Effect of Al and Ga codoping on the morphological, electronic, and optical properties of ZnO transparent conductive thin films prepared by spray pyrolysis technique

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Abstract: Codoping a semiconductor thin film with two or more dopants is a feasible technique to improve the electrical properties of the thin film. In this work, we studied the codoping of Al and Ga n-type impurities in a ZnO film (AGZO) deposited on a glass substrate by the spray pyrolysis method. The total doping concentration, [Al + Ga]/[Al + Ga + Zn], was 5 at.-% with varying Al:Ga codoping proportions of 0:5, 1.25:3.75, 2.5:2.5, 3.75:1.25, and 5:0 at.-%. The effect of Al/Ga codoping on the structural, texture, morphological, optical, and electrical properties of the AGZO films were investigated using X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscopy (SEM), UV-visible spectroscopy, and four-point probe technique, respectively. Varying Al:Ga codoping proportions significantly alter the textures and morphologies of the AGZO thin films. Thin films with higher Al doping content exhibit amorphous-like structures due to fine nano grains with high concentrations of disordered grain boundary regions. The optical transmittance spectrums show transmittance higher than 80% in the visible light region for all the codoped films. The sheet resistances and electrical resistivity of the AGZO films are significantly lower than those of the 5 at.-% Al-doped ZnO films.

Key words: Deposition, semiconductor, thin film, nanostructure, spray pyrolysis, doping

1. Introduction

Zinc oxide (ZnO) thin films have attracted considerable attention as transparent conductive nanostructure materials that have been considered for potential applications in several technological devices, such as photocatalytic material [1], piezoelectric devices [2], chemical/humidity sensors [3,4], solar cells [5,6], and photocathodic protections [7,8]. ZnO has a wide direct band gap of around 3.37 eV at room temperature resulting in good electrical and optoelectrical properties and high photosensitivity [9]. ZnO is an intrinsic n-type semiconductor whose extra free electrons are generated by defects, e.g., O vacancies and Zn interstitials [10]. However, the electrical resistivity of undoped ZnO is high as the concentration of electrons is slightly higher than that of holes [10]. Moreover, quick recombination rate of photogenerated electron–hole pairs decreases the electron concentrations resulting in low electrical conductivity that limits its electrical applications [11].

Doping atoms in ZnO is one of the techniques to enhance its optoelectrical properties. Its conductivity and transparency could be improved by doping group III atoms such as Al, B, In, and Ga. The doping of
these group III atoms in ZnO can substitute Zn atoms and provide excess free electrons, which contributes to higher electrical conductivity [12,13]. Doping of Al in ZnO has several advantages, since Al-dopant sources are low-cost and nontoxic. However, the atomic substitution of Al for Zn remains difficult for high doping concentrations due to the difference in ionic radiiuses and coordination preference [14]. Reportedly, Al atoms, whose ionic radius is 0.54 Å, can be found in both substitutional and interstitial sites [15]. Ga has an ionic radius of 0.62 Å, which is close to the Zn ionic radius of 0.74 Å [13]. Therefore, Ga atom can substitute Zn atom with minimal structural distortion and can be doped at high concentration to improve film properties [16]. However, the Ga-dopant sources are relatively expensive. Each of Al and Ga dopants provides a unique effect on the structural defects and properties of the ZnO matrix. It has been reported that codoping of both dopants in ZnO thin films led to morphological and bandgap modifications and corresponding electrical properties of the films at varying codoping concentrations [13,17–19]. Codoping of Al and Ga in ZnO films (AGZO) were reported to improve the conductivity of the ZnO films [13,18].

Numerous methods for ZnO thin film preparation include atomic layer deposition [20], sputtering [21], chemical vapor deposition (CVD) [22], spin coating [23], sol–gel [24], and spray pyrolysis [25]. Among these methods, spray pyrolysis shows many advantages such as simplicity, safety, and low cost of equipment and raw materials. Spray pyrolysis is a technique that involves atomizing a precursor solution into microdroplet aerosols. The droplets are directed toward a heated substrate to decompose and form a thin film of a desired compound. The composition of the film can be controlled by the mixtures of the precursor solutions. Both dense and porous structures can be deposited by spray pyrolysis, even on large substrates.

In prior reports on AGZO films, the films were prepared by physical deposition, such as sputtering [17,19,26], or by chemical deposition, such as sol–gel technique [13]. Only one study on AGZO films applied the spray pyrolysis technique [18]. Makuku et al. [18] reported that codoping of Al and Ga in ZnO with equal doping concentrations of Al and Ga for total codoping concentrations varied from 0 to 6 at.%. It was reported that codoping of Al and Ga improved the electrical conductivity of the AGZO films with the lowest resistivity obtained for the total codoping of 2 at.% with equal Al:Ga doping proportion [13,18].

Prior studies on AGZO focused on the effect of the varying Al:Ga codoping proportion at low total codoping concentration (<2 at.%) [13,18,19]. For high codoping concentration, the Al:Ga codoping proportion was fixed at an equal ratio. One of the key prospects of codoping technique is to expand the effective doping range to high doping concentration. Therefore, in this work, it is of interest to investigate the effect of varying Al:Ga proportions at high codoping concentration. The effect of varying Al:Ga codoping proportion for 5 at.% doping concentration on AGZO films, grown on glass substrates by the spray pyrolysis method, is investigated and reported herein. The analyses of the structural, optical, and electrical properties of AGZO thin films are reported. A total codoping concentration of 5 at.% was applied to assess the prospect of the Al/Ga codoping technique at high doping concentration. The Al:Ga codoping proportions were varied to investigate its effect on optical and electrical properties. The codoping effect on the morphology and surface textures of the thin films were also analyzed for the structure–property relations.

2. Materials and methods
2.1. Thin film preparation methods

Al/Ga-codoped ZnO (AGZO) thin films were obtained from aqueous solutions by the spray pyrolysis under ambient air atmosphere. Al and Ga were doped together by mixing proper quantities of dopant sources in a
precursor solution. The total doping concentration, \([\text{Al} + \text{Ga}] / [\text{Al} + \text{Ga} + \text{Zn}]\), was 5 at.\% with varying Al:Ga doping proportions of 5:0, 3.75:1.25, 2.5:2.5, 1.25:3.75, and 0:5. The in-house–designed spray pyrolysis setup is schematically shown in Figure 1. Flow rate of the precursor solution fed to a spray nozzle was controlled by a syringe pump. Air was directly compressed to the nozzle from an ambient atmosphere using a filter to remove moisture and dust. The solution and compressed air mixed together at the nozzle forming spray of microdroplets that were directed toward a heated glass substrate. Before deposition, the glass substrate was cleaned with acetone and deionized water in an ultrasonic bath. The mixture of 0.05 M Zinc acetate dihydrate \((\text{Zn(\text{CH}_3\text{OOH})}_2\cdot2\text{H}_2\text{O})\) in methanol was prepared as precursor. Aluminum nitrate \((\text{Al(NO}_3)_3\cdot9\text{H}_2\text{O})\) and gallium nitrate \((\text{Ga(NO}_3)_3\cdot9\text{H}_2\text{O})\) were Al- and Ga-dopant sources, respectively. The flow rates of air and the precursor solution were 0.2 kg/cm\(^2\) and 4 mL/min, respectively. The spray deposition was sprayed on the substrate for 10 min; the glass substrate was preheated at 400 °C.

![Figure 1. Schematic diagram of the spray pyrolysis unit: (a) air compressor, (b) air regulator, (c) atomizer nozzle, (d) heater, (e) temperature control, (f) solution flow control, and (g) gas exhaustion.](image)

### 2.2. Thin film characterization methods

Phase structures of the samples were investigated by X-ray diffraction (XRD) method (Cu K\(_\alpha\) radiation, \(\lambda = 0.15405\) nm, 40 kV, 30 mA) using Philips X’Pert X-ray diffractometer (Amsterdam, the Netherlands). Scanning electron microscopy (SEM, Quanta 450 FEI, Hilsboro, OR, USA) and atomic force microscope (AFM, AR MFP-3D, Oxford Instruments plc, Abingdon, UK) tapping mode were used to characterize the morphological characteristics of their surfaces. The thicknesses of the AGZO films were measured by a profilometer (Surftest SV-3000, Mitutoyo, Kawasaki, Japan).

The average crystallite sizes of the AGZO thin films were determined from SEM and XRD data by two corresponding methods: (1) an image analysis technique using ImageJ Software (LOCI, University of Wisconsin–Madison, WI, USA), and (2) Scherer’s equation, which is given as [27]:

\[
D_p = \frac{0.9\lambda}{\beta \cos \theta},
\]

where \(D_p\) is the mean crystallite size, \(\lambda\) the wavelength of the X-ray beam (Cu K\(_\alpha\) radiation: \(\lambda = 0.15405\) nm), \(\beta\) the full width at half maximum (FWHM) in radians, and \(\theta\) the Bragg’s angle.

The optical transmittance of the deposited films was measured in the wavelength range of 300–800 nm using an UV-Visible spectrophotometer (Shimadzu UV-1700, Kyoto, Japan). From the optical transmittance...
data, the bandgap energy \((E_g)\) of Al/Ga-codoped ZnO films could be acquired from the plot of \((\alpha h\nu)^2\)-vs.-\(h\nu\), based on the Tauc’s relation for a direct bandgap, given as [17,18]:

\[
\alpha h\nu \propto (h\nu - E_g)^{1/2}, \tag{2}
\]

where \(\alpha\), \(h\), \(\nu\) are the film’s absorption coefficient, the Planck’s constant, and photon frequency, respectively. The absorption coefficient can be calculated from transmittance data, using the Beer–Lambert law [18]:

\[
\alpha = \frac{1}{D} \ln \left( \frac{1}{T} \right), \tag{3}
\]

where \(D\) and \(T\) are film thicknesses and transmittance, respectively.

Sheet resistances of the films were investigated using the four-point probe method. The film resistivity properties were calculated from the sheet resistances and film thicknesses. The sheet resistance, \(R_s\), and film resistivity, \(\rho\), are derived by the equations below [28]:

\[
R_s = \frac{\pi}{\ln(2)} \frac{V}{I}, \tag{4}
\]

\[
\rho = R_s D, \tag{5}
\]

where \(V\), \(I\), \(D\) are the measured voltage, current, and the film thicknesses, respectively.

3. Results and discussion

3.1. Phase structures

The phase structures of the Al/Ga-codoped ZnO thin films (AGZO) were analyzed using XRD in the \(2\theta\) range between 20° and 80°. Figure 2 shows the representative XRD patterns of AGZO thin films with varying Al:Ga codoping proportions. The XRD patterns reveal that the films exhibit hexagonal wurtzite structure, which was referred with JCPDS 36-1451. Each of the films possesses a preferred diffraction peak of (002) plane with a minor (101) peak, which are also observed in the AGZO reported by Lee et al. [17], Ebrahimifard et al. [13], Makuku et al. [18], and Lung et al. [19]. The relative intensity of the ZnO thin film with 5 at.% Ga doping shows a strong (002) preferred orientation, which indicates that the film orientation is mostly along the c-axis of the crystallographic structure [19]. As the Al codoping concentration is increased, the (002) peak intensity significantly decreases. The crystallinity of AGZO films was aggravated by an increase in the Al doping concentration. The ZnO thin film doped with 5 at.% Al shows amorphous-like structure. This disorder effect by Al doping may be due to the atomic size difference between Zn, Al, and Ga that may distort the matrix structures and cause localized stress in the vicinity of the impurity-located sites. The Al atomic size (0.054 nm) is much smaller than that of Zn (0.074 nm), while the Ga atomic size (0.062 nm) and that of Zn atom are close. The Al atoms can be located in either substitutional or octahedral interstitial sites, while the Ga atoms can only be located in substitutional sites [14–16]. For high doping concentration, excessive dopants may reside in the interstitial sites or form oxides, which causes a reduction of crystallinity [13,29]. As a result, the doping of Al distorts the ZnO crystallographic structure and reduces its crystallinity more than the doping of Ga does [13].
3.2. Morphologies and microstructures of the thin films

The AFM images of 5 at.% Al-doped and 5 at.% Ga-doped ZnO thin films are shown in Figure 3. Different dopant metals clearly exhibited distinct surface roughness and grain sizes and shapes of the doped ZnO thin film. For Al doping, the film possesses highly uniform and fine nano grains; while the Ga-doped ZnO shows relatively coarse grains with wide grain size distribution. The Ga doping also results in a significantly rougher surface than does the Al doping. The thicknesses of the films are shown in Table 1. Ga doping appears to increase the thickness of the films, which may be due to rough surface and coarse grains of Ga-doped ZnO shown by the AFM images.

Table 1. Film thicknesses, sheet resistances, and resistivity of the AGZO films as a function of Al:Ga codoping proportions.

<table>
<thead>
<tr>
<th>Al:Ga codoping proportions (at.%)</th>
<th>5:0</th>
<th>3.75:1.25</th>
<th>2.5:2.5</th>
<th>1.25:3.75</th>
<th>0:5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness (nm)</td>
<td>53</td>
<td>71</td>
<td>69</td>
<td>83</td>
<td>131</td>
</tr>
<tr>
<td>Sheet resistance (MΩ/sq)</td>
<td>67.95</td>
<td>4.41</td>
<td>1.06</td>
<td>0.88</td>
<td>0.71</td>
</tr>
<tr>
<td>Resistivity (Ωcm)</td>
<td>360</td>
<td>31</td>
<td>7.3</td>
<td>7.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The SEM surface morphologies of the AGZO thin films with varying Al:Ga codoping proportions are shown in Figures 4a–4e. Evidently, different Al:Ga codoping proportions alter the textures of the AGZO thin films, as well as their average grain sizes and shapes. As the Al doping concentration is increased, AGZO thin films exhibit finer nano grains with uniform size and rounded shape, which corresponds well with the AFM analyses. An increase in the Ga doping content results in larger grains with oval shape, as evident in Figure 4e.
Figure 3. AFM images for two (left) and three (right) dimensional pictures of a) 5 at.% Ga-doped ZnO thin film and b) 5 at.% Al-doped ZnO thin film.

From the AFM and SEM analyses, the varied Al:Ga codoping proportions may have influenced the nucleation and growth processes during the spray pyrolysis deposition, which influenced the resultant surface textures and grains of the thin films. During the spray pyrolysis deposition, the droplets of the precursor solution were sprayed to a heated substrate. As the droplets reached the substrate’s surface, the solvent droplets evaporated, decomposed, and deposited the salt precipitates, which influenced the nucleation and diffusion for the thin film growth. Therefore, the nature of different precursors, whose evaporation and salt precipitation characteristics were varied, may influence the mechanisms for the thin film formation leading to different film textures [30]. In this case, zinc acetate dehydrate, aluminum nitrate, and gallium nitrate in methanol were used as source precursors for ZnO, Al dopant, and Ga dopant, respectively. Therefore, varying Al:Ga codoping proportions, with different precursor mixture compositions, may lead to different surface textures of the thin films.

The average crystallite sizes of the AGZO films are shown in Table 2. The two sets of crystallite size data, determined by the image analysis and Scherer’s equation, correspond well with each other. The crystallite
Figure 4. SEM images for AGZO films obtained from spray solutions with Al:Ga codoping proportions of a) 5:0 at.%, b) 3.75:1.25 at.%, c) 2.5:2.5 at.%, d) 1.25:3.75 at.%, and e) 0:5 at.%. sizes in the range 10–40 nm for all the films. The crystallite size results from the image analysis are slightly higher than those from Scherer’s equation. From the SEM images, a few grains are clustered with one another, which may have contributed to larger crystallite-size values obtained by the image analysis, as opposed to those derived from Scherer’s equation. The 5 at.% Al-doped ZnO shows considerably smaller crystallite sizes than the AGZO films and 5 at.% Ga-doped ZnO. In agreement with the structural and morphological results, the 5 at.% Al-doped ZnO exhibited uniform and continuous films with very fine nano grains and amorphous structures. A high Al doping content increased the Al atom density in the interstitial sites, which may have resulted in the segregations of insoluble Al atoms along the grain boundaries and suppressed the grain growth process resulting in very fine grains with high grain boundary concentrations. When the grains are as small as 50 nm or less, the atomic arrangement in each grain and different grains exhibit different orientations. Moreover, the grain boundary regions are highly disordered. As a result, the very fine nano grains of the 5 at.% Al-doped ZnO exhibit amorphous-like structure. For the 5 at.% Ga-doped ZnO, the average grain size was relatively large with higher crystallinity. Ga impurities can be suitable substitutional atoms in Zn lattice sites due to similar atomic sizes of Zn and Ga [14,16]. Therefore, substitutional Ga may be doped in ZnO with relatively high solubility and good doping effect. For the Al/Ga codoping, an increase in the Al content could result in insoluble Al atoms in grain boundaries that suppressed the grain growth process leading to finer grains. For low Al codoping contents at 1.25 and 2.5 at.% (Figures 4c and 4d), the grain size distribution is uniform with oval shape similar to the 5 at.% Ga-doped film, but with much smaller grain size. For the Al codoping of 3.75 at.%, the film possesses the clusters of very fine rounded grains (marked areas in Figure 4b), which are dispersed in the matrix of coarser oval grains. It is likely that there were some droplets that possessed high Al concentration during
the spray pyrolysis deposition. When the high-Al-content droplets were deposited on a substrate, the resultant grains' size and shape were identical to those of the 5 at.% Al-doped ZnO.

![Figure 5](image-url)

**Figure 5.** Optical transmittance spectra of Al/Ga-codoped ZnO thin films over the wavelength range of 300–800 nm. The Al:Ga codoping proportions are 5:0, 3.75:1.25, 2.5:2.5, 1.25:3.75, and 0:5 at.%.

**Table 2.** Average crystallite sizes of the AGZO films as a function of Al:Ga codoping proportions.

<table>
<thead>
<tr>
<th>Al:Ga codoping proportions (at.%)</th>
<th>Crystallite sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Image analysis</td>
</tr>
<tr>
<td>5:0</td>
<td>23</td>
</tr>
<tr>
<td>3.75:1.25</td>
<td>31</td>
</tr>
<tr>
<td>2.5:2.5</td>
<td>34</td>
</tr>
<tr>
<td>1.25:3.75</td>
<td>36</td>
</tr>
<tr>
<td>0:5</td>
<td>41</td>
</tr>
</tbody>
</table>

### 3.3. Optical transmittance and the bandgap energy of the thin films

The optical transmittance spectra (wavelength range 300–800 nm) of the AGZO films for varying Al:Ga codoping proportions are plotted in Figure 5. The results show that all the codoped films are highly transparent over the visible region; the average optical transmittance values of all the films are higher than 80% in the visible and near infrared region. The transmittance values of all the films fall off for wavelengths shorter than 380 nm, which are in the UV range, due to the band absorption of the ZnO films. The optical transmittance over visible light region of 5 at.% Ga doping ZnO is higher than those of the 5 at.% Al-doped ZnO and AGZO films. From the AFM and SEM results, the grains of Al-doped ZnO and AGZO are finer than those of Ga doping ZnO. Moreover, the codoping Al significantly reduces grain sizes of the films. Small grain sizes result in large grain boundary density, which is one of the main light scattering defects. As a result, the visible light transmittance of
Al-doped ZnO and AGZO is significantly lower than that of Ga-doped ZnO. Doping more Ga contents slightly increases the transmittance over the visible light region. 

Figure 6. The Tauc’s plots for determining the bandgap energy of AGZO films with varying Al:Ga codoping proportions of 5:0 at.%, 3.75:1.25 at.%, 2.5:2.5 at.%, 1.25:3.75 at.% and 0:5 at.%. 

The energy bandgaps of the AGZO films are derived from the Tauc’s plots of $(a h \nu)^2$ vs $-h \nu$, as shown in Figure 6. The energy bandgaps of the AGZO with Al:Ga codoping proportion of 0:5, 1.25:3.75, 2.5:2.5, 3.75:1.25, and 5:0 at.% are 3.29, 3.29, 3.28, 3.25, and 3.24 eV, respectively. An increase in Ga codoping proportion reduces the bandgap energy. The bandgap energy results correspond well with those reported by Ebrahimifard et al., where for high doping concentration, Al-doped ZnO ($E_g = 3.34$ eV) exhibits larger bandgap than Ga-doped ZnO ($E_g = 3.29$ eV) [13]. From the optical transmittance data, the transmittance of the films over the UV range is the largest for the Al-doped ZnO. Codoping more Ga proportion decreases the UV transmittance. Based on the energy gap and film thicknesses analyses, higher Ga doping proportion reduces the bandgap energy and increases the film thicknesses. Consequently, for the films with higher Ga doping proportion, more electrons absorbed photons over UV ranges, resulting in lower UV transmittance.

3.4. Electrical properties of the thin films

The electrical sheet resistances of AGZO films are shown in Table 1. The sheet resistance is clearly affected by the varying Al:Ga codoping proportions. The sheet resistance of Al:Ga codoping at 3.75:1.25 at.% was 4.41 MΩ/sq, which was significantly reduced from 67.95 MΩ/sq of the 5 at.% Al-doped ZnO. Further decrease in
the Al codoping proportion slightly decreases the sheet resistance. As discussed in the AFM and SEM analyses, a higher Al doping content led to finer grains with disorder structures and high grain boundary concentrations, which are electron-scattering barriers. The scattering of charge carriers by grain boundaries plays a dominant role in the electrical conduction mechanism in ZnO films [31]. The effects on the electrical transport are also caused by increase in barrier potentials at grain boundary due to poor crystallinity, incomplete oxidation, or chemisorbed oxygen. As a result, the electron mobility is decreased due to a higher concentration of grain boundaries. Therefore, an increase in Al doping content increases the sheet resistance of the AGZO thin films. However, for the 1.25:3.75 at.% Al:Ga codoping and the 5 at.% Ga doping, their sheet resistances are close at 0.88 and 0.71 MΩ/sq, respectively.

The electrical resistivity results of the AGZO films are summarized in Table 1. The resistivity of 5 at.% Al-doped ZnO is much higher than those of AGZO films. As discussed above, Al-doped ZnO exhibits fine amorphous-like grains with high grain boundary concentration leading to high electron scattering rate and high resistivity. Moreover, it has been reported that Ga-doped ZnO is more stable n-type ZnO than Al-doped ZnO [12,13]. For high doping concentration, Al dopants are more likely to form oxide compounds resulting in higher electrical resistivity than do the Ga dopants [12]. Also, the bandgap energy of AGZO appears to decrease with increasing Ga codoping proportion. Lower bandgap energy results in larger amounts of free electrons leading to lower resistivity. The minimum resistivity is obtained from the 2.5:2.5 and 1.25:3.75 at.% AGZO films. The codoping of Al:Ga improves the conductivities as compared to pure doping of Al or Ga. The resistivity values of the 2.5:2.5 and 1.25:3.75 at.% AGZO films (7.3 Ωcm) are close to those of 2:2 at.% AGZO (11 Ωcm), reported by Ebrahimifard et al. [13]. This demonstrates the feasibility of using Al/Ga codoping in order to reduce the dopant cost by partially substituting Ga dopants with Al dopants, while improving the electrical properties of the ZnO thin films. However, the minimum resistivity obtained from this work is relatively high to be applied as high-performance transparent conductive electrodes. The AGZO electrical properties may be improved by heat treatment process. Lee et al. showed that the AGZO resistivity can be reduced from 10 Ωcm to 1.1 × 10⁻³ Ωcm by annealing the films at 450 °C [17]. Therefore, the heat treatment of the highly doped AGZO should be investigated further to improve its performance.

4. Conclusion

Al/Ga-codoped ZnO thin films (AGZO) were prepared on glass substrates by a spray pyrolysis method with varying Al:Ga codoping proportions and total codoping concentration of 5 at.%. The Al-doped ZnO showed highly uniform, fine nano grains with round shapes, while the Ga-doped ZnO possessed coarse nano grains with an oval shape. The thin films with higher Al doping content exhibited more amorphous-like structures due to fine nano grains with high concentrations of disordered grain boundary regions. The optical transmittance spectrums showed transmittance higher than 80% in the visible light region for all the codoped films. The sheet resistances and resistivity of the AGZO thin films are significantly lower than those of the 5 at.% Al-doped ZnO. An increase in the Al codoping content in the AGZO films slightly increase their sheet resistance and resistivity due to finer grains with higher concentrations of grain boundaries. For both the 1.25:3.75 at.% Al:Ga codoping and the 5 at.% Ga doping, their sheet resistances are fairly close at 0.88 and 0.71 MΩ/sq, respectively. The minimum film resistivity of 7.3 Ωcm is obtained from 2.5:2.5 and 1.25:3.75 at.% AGZO films.
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