC sputtering current applied on both targets was kept at 400 mA. The thickness of all the ZAO films was maintained at 800 nm by controlling the deposition time. Film thickness was measured using a surface profiler (AMBIOS XP-2). The structure of the films was characterized by X-ray diffractometer (XRD, Philips PANalytical X'Pert, CuKa). Electrical resistivity, mobility and carrier concentration were measured using a Hall automatic measuring system (ACCENT HL5550 LN2, USA). Because the ZAO films are one kind of n-type high degenerate semiconducting material with high conductivity, there is no need to plate metal electrodes on the samples measured by the machine above. The optical transmission spectra of films were recorded by the UV–VIS–IR pectrophotometer (VARIAN CARY5000).

3. Results and discussion

3.1. The distance between substrate and plasma dependence of structural, electrical and optical properties of the ZAO thin films

The distance between substrate and plasma is from 0 mm to 35 mm. The gas flow of Argon is 40 sccm.

3.1.1. Structure analysis.

XRD patterns of ZAO films deposited on different distances are shown in Fig. 1. All ZAO films show (002) and (004) diffraction peaks, indicating a polycrystalline structure with a preferential orientation of c-axis perpendicular to the substrate. Grain pitch and (002) peak’s angle of ZAO as a function of the distance between substrate and plasma are shown in Fig. 2. As the distance between substrate and plasma increases, (002) peak’s angle of ZAO films decreases gradually, and depart from (002) peak’s angle of ZnO films ($34.45^\circ$); Grain pitch of ZAO films increases gradually, and departs from that of ZnO film (0.2603 nm).

This means that: as the distance between substrate and plasma increases, Lattice distortion intensifies and residual stress of the films increases.

The crystal size of ZAO films with different distance can be evaluated from the full-width at halfmaximum (FWHM) of (002) peak using Scherrer’s formula \cite{19}:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

(1)

Where $\lambda$, $\theta$ and $\beta$ are the X-ray wavelength, Bragg diffraction angle and FWHM, respectively.

The calculated values of crystal sizes of ZAO films are about 33 nm.

Figure 1. XRD patterns of ZAO films deposited at different distance
Deposition rate of ZAO films as a function of the distance between substrate and plasma is shown in Fig.3. Deposition rate of ZAO films decreases linearly with the increase of the distance.

![Graph showing deposition rate vs distance](image)

**Figure 3.** Deposition rate of ZAO films as a function of the distance between substrate and plasma

### 3.1.2. Electrical properties.

The resistivity and hall mobility of the ZAO films deposited at various distances between substrate and plasma are shown in Fig. 4. The resistivity decreases to a minimum of $3.3 \times 10^{-3} \Omega \text{cm}$ at 14mm.

The hall mobility increases with the distance between substrate and plasma, and reaches a maximum of 24.2 cm$^2$/Vs at 14mm, and then decreases as the distance increases to 35mm. The carrier concentration has the same trend with the carrier mobility. The improvement of conductivity is caused
by the improved crystallinity and decreases amount of interstitial atoms. When the distance between substrate and plasma is short, the deposition rate is so fast that the ions sputtered are covered by the latter ones before they move to the lowest position of energy at the substrate and trapped in the non-equilibrium position. So the film’s crystallinity is poor. As the distance increases, the deposition rate decreases gradually, the crystallinity improves, many carriers are released from the poorly crystallized areas, thus causing the increase in carrier concentration and mobility. However, when the distance is too long, energies of the ions sputtered are so low that they aren’t able to shift to the lowest position of energy at the substrate. That makes the increase of amount of interstitial atoms and defects.

### 3.1.3. Optical properties

The effects of the distances between substrate and plasma on optical properties are depicted in Fig. 5. A transmission of all films reached nearly 80% in visible region. In this work, the transmission of the ZAO film prepared at 0mm was lower than that at 14mm at near-UV spectral region but higher at infrared spectral region. Furthermore, there is a “blue-shift” phenomena found, which is caused by effect of Burstein-Moss[20]. The transmission of films deposited at 14mm is over 80% in visible region, which was mainly due to the good crystallinity. The fluctuation in Fig. 5 is caused by interference effect of the incident light, it means that the uniformity of the film deposited is good.

![Figure 4](image1.png)

**Figure 4.** Resistivity and hall mobility of the ZAO films as a function of the distances between substrate and plasma.

![Figure 5](image2.png)

**Figure 5.** Transmission of the ZAO as a function of the wavelengths at the different distance between substrate and plasma.
3.2. The effects of the gas flow of Argon and the distance between substrate and plasma on the properties of the ZAO thin films
The gas flow of Argon is from 10sccm to 50 sccm. The distance between substrate and plasma is 35mm.

3.2.1. Structure analysis.
XRD patterns of ZAO films deposited on different gas flow of Argon are shown in Fig. 6. All ZAO films show (002) and (004) diffraction peaks, indicating a polycrystalline structure with a preferential orientation of c-axis perpendicular to the substrate. As the gas flow of Argon increases, (002) peak’s angle of ZAO films departs from (002) peak’s angle of ZnO films(34.45°); Grain pitch of ZAO films departs from that of ZnO film(0.2603nm). Diffraction angle’s change origins from the substitute Al $^{3+}$ for Zn $^{2+}$. The atomic radius of Al $^{3+}$ is smaller than that of Zn $^{2+}$, this causes the Lattice distortion and residual stress of the films. If we anneal the film in Argon, that situation will improve. Grain size is about 33nm.

![Figure 6. XRD patterns of ZAO films deposited on different gas flow of Argon](image)

3.2.2. Electrical properties
ZAO is one kind of n-type and wide band gap semiconducting oxide. Carriers in the film are mostly from the absence of oxygen and the substitute Al $^{3+}$ for Zn $^{2+}$. The latter one is the main source of carriers. So the carrier concentration is dependent on Al concentration in the film of ZAO. The gas flow of Argon has important influence on the absence of Oxygen and the substitute Al $^{3+}$ for Zn $^{2+}$.

The resistivity and carrier concentration, deposition rate of the ZAO films deposited at various gas flows of Argon is shown in Fig. 7, Fig. 8 respectively. The resistivity decreases with the gas flow of Argon and reaches a minimum of $4.26 \times 10^{-4}$ $\Omega \text{cm}$ at 20sccm, and then increases as the gas flow increases to 50sccm. The carrier concentration has the opposite trend with the resistivity. It reaches a maximum of $1.8 \times 10^{21} \text{cm}^{-3}$ at 20 sccm. However, the hall mobility has the opposite trend with the carrier concentration, it reaches a minimum of 8.16 cm$^2/(Vs)$ at 20sccm. It is probably because the scattering between the carriers which cause the decrease of mobility. The improvement of conductivity is caused by the improved crystallinity and decreases amount of interstitial atoms. When the gas flow of Argon is small, the deposition rate is so low that energies of the ions sputtered are too low to make them shift to the lowest position of energy at the substrate. So the crystallinity of film is poor. As the gas flow increases, the deposition rate increases gradually, the crystallinity improves, then carrier concentration increases and the scattering between the carriers causes the decrease of mobility. However, when the gas flow is too big, the deposition rate is too fast, the ions sputtered were covered by the latter ones before they moved to the lowest position of energy at the substrate. So the film’s
crystallinity is poor. That makes the increase of amount of interstitial atoms and defects. So the changes mentioned above exist.

4. Conclusion
Through extensive research on the performance of ZAO films, high-quality ZAO films by controlling the distance between substrate and plasma and the gas flow of Argon in fabricated process were obtained. All ZAO films exhibit a strong (002) c-axis oriented normal to the substrate. When the distance between substrate and plasma increased from 0 to 35 mm, the lattice distortion intensifies and the residual stress of the films increase; the deposition rate of ZAO films decreases linearly, and the resistivity decreases to a minimum and then increases, while the hall mobility has an opposite tendency with the resistivity. At 14mm, the ZAO film was obtained with a minimum resistivity of
3.3×10^{-4}\ \Omega \text{cm}, a maximum hall mobility of 24.2 cm^2/Vs and a transmission over 80% in the visible range. When the gas flow of Argon increased from 10 to 50 sccm, the deposition rate of ZAO films increases, the resistivity decreases to a minimum and then increases, however, the carrier concentration has the opposite trend with the resistivity. At 20 sccm, the ZAO film was obtained with a minimum resistivity of 4.26×10^{-4}\ \Omega \text{cm}, a maximum carrier concentration of 1.8×10^{21}\text{cm}^{-3} and a transmission over 80% in the visible range. Therefore, the ZAO thin films are suitable for the window layers of n-i-p thin film solar cells or transparent conductive films.

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