Influence of various thickness metallic interlayers on opto-electric and mechanical properties of AZO thin films on PET substrates

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Various thickness metallic interlayers to improve the opto-electric and mechanical properties of aluminum-doped zinc oxide (AZO) thin films deposited on flexible polyethylene terephthalate (PET) substrates are studied. The effects of the interlayers on the resistance and transmittance of the AZO thin films are discussed. The result shows that the metallic interlayers effectively improve the electric resistance but reduce the optical transmittance of the AZO thin films. These phenomena become more obvious as the interlayer thickness increases. However, the AZO with an aluminum interlayer still behaves an acceptable transmittance. Moreover, mechanical tests indicate that the aluminum interlayer increases the hardness and modulus, and reduce the residual stress of the AZO thin films. In contrast, the silver and copper interlayers decrease the AZO’s mechanical properties. Comparing to those without any interlayer, the results show that the best interlayer is the 6 nm thick aluminum film.

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1. Introduction

Aluminum-doped zinc oxide (AZO) films become widely used transparent conductive oxide (TCO) thin films in optoelectronic devices such as solar cells and displays because of its low cost and toxic free [1–6]. Although AZO thin films possess low cost advantage, its electrical and optical properties are normally worse than those of indium tin oxide (ITO) films [7,8]. Therefore, how to deposit a high quality AZO film becomes an important issue in the TCO applications. The basic idea to improve the electric properties of the AZO film is to raise the aluminum doped rate. But, Park et al. [1] showed that not all aluminum atoms in the film are activated and they also found the saturated doped rate is 3 wt %. Other methods were reported, such as elevating the substrate temperature during AZO sputtering [9,10] or using high RF sputtering power [4]. However, the elevated temperature or power may lower the optical property and even the film adhesion [3,5].

AZO thin films deposited on flexible substrates are gaining a great interest in the last decade [11,12]. It is because the flexible substrates provide advantage such as lighter weight, higher shock resistance, flexible stock, and roll-to-roll processing. However, the disadvantage of flexible substrates is lack of providing mechanical support, inducing cracking or peeling in the thin films [13]. The defects sequentially affect the optical and electric behaviors of the thin films. It is also difficult to deposit high quality AZO thin films on some flexible substrates, such as polymers, because of the limit of depositing and annealing temperature [14]. Therefore, it is necessary to find a substitutive solution to improve the opto-electric and mechanical properties of the AZO thin films on flexible substrates.

In this work, a systematic study of various interlayers with various thicknesses to improve the quality of AZO/PET structures is presented. Three metal interlayers (silver, aluminum, and copper) with three thicknesses (6, 8, and 10 nm) are sputtered between the AZO film and the PET substrate. Electric resistance and optical transmittance of the AZO thin films are measured by a four-point probe and an UV/Vis/NIR spectrophotometer. Further observation on microstructure and mechanical properties are tested by X-ray diffraction and nanoindentation. All the results are compared to those without any interlayer.

2. Experiments

AZO thin films combined with three metallic interlayers, including silver, aluminum, and copper, are studied in this work. All the thin films are deposited by sputtering, where the sputtering parameters are listed in Table 1. The target of AZO uses 98 wt% ZnO added 2 wt% Al2O3, and all interlayers use pure metallic targets. To ensure the thin film quality, the sputtering pressure, Ar gas flow, and RF power are slightly adjusted for various targets. Three thicknesses of interlayers, including 6, 8, and 10 nm, are considered. The metallic interlayers are first sputtered on the PET substrate, and then the AZO film is sputtered on the top of the interlayer. In all cases, the PET substrate is 20 mm × 20 mm, 188 μm-thick, and the AZO film is 200 nm-thick. Before sputtering, all the substrates are carefully...
cleaned in an ultrasonic bath and treated by O₂ plasma. The final film thickness is confirmed by a Kosaka ET4000 surface profiler, where all the thickness tolerances are controlled within 3% and the surface roughnesses are less than 3 nm. A grazing-incidence XRD machine (PANalytical X’Pert PRO MPD) with a copper anode (λ = 0.154 nm) is utilized in the microstructure analysis. The phase structure and crystallite grain size can be determined from the XRD patterns in the usual 2θ geometry. According to the Scherrer formula [15,16], the grain size D is defined as

\[ D = \frac{k\lambda}{\cos \theta \cdot B} \]  

with the correction factor \( k \approx 1.05 \), the X-ray wavelength \( \lambda \) (= 0.154 nm), the diffraction angle \( \theta \), the full width at the half maximum (FWHM) \( B \), and the broadening peak width \( B_0 \). The values \( B \) and \( B_0 \) can be obtained from the 2θ diagram of XRD. The grain size is then determined by substituting these data into Eq. (1).

The residual stresses of thin films can be calculated based on the biaxial strain model. The strain along the c-axis can be estimated by the relation

\[ \varepsilon_f = \frac{d_{\text{film}} - d_{\text{bulk}}}{d_{\text{bulk}}} \]  

where \( d_{\text{bulk}} \) is the unstrained lattice constant of bulk AZO and \( d_{\text{film}} \) is the lattice constant of the AZO films measured by XRD. The film stress (\( \sigma_f \)) parallel to the film surface has been used as following formula, which is valid for a hexagonal lattice [12,17]:

\[ \sigma_f = \frac{2c_{13}^2 - c_{33}(c_{11} + c_{12})}{2c_{13}} \cdot \varepsilon_f \]  

where \( c_{ij} \) denotes the elastic constants of single crystalline AZO. The constants \( c_{11} = 208.8 \text{ GPa} \), \( c_{13} = 213.8 \text{ GPa} \), \( c_{12} = 119.7 \text{ GPa} \), and \( c_{13} = 104.2 \text{ GPa} \) are used in this work [12,17]. The calculated stress and grain size are shown in Table 2. The negative stress denotes the compressive state of the film.

Typical nanoindentation experiments are performed by using a Hysitron Triboindenter fitted with a standard Berkovich indenter. The loading time, holding time, and unloading time of the indentation tests are all 5 s. The peak load is carefully controlled so that the indentation depth is always less than 20% of the film thickness for each specimen. A standard analysis to determine the hardness and elastic modulus from the unloading load–depth curve is conducted according to the Oliver and Pharr method [18,19]. Following the Oliver and Pharr method, the hardness and reduced modulus can be determined by

\[ H = \frac{P_{\max}}{A}; \quad E_r = \frac{S}{2\beta} \cdot \sqrt{\frac{\pi}{A}} \]  

where \( P_{\max} \) represents the peak load, \( A \) is the projected contact area, \( S \) denotes the slope of the initial portion of the unloading curve, and \( \beta \) is a constant that depends on the geometry of the indenter, \( \beta = 1.034 \) for Berkovich indenter. The hardness is the mean pressure that a material can support under load. The elastic modulus can be determined from the reduced modulus by subtracting the elastic deformation occurs in the indenter.

Electrical sheet resistance of the thin films is examined using a four-point probe (QUATEK 5610Y/QT-50). Optical transmittance of the specimens is measured using an UV/VIS/NIR spectrophotometer (BWTEK RTC112) with normal incidence in the visible wavelength ranged from 400 to 800 nm, taking the air as reference.

3. Results and discussion

In the XRD analysis, Fig. 1 shows the diffraction patterns of AZO thin films with various silver interlayer thicknesses. Three XRD peaks, (0 0 2), (1 0 2), and (1 0 3), of AZO are identified, showing the preferred orientation (0 0 2) texture at 2θ = 34.3° for all cases. It also illustrates the intensity of the (0 0 2) peak increases with the interlayer thickness, where the detail values are listed in Table 2. Fig. 2 shows the XRD patterns of AZO with various aluminum interlayer thicknesses. Similar three peaks and the preferred orientation are found. In contrast, the intensity of the (0 0 2) peak decreases with the interlayer thickness, where the detail values are listed in Table 3. The XRD patterns of AZO with various copper interlayer thicknesses are shown in Fig. 3. It shows the intensity of the preferred orientation (0 0 2) decreases with the interlayer thickness, also listed in Table 4. Comparing Figs. 1–3, the XRD results illustrate AZO with silver and aluminum interlayers have higher intensity, which means the silver and aluminum interlayers improve the microstructure of the AZO film. Furthermore, the XRD intensity of AZO with the copper interlayer is even less than that without the interlayer, meaning the copper interlayer is helpless to the AZO microstructure.

Table 1
Sputtering parameters.

<table>
<thead>
<tr>
<th>Film type</th>
<th>AZO</th>
<th>Ag</th>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>98 wt% ZnO + 2 wt% Al₂O₃</td>
<td>99.99 wt% Ag</td>
<td>99.99 wt% Al</td>
<td>99.99 wt% Cu</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Pre-sputtering pressure (Torr)</td>
<td>5 × 10⁻⁶</td>
<td>5 × 10⁻⁶</td>
<td>5 × 10⁻⁶</td>
<td>5 × 10⁻⁶</td>
</tr>
<tr>
<td>Sputtering pressure (Torr)</td>
<td>1.6 × 10⁻²</td>
<td>7.5 × 10⁻³</td>
<td>4.8 × 10⁻³</td>
<td>7.5 × 10⁻³</td>
</tr>
<tr>
<td>Sputtering Ar gas flow (sccm)</td>
<td>70</td>
<td>50</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>100</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Pre-sputtering time (min)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Sputtering time (s)</td>
<td>540</td>
<td>20/30/50</td>
<td>30/40/50</td>
<td>50/60/70</td>
</tr>
<tr>
<td>Film thickness (nm)</td>
<td>200</td>
<td>6/8/10</td>
<td>6/8/10</td>
<td>6/8/10</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of AZO/Ag/PET.
Table 2
Opto-electric and mechanical properties of AZO/Ag/PET.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>AZO/6 nm Ag/PET</th>
<th>AZO/8 nm Ag/PET</th>
<th>AZO/10 nm Ag/PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD (0 0 2) intensity (cps)</td>
<td>46,610</td>
<td>42,138</td>
<td>40,664</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>16.9</td>
<td>16.3</td>
<td>16.6</td>
</tr>
<tr>
<td>Residual stresses (GPa)</td>
<td>−1.07</td>
<td>−1.07</td>
<td>−1.07</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>4.0</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>17.0</td>
<td>16.4</td>
<td>15.7</td>
</tr>
<tr>
<td>Sheet resistance (Ω/□)</td>
<td>125</td>
<td>41</td>
<td>24</td>
</tr>
<tr>
<td>Transmittance (%)</td>
<td>65.9</td>
<td>63.2</td>
<td>59.0</td>
</tr>
</tbody>
</table>

Table 3
Opto-electric and mechanical properties of AZO/Al/PET.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>AZO/6 nm Al/PET</th>
<th>AZO/8 nm Al/PET</th>
<th>AZO/10 nm Al/PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD (0 0 2) intensity (cps)</td>
<td>38,783</td>
<td>43,111</td>
<td>42,994</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>16.9</td>
<td>16.9</td>
<td>16.9</td>
</tr>
<tr>
<td>Residual stresses (GPa)</td>
<td>−1.07</td>
<td>−0.94</td>
<td>−0.88</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>4.0</td>
<td>4.6</td>
<td>5</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>18</td>
<td>18.6</td>
<td>20</td>
</tr>
<tr>
<td>Sheet resistance (Ω/□)</td>
<td>3000</td>
<td>155</td>
<td>145</td>
</tr>
<tr>
<td>Transmittance (%)</td>
<td>90.6</td>
<td>88.8</td>
<td>76.9</td>
</tr>
</tbody>
</table>

Table 4
Opto-electric and mechanical properties of AZO/Cu/PET.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>AZO/6 nm Cu/PET</th>
<th>AZO/8 nm Cu/PET</th>
<th>AZO/10 nm Cu/PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD (0 0 2) intensity (cps)</td>
<td>42,571</td>
<td>38,959</td>
<td>31,319</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>17.0</td>
<td>16.6</td>
<td>17.0</td>
</tr>
<tr>
<td>Residual stresses (GPa)</td>
<td>−1.01</td>
<td>−1.07</td>
<td>−1.14</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>4.3</td>
<td>3.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>17.4</td>
<td>16</td>
<td>17.8</td>
</tr>
<tr>
<td>Sheet resistance (Ω/□)</td>
<td>141</td>
<td>59</td>
<td>40</td>
</tr>
<tr>
<td>Transmittance (%)</td>
<td>71.8</td>
<td>70.3</td>
<td>68.5</td>
</tr>
</tbody>
</table>

Fig. 4 shows the grain size of AZO thin films with various interlayer thicknesses. Based on the Scherrer equation shown in Eq. (1), the grain size can be determined from the XRD patterns. Fig. 4 shows the grain size of AZO thin films with the aluminum interlayer increases from 16.9 nm to 17.3 nm as the interlayer thickness increases from 6 nm to 10 nm. Similar tendency is found for the cases of silver and copper interlayers, in which the grain size lowers as the interlayer thickness increases from 6 nm to 8 nm and then returns to the same value as the thickness increases to 10 nm. It emphasizes that only the aluminum interlayer can effectively improve the crystalline of the AZO thin films.

Fig. 4 shows the residual stress of AZO thin films with various interlayer thicknesses. Based on the biaxial strain model shown in Eq. (3), the residual stress of the thin film can be determined from the XRD results. Fig. 5 shows all the residual stresses for all cases are compressive, and vary from −1.15 GPa to −0.85 GPa. It shows the average residual stresses of AZO/Ag/PET are −1.07, −1.07, and −1.01 GPa for 6, 8, and 10 nm silver interlayers. The average residual stresses of AZO/Al/PET decreases from −0.94 to −0.88 GPa as the aluminum interlayer thickness increases from 6 to 10 nm. The average values of AZO/Cu/PET are −1.01, −1.07, and −1.14 GPa for
6, 8, and 10 nm copper interlayers. Note that the residual stress of the AZO thin film without any interlayer (AZO/PET), is −1.07 GPa, meaning that only the aluminum interlayer can reduce the amplitude of the residual stress of the AZO films.

There are two commonly used techniques in thin film stress measurement. One is the substrate curvature method which measures the substrate curvature change before and after thin film deposition [20]. The other non-destructive technique has been frequently used for thin film stress measurement is call sin² ψ method [21]. The basic concept of the sin² ψ method analysis is that the lattice spacing varies with the orientation of the lattice planes with respect to the loading direction. The film stress can be determined from the linear regression of the XRD peak shift. However, the accuracy of the sin² ψ method strongly depends on the crystallinity of the thin film. In this work, therefore, we use the biaxial strain model instead of the substrate curvature and sin² ψ methods because it is difficult to measure the curvature of the flexible substrates and to identify enough XRD peaks of the AZO films (see Figs. 1–3).

The residual stress of a thin film is the sum of the intrinsic stress, the thermal stress, and the external stress. The intrinsic stress is due to the deposition defects and lattice mismatch between the thin film and the substrate. The thermal stress is caused by the thermal mismatch between the thin film and the substrate, and the temperature difference between the deposition and the ambient during stress measurement. The external stress denotes the stress resulting from an external mechanical load.

Note that the experimental results show that the aluminum interlayers effectively reduce the amplitude of the residual stress of the AZO films. It is because the aluminum interlayer provides a buffer layer between the polymeric substrate and the oxide thin film, which improve the crystallinity of the AZO film. In other words, it is easier to deposit AZO on the aluminum interlayer than on silver or copper interlayers. Referring to microstructures shown in Fig. 4 and Tables 2–4, the results illustrate that AZO thin films deposited on the aluminum interlayer surface have better crystallinity than on other surfaces. Liu et al. [12] also reported that the amplitude of the compressive stress of the sputtered zinc oxide films reduces as the crystal grain size increases, which agrees well with this work.

Moreover, the interlayer reduces the thermal mismatch between the substrate and the thin film. The thermal stress of a thin film deposited a substrate can be simply calculated from the temperature change (ΔT) and mismatch of coefficient of thermal expansion (CTE) as:

$$
\sigma_f = \frac{\Delta T(\alpha_s - \alpha_f)E_f}{1 - \nu_f}
$$

where α denotes CTE and the subscripts s and f indicate the substrate and the thin film. The CTEs of AZO, PET are 5.4, 62 × 10⁻⁶/°C, and of Ag, Al, Cu are 20, 25, 18 × 10⁻⁶/°C, respectively [22]. The metallic interlayers can reduce the CTE mismatch thus decreasing the thermal stress during the AZO film deposition. However, referring to Fig. 4 and Table 4, it is difficult to deposit silver thin films on the PET substrate, which results in worse crystallinity and higher residual stress of AZO films in the silver interlayer cases.

The elastic modulus and hardness of various AZO thin films measured by nanoindentation are shown in Figs. 6 and 7. They show...
that, as the interlayer thickness increases, the moduli and hardnesses of AZO with aluminum (AZO/Al/PET) increases, and those of AZO with copper interlayers (AZO/Cu/PET) almost remain constant, but those of AZO with silver interlayer (AZO/Ag/PET) decrease. The detail values are listed in Tables 2–4. The modulus and hardness of AZO without any interlayer are also list in Table 3. Figs. 6 and 7 emphasize that only aluminum interlayer improves the modulus and hardness of AZO/PET.

Nanoindentation results strongly depend on the indentation depth and substrate effects. Although many modified formulations proposed [23,24], it is still difficult to separate the thin film’s properties from the nanoindentation results, especially for flexible substrates. However, the nanoindentation tests provide relative comparison of mechanical behaviors among various interlayers.

Similarly, the result that the aluminum interlayer increases the modulus and hardness of AZO/PET is consistent with the improvement of the microstructure and grain size shown in Figs. 1–4. The aluminum interlayer enhances the crystallinity of the AZO films thus raising the hardness and modulus, which agrees well with other reports [5,12]. Furthermore, the metallic interlayers are much stiffer than the PET substrate. The mechanical support provided from the metallic interlayer also increases the hardness and modulus measured with nanoindentation.

Fig. 8 shows the sheet resistance of the AZO thin films with various interlayer thicknesses. It illustrates the sheet resistance of AZO/Ag/PET decreases from 125 to 24 Ω/□ as the Ag interlayer thickness increases from 6 to 10 nm. For AZO/Al/PET, the resistance slightly decreases from 155 to 134 Ω/□ as the Al interlayer thickness increases from 6 to 10 nm. The sheet resistance decreases from 141 to 40 Ω/□ as the copper interlayer thickness increases from 6 to 10 nm. Referring to the result without the interlayer listed in Table 3, it indicates the sheet resistance of AZO/PET is 3000 Ω/□, which is much higher than those with the interlayer. The resistance of the AZO/PET is unacceptable in the applications of conductive films. The result emphasizes that the interlayer effectively improves the electric resistance of the AZO thin films which already reach applicable levels.

Fig. 9 exhibits the optical transmittance spectra of AZO thin films with various silver interlayer thicknesses. It shows the transmittance decreases as the interlayer thickness increases. With 6 nm silver interlayer, the average transmittance is 65.9%. And then, the average transmittance decreases to 59.0% as the silver interlayer increases to 10 nm. Fig. 10 exhibits the transmittance spectra of AZO thin films with various aluminum interlayer thicknesses. Similarly, the transmittance decreases as the interlayer thickness increases. Fig. 10 shows the average transmittance decreases from 88.8% to 76.9% as the aluminum interlayer thickness increases from 6 nm to 10 nm. Note that the average transmittance of the AZO thin film without any interlayer is 90.6%. Fig. 11 exhibits the AZO transmittance with various copper interlayer thicknesses, showing the average transmittance is 70.3% with 6 nm aluminum interlayer, and it slightly decreases to 68.5% as the aluminum interlayer increases.
to 10 nm. Comparing Figs. 9–11, the transmittance of the AZO films decreases as adding an interlayer, silver interlayer especially. However, the average value of the AZO film with 6 nm aluminum interlayer decreases slightly and still maintains an acceptable 88.9% transmittance.

All the experimental results, including XRD (0 0 2) peak intensity, grain size, residual stress, hardness, elastic modulus, sheet resistance, and average transmittance, of the AZO/Ag/PET specimens are listed in Table 2. All the results of AZO/Al/PET and AZO/Cu/PET specimens are also listed in Tables 3 and 4, respectively. Furthermore, the opto-electric and mechanical properties of AZO thin films without any interlayer, denoted as AZO/PET, are listed in Table 3 for comparison. Tables 2–4 only list the average values, where the error bars of the standard deviation for each experimental result are indicated in Figs. 6–8 individually.

4. Conclusions

The effects of various interlayers on the opto-electric and mechanical properties of transparently conductive AZO thin films deposited on flexible PET substrates are studied in this work. Comparing to the case without any interlayer, the results of the characteristic testing show that the metallic interlayers can effectively improve the electric resistance but reduce the optical transmittance. These phenomena become more obvious as the interlayer thickness increases. For various interlayers, the silver has the best resistance and the aluminum behaves the best transmittance. Moreover, the aluminum interlayer increases the hardness and modulus of the AZO thin films, but the silver and copper interlayers slightly decrease the mechanical properties. The aluminum interlayer also decreases the residual stresses of the AZO films. In summary, the aluminum interlayers are the most beneficial to the AZO thin films on flexible substrates.

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