Room Temperature Sputtered Aluminum-Doped ZnO Thin Film Transparent Electrode for Application in Solar Cells and for Low-Band-Gap Optoelectronic Devices

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ABSTRACT: Aluminum-doped zinc oxide (AZO) is a popular, low-cost, nontoxic material that finds application as a transparent conducting electrode in photonic, sensing, and photovoltaic devices. We report the AZO thin films with a high figure of merit on large-area glass substrates by direct current magnetron sputtering without any intentional substrate heating. Furthermore, a simple thermal post-treatment to improve the transmittance of AZO thin film in the infrared region for its application in low-band-gap devices is presented. High optoelectronic properties are obtained by optimizing oxygen content during the sputtering process. The structural, morphological, optoelectrical, and photoluminescence characterization of cold sputtered AZO films is investigated for its latent applications. AZO thin films with an electrical sheet resistance of 8.8 Ω/□ and a visible light transmittance of 78.5% with thickness uniformity above 95% are achieved on 300 mm × 300 mm glass substrate. The AZO film with optimized process conditions is employed as a transparent electrode to fabricate a copper–indium–gallium–selenide-based thin film solar cell, demonstrating 11.8% power conversion efficiency. The AZO film with optimized sputter conditions was post-treated in ambient conditions with an Al blanket to suppress the resistivity by proper organization of the defects due to Al3+ consumption and point defects, resulting in improved transparency (85%) in the infrared region with a sheet resistance of 40 Ω/□. This has great potential for developing scalable and low-cost AZO thin films for transparent electrodes in a wide range of the spectrum.

1. INTRODUCTION

Aluminum-doped zinc oxide (AZO) is an emergent prevalent transparent conducting oxide-based electrode material owing to its tunable optoelectronic properties, profusion in the earth’s crust, as well as nontoxicity.† It has analogous electrical and optical properties like conventional indium-doped tin oxides and fluorine-doped tin oxide.5 AZO-based thin films are widely used in photonic devices such as light-emitting diodes, flat panel displays,7 thin film solar cells,5,8 as well as various sensing devices.7 Typically, the above applications demand high transmittance (>80%) in the visible region as well as metal-like conductivity (sheet resistance <10 Ω/□). Various vacuum-based popular techniques such as sputtering,† pulsed laser deposition,10 electron beam evaporation,11 as well as non-vacuum techniques such as chemical vapor deposition,12 spray pyrolysis,13 chemical bath deposition,14 and sol–gel deposition15 are well reported for coating AZO thin films on different substrates. Most of the technique’s require either high substrate temperature or thermal post-treatment to prepare AZO thin films with high figures of merit (FOM). Of the above processes, direct current (DC) magnetron sputtering is an industrially acceptable technique. It can produce highly transparent conductive thin films with good scalability on a large area with a faster deposition rate. Properties of sputtered AZO thin films are largely determined through controlled process parameters; base vacuum, gas pressure, power density, and substrate temperature during sputtering.17 In line with this, in our earlier work, we optimized these sputtering process parameters to attain high electrical conductivity and transmission in AZO film while heating the glass substrate during sputtering.18 However, high-temperature sputtering damages underlying layers/coatings while employing this top contact on devices; therefore, it could not be used for various temperature-sensitive devices such as organic and perovskite-based solar cells or light-emitting diodes19,20 Consequently, it is necessary to develop a low/room temperature DC magnetron sputtering process for producing quality AZO thin films without compromising much with its optical and electrical properties. Moreover, to advance optoelectronic properties, oxygen partial pressure during sputtering needs to be perfected.

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The room temperature sputtered AZO thin films were employed to control defect states eventually responsible for optical transmission of coated thin films. This study aims to find optimal oxygen flux required for DC sputtering to achieve desired conductivity and transmittance in AZO thin films on 30 cm × 30 cm glass without heating during the process for its application in temperature-sensitive multilayer structures and photonic and electronic devices. The room temperature sputtered AZO thin film with optimized conditions is validated by being employed as a transparent electrode in the CIGS solar cell, demonstrating a potential alternative of indium-doped tin oxide (ITO) as a scalable and low-cost transparent conducting oxide (TCO) electrodes for low-band-gap optoelectronic devices.

### 2. Experimental Section

AZO thin films were sputtered on 30 cm × 30 cm × 3 mm glass substrates cleaned using a glass washing machine (Miele, Germany). The cleaning cycle includes treatment using alkali, neutralizing agents, followed by deionized water. Details of surface treatment are described in our previous work.\(^{26}\) The AZO sputtering was carried out in a high-vacuum DC magnetron sputtering system armed with cylindrical rotating targets (Vertisol 600, Singulus Technologies, Germany). The bonded tube target of 60 cm with an inner diameter of 12.5 cm and a thickness of the AZO material of 1.5 cm was used in this study. The fixed material composition of the target, Al:ZnO (2.98 wt%), was maintained at 8 cm away from the substrate for all of the depositions reported here. The inline sputter is metered to coat vertically leaning substrates, 30 cm × 30 cm, capable of traveling at a constant linear velocity of 50 cm/min. A base vacuum of 2 × 10^{-6} mbar was achieved in the deposition chamber before commencing with AZO sputtering. The argon (Ar) and a mixture of argon/oxygen (Ar/O\(_2\)) (95:5%) gas flow rates were accustomed to regulate the oxygen partial pressure during sputtering without affecting the overall deposition pressure. The overall oxygen content in plasma gas was varied from 0 to 5%. All other sputtering process parameters, including power set to 4000 W, a deposition pressure of 2.7 × 10^{-3} mbar, and a substrate temperature of 300 K, were kept constant for all samples. The above-selected parameters were optimized previously by our group; details can be found in our previous publication.\(^{1}\) The AZO thin film with optimized conditions was validated by employing as a top electrode for copper–indium–gallium–selenide (CIGS) thin film solar cell. The device was fabricated in a AZO (900 nm)/ZnO(40 nm)/CdS (50 nm)/CIGS (1.5 μm)/Mo (800 nm)/SLG (3 mm) substrate configuration; the other experimental details on device fabrication can be found in our previously published work.\(^{29}\) Further, AZO thin films sputtered with optimized conditions (1% oxygen flux) were post-treated at 500 °C for 30 and 60 min with an Al blanket, and the schematic is presented in Figure S1 of the Supporting Information.

The thickness and uniformity of the as-deposited AZO films were evaluated using an XRF system (Helmut Fischer, Switzerland). The thickness of the AZO-coated SLG was mapped at 36 different locations on the 300 mm × 300 mm glass to ensure uniformity. All of the sputtered AZO films’ electrical properties were assessed at nine different locations using four-point probe equipment (Loresta GP, Mitsubishi, Japan) in a four-point collinear probe configuration. Hall effect measurements (Ecopia HMS S500) were carried out using the Van der Pauw configuration to confirm resistivity, carrier concentrations, and mobility of sputtered AZO thin film samples with a size of 10 mm × 10 mm. Phase and crystallite size analysis was done using X-ray diffraction (XRD) patterns recorded on a D8 Advance XRD system (Bruker) equipped with a Cu Kα source (1.54 Å). Field emission scanning electron microscopy (FESEM, Zeiss, Germany) was used to observe and record the surface and cross-sectional micrographs. Optical properties of the sputtered AZO thin films were investigated using a UV–visible–NIR spectrophotometer (Varian, Cary 5000). Photoluminescence (PL) spectra (Horiba Instruments Inc., USA) were recorded at an excitation wavelength of 325 nm. A standard Scotch tape test method was used to validate the adhesion of the AZO films to SLG. The current–voltage (I–V) characteristics of the CIGS device

### Table 1. Summary of AZO Thin Film Thickness, Electrical, Optical Properties, and Figure of Merit Sputtered at Different Oxygen Content and Electrical and Optical Properties of AZO Thin Film (1% O\(_2\) Content) Annealed for 30 and 60 min

| % O\(_2\) content | thickness (nm) | standard deviation (nm) | COV (%) | resistivity ×10\(^{-3}\) (Ω-cm) | sheet resistance (Ω/□) | % transmittance (400–700 nm) | band gap (eV) | figure of merit (Ω\(^{-1}\)) |
|------------------|----------------|------------------------|---------|-----------------------------|-------------------------|---------------------------|---------------|-----------------------------|
| 0                | 1044           | 15                     | 1.39    | 0.88 ± 0.04                 | 8.4 ± 0.1               | 68.45                     | 3.54          | 8.1                         |
| 0.5              | 1090           | 27                     | 2.48    | 1.10 ± 0.05                 | 10.1 ± 0.5              | 76.06                     | 3.50          | 7.5                         |
| untreated        | 1038           | 26                     | 2.49    | 0.91 ± 0.04                 | 8.8 ± 0.3               | 78.52                     | 3.48          | 8.9                         |
| 1 (500 °C/30 min)| 1037           | 25                     | 2.46    | 2.15 ± 0.04                 | 24.6 ± 0.2              | 80.26                     | 3.47          | -                           |
| 1 (500 °C/60 min)| 1035           | 24                     | 2.48    | 4.37 ± 0.05                 | 45.8 ± 0.3              | 85.56                     | 3.45          | -                           |
| 2                | 996            | 18                     | 1.79    | 2.82 ± 0.02                 | 28.2 ± 0.4              | 78.32                     | 3.40          | 2.7                         |
| 5                | 918            | 19                     | 2.02    | 20.24 ± 0.7                 | 220.5 ± 8               | 80.05                     | 3.34          | 0.36                        |
was measured in standard test conditions (illumination intensity of 1000 W/m², at 25 °C) using a solar simulator (94123A; Oriel Instruments). Surface topography of the AZO films with 1% oxygen flux post-treated at 500 °C for 30 min and at 500 °C for 60 min was scanned on the area of 500 μm × 500 μm with a stylus profilometer (Bruker DektakXT) equipped with a stylus with a curvature radius of 50 nm and a nominal vertical resolution below 1 nm.

3. RESULTS AND DISCUSSION

AZO thin films were coated on large-area glass by DC magnetron sputtering using a rotating cylindrical Al:ZnO (2.98%) target without heating the substrate during the process. Experiments were designed with a variation of plasma oxygen content during sputtering to achieve AZO thin films with high thickness homogeneity, low resistivity, and maximum optical transmission. The average optoelectrical properties of AZO thin films cold sputtered over a 30 cm × 30 cm glass substrate at varied oxygen contents along with 1% O₂ content samples annealed at 500 °C for 30 and 60 min are summarized in Table 1.

3.1. Thickness Uniformity. The optoelectrical properties of films are often reliant on thickness uniformity. Therefore, it is extremely important to have a high degree of thickness homogeneity over a large area for efficient device performance.

An XRF mapping of the AZO thin film on 30 cm × 30 cm glass acquired for the AZO thin films with optimized oxygen flux is shown in Figure 1. AZO thin films are found to slightly profuse in the central area compared to that of the top and bottom ends. The variation in thickness can be attributed to the distribution of slightly more intense plasma toward the central region and less toward the top and bottom edge. This trend was witnessed to be steady with all samples regardless of oxygen flux. All of the AZO films deposited on glass confirmed a uniformity better than 95% over a full area of 30 cm × 30 cm. All of the cold-sputtered films exhibited excellent adhesion to glass regardless of oxygen gas flux, as confirmed by the Scotch tape test.

3.2. Structural and Morphological Analysis. Figure 2 displays X-ray diffraction patterns of cold-sputtered AZO thin films on glass obtained with different oxygen fluxes. The major XRD peaks of all samples were observed to be sharp and intense, indicative of good crystallinity. All AZO films unveiled a hexagonal wurtzite structure, matching with reference (ICDD: 01-089-1397) as well as previous relevant reports. All films show the preferred orientation in the plane (002) along the c-axis, suggesting columnar progression. The intensity of diffraction peaks was found to increase by an increase in oxygen flux. Using X-ray diffraction patterns of all of the samples, crystallite sizes were estimated following Scherrer’s equation. An increase in average crystallite size from about 6 nm for zero oxygen flux to 20 nm for samples sputtered with 5% oxygen flux is noted, which can be attributed to variation in deposition rate due to an increase in oxygen content during sputtering.

Figure 3 presents the FESEM surface and cross-sectional morphology of AZO thin film sputtered with different oxygen fluxes. Coarsening of grains is clearly noticed with increment in oxygen flux, which is indicative of improvement in crystallinity. All of the films were dense and void-free irrespective of oxygen flux. The pore-free dense nature of AZO thin films was confirmed from cross-sectional morphology.

3.3. Electrical Properties. Figure 4a–d presents the variation of average sheet resistance, mobility, carrier concentration, and electrical resistivity of AZO thin films sputtered with variable oxygen flux, as measured by the Hall technique. Hall measurements revealed all samples exhibit n-type electrical conductivity regardless of oxygen flux. The Hall measurements were all in good agreement with readings taken by a four-probe meter over multiple locations on a 30 cm × 30 cm area. The spatial variations in electrical properties were less than 5%, consistent with thickness uniformity. The electrical characteristics of AZO thin films originated from the substitution of Al³⁺ ions on the Zn²⁺ ions site and Al₁, Zn interstitial atoms. The relationship between the resistivity (ρ), carrier concentration (n), charge of carrier (e), and mobility (μ) is expressed based on the following equation:

\[ \rho = \frac{1}{ne\mu} \]  
\[ (1) \]

The resistivity and sheet resistance of sputtered AZO thin films were augmented with an increase in oxygen flux (Figure 4a,d). From eq 1, the high resistivity of AZO thin film is caused by the lower product of the \( n \) and \( \mu \). The increment was observed despite improvement in crystallinity.

Typically, improvement in crystallinity leads to improved conductivity. Increased oxygen flux during sputtering is expected to passivate the oxygen vacancy; Al and O₂ react to form Al₂O₃, leading to a decrease in the substitution of Al³⁺, which eventually decreases the carrier concentration (Figure 4c). Figure 4b presents the Hall mobility variation with O₂ flux.
in the AZO thin film. With rising O$_2$ flux, the Hall mobility decreases. In the present work, the Hall mobility of AZO thin film with a carrier concentration of 10$^{20}$–10$^{21}$ cm$^{-3}$ mainly results from the ionized impurity scattering rather than grain boundary scattering, consistent with an earlier report. Therefore, the Hall mobility of AZO films decreases owing to an increase in ionized impurity scattering. In this study, the impact of carrier concentration is dominant compared to the
crystallinity on electrical properties of cold-sputtered AZO films. The resistivity of the AZO thin film increased drastically after increasing O₂ flux to more than 1%.

### 3.4. Optical Properties

The transmittance band of sputtered AZO films on glass at different oxygen fluxes was recorded over the 300–1800 nm, as shown in Figure 5a. The overall visible light transmission was within 65–80%, while the absorption edge was near 350 nm for all films on glass. The transmission band unveiled substantial interference fringes from all samples, which was established due to the high planar surface of all sputtered films, consistent with surface morphology correlation. The transmittance of AZO films was found to be low in the IR region for samples sputtered with low oxygen flux. This can be attributed to reflection losses incurred in the presence of high metal interstitial defects with oxygen vacancies. The optical absorption coefficient (α) was determined from transmittance (T) measurement using eq 2.

$$\alpha = -\frac{1}{d} \ln T$$

where d is film thickness. The optical band gap energy was calculated using these absorption coefficient values. The band gap of an AZO thin film was found using the Tauc technique, which consisted of extrapolating the (hν)² plot with photonic energy for direct transition for AZO films, as shown in Figure 5b.

With an increase in oxygen flux, optical transmittance increased while the band gap decreased as the adequate quantity of oxygen plasma gas was present during sputtering. The higher metal interstitial defects lead to increased carrier concentration, increasing the band gap, consistent with explanation by the Burstein–Moss effect. PL of all prepared films was recorded to understand the defect levels in the sputtered films with varied oxygen flux. Figure 6 presents the photoluminescence spectrum of AZO thin films sputtered with various O₂ gas content.

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**Figure 6.** Photoluminescence spectrum of AZO thin films sputtered with various O₂ gas content.

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PL spectrum of AZO films sputtered with variable oxygen flux measured in the wavelength range of 400–600 nm under the excitation of 325 nm. Two distinct peaks appear for all of the samples. The peak at 440 nm is attributed to a zinc interstitial defect, as shown in the inset of Figure 6, whereas the peak at 530 nm indicates a metal antisite defect. The intensity of the peak at 530 nm reduces with increased oxygen flux, consistent with carrier concentration variation, as supported by previous reports.

Based on our experiments and results, detailed investigation, and analysis, it was perceived that the sputtering conditions had an abundant impact on electrical resistivity and optical transmittance of AZO films. For cold-sputtered AZO thin film samples, defects such as vacancies and antisites are very dependent on oxygen flux. The formation of oxygen vacancies also compliments the creation of interstitials and vice versa. With a slight variation in oxygen flux, there is a substantial variation in optoelectronic properties. The electrical resistivity and optical transmittance of the AZO films are not independent of each other; therefore, to correctly define effectiveness, a FOM is proposed using eq 3, as presented in Table 1.

$$\text{FOM} = \frac{T_{\text{vis}}}{R_s}$$

where $T_{\text{vis}}$ denotes the average transmittance in the visible region (400–700 nm) and $R_s$ signifies electrical sheet resistance. The AZO thin films cold-sputtered at 1% oxygen flux were found to be optimal, resulting in electrical resistivity of $9.1 \times 10^{-4} \Omega \cdot \text{cm}$ and optical transmittance of 78.5% in the visible range. The FOM of AZO thin films achieved in this work compared to that in the reported literature considering identical preparation conditions was found to be the best, as summarized in Table 1 of the Supporting Information. Moreover, the optimized cold-sputtered AZO thin films have equivalent properties if compared with other transparent conducting oxides, Sn:In₂O₃ and F:SnO₂ films prepared in identical conditions, ideal for large-area photonic device applications. In order to demonstrate the application of the cold-sputtered AZO film deposited at 1% oxygen flux, we employed the front contact on the ZnO/CdS/CIGS/Mo/SLG stack of the solar cell. The dark and AM1.5G illumination I–V curve of the fabricated CIGS solar cell demonstrated a power conversion efficiency of 11.8%, and the typical configuration of the solar cell is presented in Figure 7.

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**Figure 7.** Dark and AM1.5G illuminated I–V curve of the CIGS solar cell fabricated from cold-sputtered AZO thin films developed in this work. Cell configuration and processes adopted are indicated in the inset.

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The AZO films with optimized sputter conditions were further post-treated to improve the transmittance in the infrared region as it is essential for low-band-gap optoelectronic applications. It is important to note that increasing oxygen flux resulted in high transmission in the IR spectrum. However, the conductivity of the film decreases owing to the passivation of an oxygen vacancy, out-diffusion of interstitial defects, and metal ions from the lattice. In this study, we have adopted a simple and novel approach for annealing AZO
thin films with an Al blanket in the air (schematic presented in Figure S1 of the Supporting Information), which is expected to compensate the inevitable out-diffusion of point defects in Al\(^{3+}\) and Zn, and improve the transmission in the IR region without compromising conductivity. The annealing of an AZO thin film deposited with 1\% oxygen flux was performed at 500 °C for 30 and 60 min. The coarsening of grains with an increase in the treatment time is evident from the FESEM micrographs (Figure S2 in the Supporting Information), and an increase in the XRD peak intensity reflects the improvement in crystallinity (Figure S3 in the Supporting Information). The average sheet resistance and transmission of the films are measured and compared with untreated AZO film. The sheet resistance of AZO films annealed for 30 and 60 min was found to be 24.6 and 45.8 Ω/□, respectively, as presented in Table 1. The high sheet resistances of the thermally treated AZO films, compared to that of the untreated, indicates the lower carrier concentration stemming from the consumption of points defects such as Al\(^{3+}\) in the form of Al\(_2\)O\(_3\) and out-diffusion of Zn\(_3\) and V\(_{\text{Zn}}\) defects from the lattice. The decrease in carrier concentration is further reconfirmed by the current−voltage characteristic measured in dark conditions by applying silver contact on top of the films (Figure S4 of the Supporting Information). The sample annealed for 60 min unveiled the lowest current compared to the others, consistent with the sheet resistance value.

However, the sheet resistance is still in the working range (compensated by the Al blanket) and did not increase as expected. Interestingly, the average transmission in the IR region (800−1500 nm) is improved from 65 to 85\% for the 60 min annealed sample, as shown in Figure 8. The increased transmission is attributed to the passivation of oxygen vacancy and reduced scattering. The representative pictures of the untreated and post-treated AZO thin films on a glass substrate. Logo used with permission.

No peak shifting is detected with an increase in oxygen flux; however, the annealing of AZO thin film resulted in shifting of the PL peaks with minor intensity variations (Figure 9). Previous reports suggested that shifting in PL peaks for AZO thin film is attributed to either disparity in film thickness or defect levels.\(^{41,42}\)

Figure 8. Optical transmittance spectrum of AZO films on glass with 1\% O\(_2\) gas content annealed for the different duration (inset: schematic of the positioning of defects levels), including representative pictures of the untreated and post-treated AZO thin films on a glass substrate. Logo used with permission.

Figure 9. Photoluminescence spectrum of AZO thin films of 1\% O\(_2\) content annealed for the different duration (inset represents the Zni defects).

No considerable change in the film thickness was recorded, as confirmed from the XRF result enumerated in Table 1. Therefore, the only possible reason for the shifting of PL peaks could be the disparity in defects levels in the conduction and valence bands. The reduction in the intensity of PL peaks appeared at 440 and 530 nm, with increasing annealing time, which directs a reduction in deep-level defects (i.e., Zn\(_3\) and O\(_{\text{Zn}}\)/O\(_{\text{Al}}\)) consistent with I−V and sheet resistance results. The PL peaks positioned at 440 and 530 nm, 442.5 and 534.5 nm, and 445 and 536.5 nm correspond to AZO thin film annealed for 0, 30, and 60 min, respectively, as shown in Figure 9. A slight red shift in the PL peaks is ascribed to the defect-type Zn\(_3\) and O\(_{\text{Zn}}\)/O\(_{\text{Al}}\) in treated AZO thin films. Therefore, annealing treatment of AZO films in an Al blanket facilitated the improvement of transmission in the IR region. This can be attributed to the compensation of point defects by an Al blanket, as confirmed by the optical, electrical, and photoluminescence study; as a result, the transmission of more than 85\% in the IR region with a sheet resistance of 45.8 Ω/□ is achieved for AZO thin films annealed for 60 min.

4. CONCLUSION

Highly transparent and conductive AZO films with thickness uniformity of more than 95\% on 30 cm × 30 cm glass substrates were successfully obtained by cold DC magnetron sputtering. The optoelectrical properties of sputtered AZO films are found to be reliant on oxygen flux during sputtering. Low oxygen flux promoted defects such as oxygen vacancies, metal interstitials contributing to improving electrical conductivity, and low transmittance in the infrared region attributed to metal-like reflectance. High oxygen flux reduces oxygen vacancies and metal interstitials, promoting improved transmittance and low electrical conductivity. A trade-off was attained with optimal oxygen flux during sputtering to acquire high-quality AZO films by means of a higher figure of merit having an average electrical sheet resistance of 8.8 Ω/□ and visible light transmittance of 78.5\%, appropriate for application in temperature-sensitive multilayer structures and photonic and electronic devices. Furthermore, an improvement in the average transmission in the IR region to 85\% with a sheet resistance of 40 Ω/□ is accomplished by the unique annealing technique of AZO thin film to dope Al in the AZO lattice,
reducing the compensating defects. The enhanced transmission by Al blanket annealing is of great interest as it serves as a transparent electrode for low-band-gap optoelectronic devices and can be further fine-tuned to obtain desirable optoelectronic properties.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00830.

Literature review on sputtered AZO thin films, the schematic representation of post-treatment of AZO thin film covered in an Al blanket, surface morphology and XRD of AZO thin films sputtered with 1% O₂ flux treated for different times, and current–voltage characteristics of AZO thin films in dark conditions (PDF)

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Notes
The authors declare no competing financial interest.

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