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# Efficient Light Trapping from Nanorod-Like Single-Textured Al-Doped ZnO Transparent Conducting Films

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**Abstract:** Nanorod-like single-textured Al-doped ZnO (AZO) transparent conducting films were prepared by the simple hydrothermal growth of AZO nanorods on AZO seed layers. The structures, morphologies, optoelectronic properties and light trapping abilities of the AZO films were investigated. The morphological changes of single-textured AZO films depending on growth temperature were shown. Above all, the relation between light trapping abilities and surface morphologies of the single-textured AZO films was studied in detail. The nanorod-like single-textured AZO films prepared at 100 °C exhibited low resistivity, high total transmittance and remarkable enhancement of haze value, which can be acted as transparent electrodes for improving the conversion efficiency of Si-based thin film solar cells.

**Keywords:** Al-doped ZnO; transparent conducting films; texture; light trapping ability



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## 1. Introduction

Recently, solar cells have been applied extensively in various fields. Among these solar cells, Si-based thin film solar cells have good application prospects due to their unique advantages, such as low cost and simplified technological process. As we all know, improving the conversion efficiency has great practical significance for solar cells. As the front electrodes of solar cells, transparent conducting films with light trapping structures can enhance the light scattering ability and increase the path of incident light in the absorption layer, which could effectively improve the conversion efficiency of Si-based thin film solar cells [1,2].

Al-doped ZnO (AZO) transparent conducting films are more highly desirable for their potential applications compared with $SnO_2$:F and $In_2O_3$:Sn films, because they have good characteristics, such as abundant resources, non-toxicity, low cost and stability under a hydrogen plasma environment [3,4]. Up to now, the crater-like single-textured structures of AZO films, as mainstream light trapping structures, can be obtained by various methods, including wet chemical erosion after sputtering deposition and plasma etching, etc. And the textured AZO films present definite light trapping abilities. In the wet chemical etching process, different etchants are adopted, such as HCl, KOH and $NH_4Cl$ [5–7]. On this basis, the crater–crater-like double-textured AZO films obtained through multiple deposition and etching process have been prepared and can improve the light trapping abilities in the whole range of solar spectrum. But the process would result in the complex and high-cost preparation [8,9]. Similarly, the plasma etching process also has certain requirements for the experimental equipment [10]. As a matter of fact, the textured surface of AZO films can also be provided by nanorod array structures. AZO nanorod structures can be grown by the hydrothermal method, which has many advantages, such as low growth temperature and simple process. Although the nanorod structures of AZO films have already been obtained by many researchers [11–13], the light trapping properties of AZO transparent conducting films with nanorod structures have not been investigated yet. Therefore, in this study, we would study the light trapping abilities of nanorod-like single-textured AZO films prepared by the simple hydrothermal method in detail. The systematic study on the effect of the morphologies of nanorod-like single-textured AZO films on the light trapping properties is significant.

In this work, nanorod-like single-textured AZO transparent conducting films were prepared. The preparation of nanorod-like single-textured AZO films started with the sputtering deposition of AZO seed layers, followed by the simple hydrothermal method to grow AZO nanorods on the AZO seed layers. The morphologies, structures, optoelectronic properties and light trapping abilities of AZO films prepared at different hydrothermal growth temperatures were investigated. In particular, the surface morphological changes of single-textured AZO films depending on growth temperature were observed and presented. By controlling the morphologies of AZO films, the relation between light trapping abilities and morphologies of the nanorod-like single-textured AZO films was studied systematically.

## 2. Experimental

Firstly, AZO seed layers were prepared on glass substrates by direct current pulse magnetron sputtering with a ZnO:$Al_2O_3$ (98 wt%:2 wt%) ceramic target (Yanchuang, Shenzhen, China, 99.99%). Then, high purity Ar was introduced to the chamber, and the sputtering power of 350 W was maintained. 500-nm-thick AZO films, as seed layers, were obtained for the latter procedures.

Subsequently, AZO nanorods were grown on the surfaces of AZO seed layers directly by the hydrothermal method. $Zn(CH_3COO)_2 \cdot 2H_2O$ (Sinopharm, Shanghai, China, AR), $C_6H_{12}N_4$ (Sinopharm, Shanghai, China, AR) and $Al(NO_3)_3 \cdot 9H_2O$ (Sinopharm, Shanghai, China, AR) were directly used without further purification. As precursors, the aqueous solutions contained $Zn(CH_3COO)_2 \cdot 2H_2O$ and $C_6H_{12}N_4$ in equal concentrations of 0.1 M. Concurrently, $Al(NO_3)_3 \cdot 9H_2O$, as a dopant source, was added into the aqueous solutions. The doping ratio for [Al]/[Al + Zn] was 2 mol%. After stirring for 60 min, the mixed solution was slowly poured into a Teflon-lined autoclave apparatus with a capacity of 100 mL. And then, the autoclave was sealed and put into an oven for growing at different temperatures for 3h. After growing, the autoclave was cooled to room temperature naturally. The single-textured AZO films prepared at 70 °C, 80 °C, 90 °C and 100 °C were denoted as T-70 °C, T-80 °C, T-90 °C and T-100 °C, respectively.

The morphologies of the AZO films were analyzed by field emission scanning electron microscopy (FESEM, SIGMA HD, Zeiss, Germany) equipped with energy dispersive X-ray spectroscopy (EDX). The crystalline structures and crystallographic properties of the AZO films were identified by X-ray diffraction (XRD, X'Pert, PANalytical, The Netherlands) within a 2θ range of 10°–90°. The total and diffuse transmittance were examined by a U-3310 ultraviolet–visible spectrophotometer with an integrating sphere. A Hall measurement system (HL5500PC, Accent, UK) was utilized to measure the resistivity, carrier concentration and mobility of the AZO films.

## 3. Results and Discussion

### *3.1. Structural Properties*

In order to probe the crystal structure and phase purity of the AZO films, the XRD measurement is performed. Figure 1 displays the XRD patterns of the AZO samples prepared at various hydrothermal growth temperatures. All the samples show a high strength and acuminate diffraction peak at 2θ of about 34° and a small peak at near 72°, which correspond to the (002) and (004) planes, respectively. All the diffraction peaks are assigned to wurtzite type ZnO with preferential c-axis orientation, as reported in the JCPDS file (JCPDS No. 36-1451) [14]. No characteristic peaks for impurities such as $Al_2O_3$ are observed. Meanwhile, as the growth temperature rises from 70 °C to 100 °C, the intensity of the (002) peak is enhanced gradually, indicating that the crystalline quality is getting better and better. Furthermore, it also implies that the increase of hydrothermal growth temperature might impel the atoms to move and arrange the AZO crystal growth along the (002) orientation, and this growth trend could also be observed from the following SEM results.

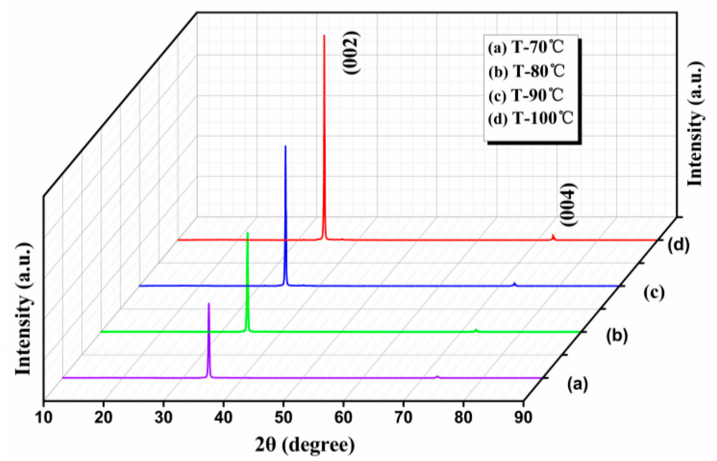


**Figure 1.** XRD patterns of all the Al-doped ZnO (AZO) films.

### *3.2. Surface Morphology*

The surface SEM images of the AZO films obtained at different hydrothermal growth temperatures are presented in Figure 2a–d, in which we can see that the surface morphologies of the AZO films are transformed in response to the growth temperature obviously. Figure 2e depicts the cross-sectional view SEM image of the T-100 °C sample, in which we can clearly see the nanorod-like structures with lengths of about 1 μm. The EDX spectrum of the T-100 °C sample is exhibited in Figure 2f, which indicates that Zn, O and Al elements exist in the films. At a low temperature of 70 °C, as shown in Figure 2a, the surfaces of the AZO films show irregular polygonal network-like structures. This may be because the nucleation and growth rates of AZO nanorods are relatively slow at low temperature, consequently suppressing the growth along the c-axis orientation of nanorods. As the growth temperature is increased to 80 °C, as Figure 2b depicts, it can be observed that the irregular polygonal network-like AZO structures are reduced and the nanorod-like structures appear. Subsequently, when increasing the temperature to 90 °C, AZO nanorods with hexagonal shape predominantly grown along the c-axis orientation can be clearly observed from Figure 2c. Furthermore, we can observe that the AZO nanorods are relatively uniform in size, resulting in a dense surface. Figure 2d shows the surface SEM image of the AZO films prepared at 100 °C. The AZO nanorods are still grown perfectly along the (002) plane, with diameters of 70–200 nm. From the above results, with the increase of growth temperature, the morphologies transform from network-like to nanorod-like structures, which corresponds to the increasing intensity of the (002) peak from the XRD results. However, at the growth temperature of 100 °C, we can see that some parts of the nanorods become bitty, and more gaps are observed among the nanorods, as presented in Figure 2d. According to the literature, the competition between growth and erosion of AZO nanorods occurs during the hydrothermal reaction [15]. As the growth temperature rises to a high temperature of 100 °C, the process of decomposing $C_6H_{12}N_4$ to produce $OH^-$ is promoted, and the growth and dissolution rates of AZO nanorods are decreased and increased, respectively. The erosion occurs on the polar plane (002) plane and side boundary of the AZO nanorods [15,16]. This process causes not only the appearance of the gaps among the nanorods, but also the uneven and rough surfaces on the films. The transformation of the observed morphology from network-like to nanorod-like structures will greatly affect the light trapping abilities of AZO films, which will be proved in the later haze results.

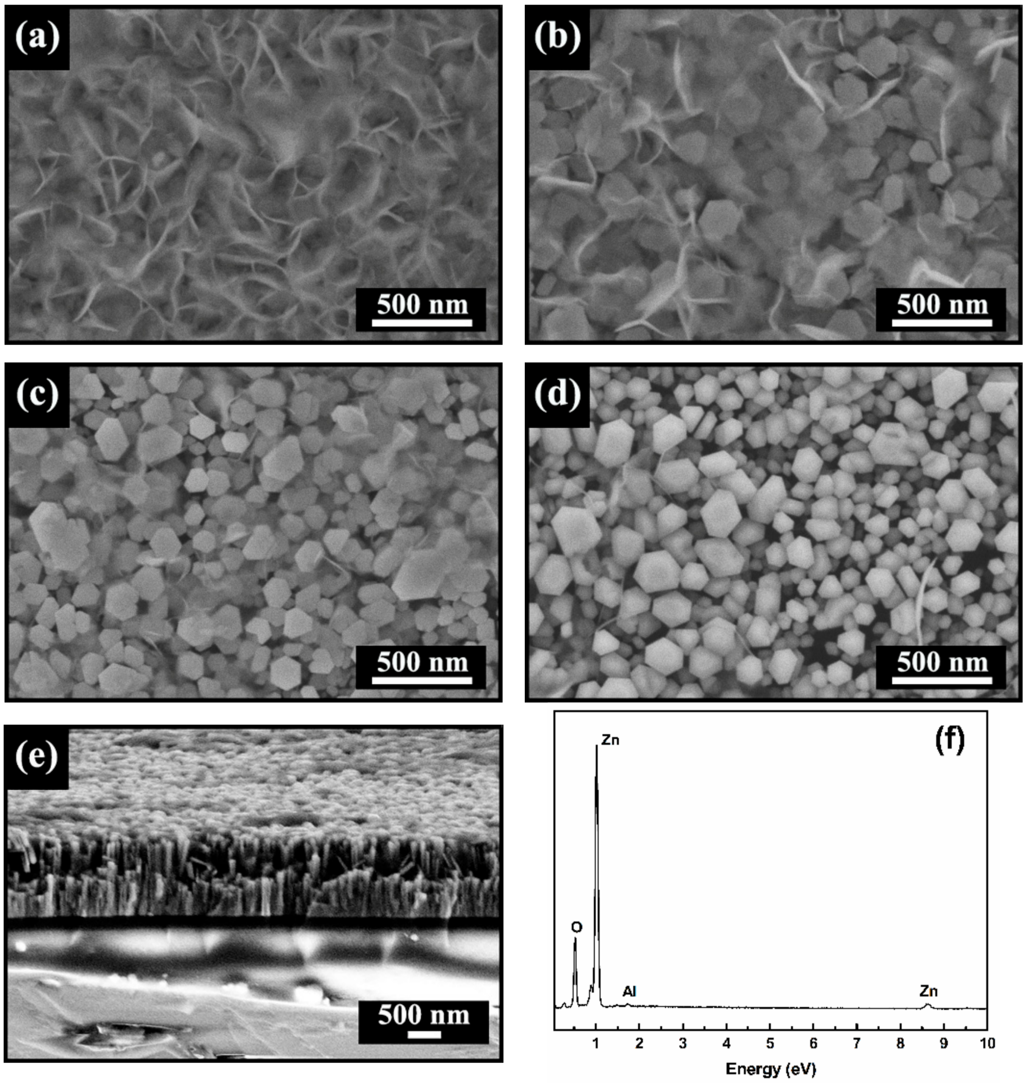


**Figure 2.** Top view SEM images of the single-textured AZO films prepared at different growth temperatures: (**a**) 70 °C, (**b**) 80 °C, (**c**) 90 °C, and (**d**) 100 °C. (**e**) Cross-sectional view SEM image of the T-100 °C sample. (**f**) EDX spectrum of the T-100 °C sample.

### 3.3. Optical Properties

Higher average transmittance value in the visible range (400–800 nm) is advantageous for the transparent conducting films used as front electrodes. The effect of growth temperature on the optical properties of single-textured AZO films is studied. Figure 3 shows the total (specular + diffused) transmittance spectra of AZO films prepared at different hydrothermal temperatures. The highest average transmittance value is 88% in the visible range for T-70 °C sample, whereas the minimum average transmittance value is 82% for T-100 °C sample. Without the influence of glass substrates (transmittance of ~90%), the average total transmittance values of all the AZO films can be above 90%, which are helpful for the performance of solar cells. Though the average transmittance value decreases with increasing the growth temperature, it can still satisfy the application of transparent conducting films. Meanwhile, the absorption edge is red shifted in the ultraviolet region, which may be due to the increase of film thickness.

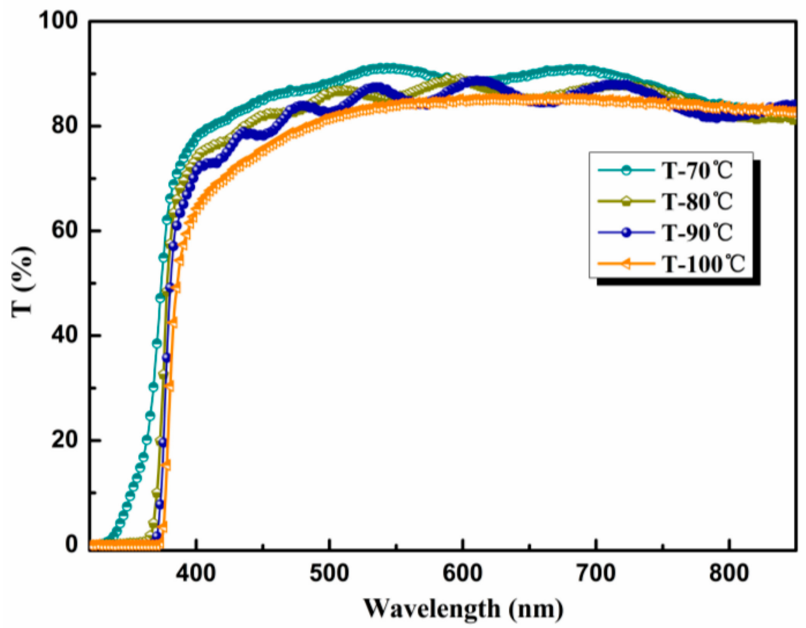


**Figure 3.** Total transmittance spectra of all the AZO films.

### 3.4. *Light Trapping Properties*

The light trapping ability is important for the photoelectric conversion efficiency of solar cells. In order to study the relation between light trapping abilities and morphologies, the haze value determined by the total and diffuse transmission ($H_T = T_{diffuse}/T_{total}$) is measured. It can be seen from Figure 4 that the haze value increases with the increasing growth temperature, revealing that the light trapping abilities of the AZO films are closely related to the surface microstructures of AZO films and the light trapping abilities are further enhanced by the nanorod-like structures of the AZO films. The nanorod-like single-textured AZO films exhibit higher haze value and better light trapping abilities in comparison with the network-like single-textured AZO films. From the SEM images and haze spectra, with the large-scale emergence of nanorod structures on the surfaces, we can see the corresponding increase of haze value. In general, the prominent light trapping ability can be provided by the rougher and less dense surface morphologies, which is confirmed in our studies. From the above SEM results displayed in Figure 2c,d, the surfaces of the nanorod-like single-textured AZO films prepared at 90 °C are denser than those of the AZO films prepared at 100 °C. The dense surfaces would greatly reduce the optical path of the light in the films, which is not favorable for improving light trapping ability. However, the AZO nanorods prepared at growth temperature of 100 °C show rougher and irregular surfaces, which can provide more scattering centers for the incoming light [17,18]. Moreover, at 100 °C, more gaps among the nanorods appear and get wider. Through these gaps and nanorods, more reflection, refraction and scattering of the incident light occur, which can greatly elongate the light path and is more conducive to the light trapping ability [19]. The nanorod-like single-textured AZO films prepared at 100 °C exhibit higher haze value (0.12) at 550 nm. As reported in our previous work [20], the crater-like single-textured AZO films prepared by wet chemical erosion after sputtering presented a haze value of about 0.13 at 550 nm. As the single-textured films, the nanorod-like AZO films in this study exhibit comparable light trapping abilities and a simpler preparation process compared with the crater-like AZO films.

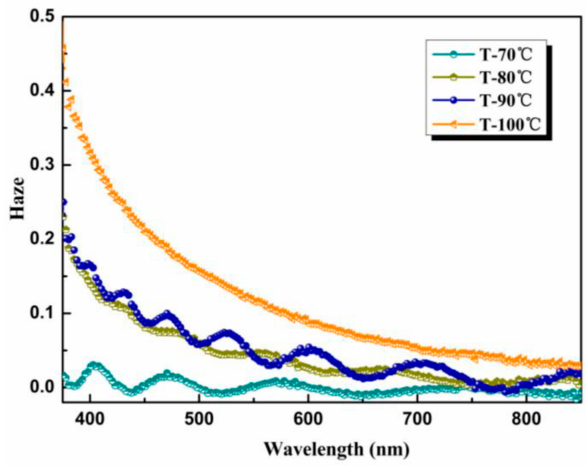


**Figure 4.** Haze spectra of the AZO films prepared at different growth temperatures.

### 3.5. Electrical Properties

To characterize the electrical properties, the resistivity, carrier concentration and mobility of all the AZO films prepared at different growth temperatures are displayed in Figure 5. From the test results, all the AZO films exhibit n-type conductivity properties. With the increase of temperature, the carrier concentration is almost constant (~$10^{20}$ $cm^{-3}$). As is well known, the resistivity is inversely proportional to the mobility and the carrier concentration [21]. Because of the almost unchanged carrier concentration, the resistivity is mainly determined by the variation trend of the mobility. From Figure 5, as growth temperature rises from 70 °C to 100 °C, the mobility increases firstly and then decreases. As a result, the resistivity shows the opposite trend with the increasing temperature. The single-textured AZO films prepared at 70 °C display the minimum mobility. From the XRD results, we can see that the crystal qualities of the samples get better gradually with increasing the growth temperature. The improvement of the crystal quality can promote the reduction of defects in the films, and thus the impurity scattering is reduced. Therefore, the corresponding mobility can be effectively enhanced at higher growth temperature. In addition, when the growth temperature is increased from 80 °C to 100 °C, the mobility is slightly decreased. It can be seen from the SEM results that as the growth temperature rises from 80 °C to 100 °C, the surface roughness of the samples is increased due to the appearance of nanorod structures and gaps among the nanorods, which might lead to the slight decrease of mobility. The resistivities of all the AZO films keep the order of $10^{-3}$ Ω·cm and the resistivity of the AZO films prepared at 100 °C is $2.24 \times 10^{-3}$ Ω·cm, which is suitable for application in the transparent front electrodes.

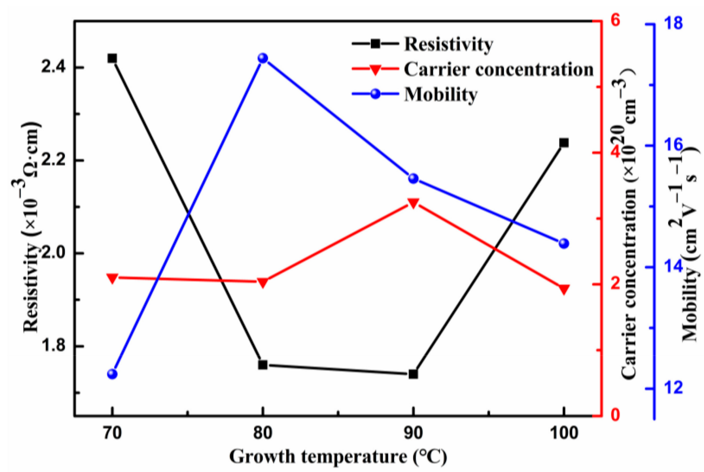


**Figure 5.** Electrical properties of the AZO films prepared at various growth temperatures.

## 4. Conclusions

In general, nanorod-like single-textured AZO transparent conducting films with good light trapping abilities were prepared by a simple hydrothermal process on the AZO seed layers. The XRD patterns showed a strong diffraction peak, which indicated the high crystallinity of all the samples. And the (002) preferred orientation peak indicated a typical hexagonal wurtzite structure of ZnO. With the increase of growth temperature, the surface morphologies transformed from network-like to nanorod-like structures. The nanorod-like single-textured AZO films prepared at 100°C displayed higher haze value, which indicated good light scattering abilities. In addition, the films also exhibited a low resistivity in the order of $10^{-3}$ Ω·cm and a high total transmittance above 80%. From the results, the nanorod-like single-textured AZO films show satisfactory optoelectronic properties and good light trapping abilities, which are suitable for front electrodes of Si-based thin film solar cells.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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