Study the Effect of ZnO/Cu/ZnO Multilayer Structure by Radio Frequency Magnetron Sputtering for Flexible Display Applications

Himadri Sekhar Das,¹,²,∗ Gourisankar Roymahapatra,² Prasanta Kumar Nandi¹ and Rajesh Das²

Abstract

ZnO/Cu/ZnO multilayer structured glass and Polyethylene naphthalate (PEN) with different thickness of copper (Cu) layer were prepared by RF magnetron sputtering at room temperature. The electrical resistivity of the films were achieved 8.6×10⁻⁵ Ω·cm and 4.5×10⁻⁴ Ω·cm, carrier concentration of 5.32×10²¹ cm⁻³ and 1.36×10²¹ cm⁻³, low sheet resistance of 12 Ω/cm² and 16 Ω/cm² respectively on glass and PEN substrate respectively with optical transmission of more than 80% for both cases at the optimum copper layer thickness. Conduction mechanism of the multilayer structure has been explained in terms of metal to oxide carrier injection with the variation of the thickness of the Cu layer. Different optimization procedures were used to achieve good optically transparent and electrically conductive films. The structural characterizations of multilayer films were carried out by X-ray diffraction (XRD); surface morphology, and topography were performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) respectively. The value of sheet resistance of the structure was influenced by the deposition condition of both layers. Effect of substrate and thickness of the Cu layer was investigated and illustrated.

Keywords: RF magnetron sputtering; Flexible Display Applications; ZnO/Cu/ZnO Multilayer Structure.

1. Introduction

Transparent and conducting oxide (TCO) is a type of materials which can show conductivity and transparency simultaneously.¹⁻²¹ TCO films show excellent electrical resistivity in the order of 10⁻⁴ Ω·cm to 10⁻³ Ω·cm with optical transmission more than 90%. This balanced electrical and optical properties of TCO makes it useful for a wide range of applications in flat-panel displays, solar cells, gas sensors, thin film transistor (TFT), liquid crystal displays (LCD), photovoltaic devices, organic light emitting diodes (OLEDs) and smart windows.¹⁻⁸ TCO films can be deposited by different deposition techniques such as spray pyrolysis,⁹ sol–gel process,¹⁰ pulsed laser deposition,¹¹ thermal evaporation,¹² chemical vapor deposition,¹³ electron beam deposition¹⁴ and radio frequency (RF) magnetron sputtering¹⁵⁻¹⁷ on various substrate. Among different deposition techniques RF magnetron sputtering technique is more beneficial due to its uniformity and high deposition rates.¹⁸,¹⁹

Indium tin oxide (ITO) and Fluorine doped tin oxide (FTO) are commercially established as highly efficient TCO materials. These materials show excellent electrical conductivity with high optical transmission in the visible region of the solar spectrum. Cost and availability of indium materials influenced the thinking of researchers to find out alternative TCO materials. Different doped (Al, Ga, In) zinc oxide (ZnO) films exhibit good electrical conduction and optical transmission in the visible region.²⁰⁻²¹ In different experiment many groups have shown the promising results of electrical resistivity (10⁻⁴ Ω·cm) and high optical transmission (more than 90%) in case of doped Zinc oxide (ZnO)²²,²³ thin films. The results such as, conductivity, optical transmission and sheet resistance of doped ZnO thin film, makes itself an alternative TCO material. Such types of properties make ZnO films as appropriate materials for optoelectronic devices, solar cells and OLEDs. ZnO materials have some advantages such as easy availability, low cost, good radiation resistance, good conductivity and high optical transmission.²⁴ Only there is a limitation for increasing the conductivity, as it is known that the conductivity can increases with increasing the carrier

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concentration, due to its ionized impurity scattering. It is found that synthesized ZnO thin films at a temperature from 200 to 300 °C are polycrystalline and textured. ZnO thin films, which are synthesized using pure Ar plasma gas, are highly porous and show very good optical transmittance and absorption spectra (near 380 nm). Abed et al. has studied the effect of RF magnetron on conventional solid state target based on ZnO-MgO:Al₂O₃ (10:2 wt %) material on glass and silicon substrates at the different working pressures. The resistivity of 8.8×10⁻² Ω·cm was achieved by the sample deposited at the lowest working pressure of 0.21 Pa. Recently, annealing effect on the structural and optical behavior of (ZnO:Eu³⁺) thin film growth been studied by Otieno et al. In our recent publication, we have studied the effect of substrate and substrate temperature on microstructure of magnetron sputtering doped-ZnO thin films. For few applications where low sheet resistance and high optical transparency required still not achieved. Different research groups had reported the dielectric-metal-dielectric thin film with different metal such as silver, Ag and Cu with increasing conductivity and high optical transmission. Among them, introduction of Cu layer in multilayer structure play significant role to increasing the conductivity of thin film. But the reports on the effect of thin Cu layer in multilayer structure are very few. In order to improve the overall performance of the transparent conductive films, Rasheed et al., Wang et al., and Toma et al. studied structural, electrical and optical properties of ZnO/Cu/ZnO multilayer film stacking using Cu film as a sandwich layer. The results showed that ZnO/Cu/ZnO multilayer film has good crystalline properties and with an increasing Cu layer thickness, a visible light transmittance of the multilayer film is reduced, while the electrical performance improved significantly. Sahu et al. studied the influence of post growth annealing on the structural, electrical and optical properties of the multilayer ZnO/Cu/ZnO films, prepared on glass substrates by simultaneous RF magnetron sputtering of ZnO and dc magnetron sputtering of Cu. Recently scientists are focusing their work to develop and replace the glass substrate to a flexible substrate for the application in display, optoelectronics and mobile. Light weight, thermally stable, chemically resists and dimensionally stable properties are preferred for a flexible substrate. Among

![Fig. 1](image_url)
the different alternative flexible substrate polyethylene naphthalate (PEN) was one of them studied recent past by different research group. In this paper, we have studied the optical, electrical properties and figure of merit of ZnO/Cu/ZnO multilayer structure by optimizing ZnO and Cu thickness at room temperature on glass and polyethylene naphthalate (PEN) substrate.

2. Experimental

Coating of ZnO and Cu multilayer thin films was performed on glass and PEN substrates by dual-target RF magnetron (powered at 13.56 MHz radio frequency) sputtering system room temperature (RT) under non reactive environment with RF power 100W. ZnO and Cu disc with a purity of (99.99 %) having 2 inch diameter and 5 mm thickness were used as sputtering target. The process chamber is evacuated up to a base vacuum of 2.4×10⁻⁶ torr. Target to substrate distance was kept at 6 cm for all experiments. Argon used as inert gas ambient and constant at 40 sccm throughout the entire deposition process. Before final deposition pre-sputtering of ZnO target is done in pure argon plasma atmosphere for about 15 min in order to remove the surface oxide layer of the target. And before that the glass substrate was cleaned properly with soap, methanol and ultrasonic bath.

The thickness of the film was measured using a digital thickness monitor (DTM) attached with RF magnetron sputtering system. The electrical properties of the multilayer (ZnO/Cu/ZnO) films were studied by Ecopia-HMS-3000 set-up. Optical transmittance and absorbance data of multilayer thin films were measured using UV-VIS spectrophotometer. Structural characterization of the films was carried out by X-ray diffraction (XRD) (Philips PW 1710 diffractometer) (Cu Ka, k = 1.54178 Å, 2θ scan mode). The surface morphology and topography were performed by Atomic Force Microscopy (AFM) (Tap 300 G).

3. Result and Discussion:

ZnO/Cu/ZnO films show promising electrical properties with \( \rho = 8.6 \times 10^{-5} \, \Omega \cdot \text{cm} \), \( R_{sh} = 12 \, \Omega / \text{cm}^2 \) and \( \rho = 4.5 \times 10^{-4} \, \Omega \cdot \text{cm} \) with \( R_{sh} = 16 \, \Omega / \text{cm}^2 \) and optical transmission of 86% and 84%, respectively on glass and PEN substrate. The resistivity, mobility and carrier concentration have been estimated from Hall measurements. The dependence of the resistivity, Hall mobility and carrier concentration of ZnO/Cu/ZnO multilayer with variation of Cu layer thickness are shown in Fig. 1. It shows (Fig. 1) the sheet resistance \( (R_s) \) as a function of the Cu layer thickness. Sheet resistance was decreases with increases of Cu layer thickness. Similar kind of result has been reported by Luan et al in another study. With increasing the Cu thickness the surface of the Cu thin films shows shifted from island state to continuous state. After formation of the continuous film sheet resistance begins to decrease. Mobility factor don’t have any effect on the sheet resistance. Mobility of multilayer film with different thickness of the copper layer is shown in Fig. 1. Mobility of the multilayer was increases with the thickness of the Cu layer.

The optical transmittance of the multilayer (ZnO/Cu/ZnO) thin films on Glass and PEN substrate are shown in Fig. 2. The thin films of multilayer show the highest transmittance 86% and 84% on glass and PEN substrate respectively, in the visible region of the solar spectrum. As the thickness of Cu layer increases from 2 nm to 8 nm optical transmittance decreases from 85% to 80% and 82% to 78% on glass and PEN substrate respectively. The decrease of transmittance in the higher region of the solar spectrum (near-infrared) results from the increase of reflectance and absorption which is attributed to the plasma resonance of the electron gas in the conduction band. The quality of good transparent conducting films can be judge by the figure of merit (FOM). Figure of merit was calculated by the equation \( \phi = 10^5 T / R_s \) where \( (T) \) transmittance and \( (R_s) \) sheet resistance. In case of glass and PEN substrate multilayer film (with 4nm Cu layer) shows (Fig. 1) highest FOM \( 1.84 \times 10^{-15} \, (\Omega \cdot \text{cm}^2)^{-1} \) and \( 1.09 \times 10^{-18} \, (\Omega \cdot \text{cm}^2)^{-1} \), respectively. Higher value of figure of merit means better performance of transparent conducting oxide film. The electrical and optical properties multilayers are mainly depended on the Cu properties.

![Fig. 2 Optical Transmission of ZnO(50nm)/Cu(4nm)/ZnO(50nm) multilayer on Glass (1) and PEN substrate (2).](image-url)
gradually decreases. This is a sharp indication of improved crystallinity with increase of the Cu thickness. Optimum electrical and optical properties were achieved for multilayer with 4nm Cu layer.

Optical band gap of the ZnO/Cu/ZnO multilayer on glass and PEN substrate is shown in Table 1. Variation of band gap was shown with different thickness of the Cu layer. Optical bandgap was calculated by using the equation

\[ \alpha h\gamma \propto (h\nu - E_g) \]

where \( \alpha \) stands for the absorption coefficient, \( h\nu \) optical energy and \( E_g \) represents the optical band gap. It is clear from the table that optical bandgap increases with decreasing Cu thickness. Decreasing of bandgap may be some Cu atoms permeate ZnO at the interface of the ZnO/Cu/ZnO multilayer. The value of bandgap with different thickness shows lower than the bulk of ZnO (3.37 eV).

**Table 1.** Band gap of multilayer with different thickness of Cu are on Glass and PEN substrate.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>ZnO/Cu/ZnO</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>ZnO(50nm)/Cu(2nm)/ZnO(50nm)</td>
<td>3.20</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(4nm)/ZnO(50nm)</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(6nm)/ZnO(50nm)</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(8nm)/ZnO(50nm)</td>
<td>3.12</td>
</tr>
<tr>
<td>PEN</td>
<td>ZnO(50nm)/Cu(2nm)/ZnO(50nm)</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(4nm)/ZnO(50nm)</td>
<td>3.16</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(6nm)/ZnO(50nm)</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>ZnO(50nm)/Cu(8nm)/ZnO(50nm)</td>
<td>3.11</td>
</tr>
</tbody>
</table>

ZnO and Cu have work function of 5.4 eV and 4.5 eV respectively. It is clear from the figure that the work function of copper is lower than the ZnO film and an accumulation layer form at the interface due to transfer of electrons from the metal to the semiconductor. Energy band diagram of the Cu/ZnO structure under isolation and interfaced shown in Fig. 4(a) and 4(b), respectively. During the interface of Cu and ZnO (Fermi level) aligns in the interface region and due to transfer of electrons from copper to ZnO. Transfer of electrons makes the valence and conduction bands of ZnO bend downward [Fig. 4(b)]. Work function difference of Cu and ZnO are large as a result significant of carriers into the ZnO semiconductor layer.

![Fig. 3 XRD patters of ZnO/Cu/ZnO multilayer structure with the different thickness of Cu layer on Glass and PEN substrate.](image)

It is clearly seen that the substantial decreases in resistivity and sheet resistance of the multilayer structure. Fig. 1 shows that Cu thickness, the ZnO/Cu/ZnO multilayer structure has a lower Hall mobility at 4 nm Cu layer in both glass and PEN substrate. This result suggests that most of the current passes through ZnO layer with a thin Cu layer which act as discontinuous scattering sites that reduce the mobility. It is clearly seen from the Fig. 1 as the thickness of Cu layer increases, the carrier concentration increases from \(8.68 \times 10^{20}\) cm\(^{-3}\) to \(7.68 \times 10^{22}\) cm\(^{-3}\) and \(7.20 \times 10^{20}\) cm\(^{-3}\) to \(8.21 \times 10^{20}\) cm\(^{-3}\) respectively for glass and PEN substrate. Also, the mobility increases from 16.24 cm\(^2\)/Vs to 17.02 cm\(^2\)/Vs for glass substrate. These results indicating that the Cu layer becomes near continuous to electron conduction and a large amount of current to pass through it. Basically, the sandwich layer of two ZnO and thin Cu layer a parallel network of electrical resistors. The amount of current flowing through each of the individual layers in turn is inversely to their resistance. Resistivity of the multilayer reduces from \(4.2 \times 10^{-4}\) Ω·cm to \(8.6 \times 10^{-5}\) Ω·cm,
Fig. 5 AFM images of ZnO/Cu/ZnO thin film on a) Glass (Cu 2nm) b) Glass (Cu 4nm) and c) PEN substrate (4nm).

5.0 × 10⁻⁴ Ω-cm to 4.5 × 10⁻⁴ Ω-cm for glass and PEN substrate respectively with the increasing of the thickness of the Cu layer. Multilayer of ZnO/Cu/ZnO with 4nm Cu thickness shows better percolation threshold.

The surface topography of ZnO/Cu/ZnO thin films grown on glass and PEN substrate are shown in AFM image (Fig. 5). Fig. 5(a) and Fig. 5(b) show the AFM image of ZnO/Cu/ZnO on glass substrate with Cu thickness of 2 nm and 4 nm respectively. From this figure it is clear that Fig. 5(a) shows non-uniform of crystallites with amorphous phase whereas Fig. 5(b) shows uniform spherical grain distribution. Also the surface looks very smooth these properties appropriate for display applications. Surface morphology of Multilayer films with Cu 4 nm deposited on PEN substrate shown in Fig. 5(c). Surface on PEN substrate also looks smooth which was appropriate for display applications.

Table 2. Surface roughness, grain size of ZnO/Cu/ZnO multilayer with different thickness of Cu films.

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>Variation of Cu (nm)</th>
<th>Surface roughness (δrms in nm)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>2</td>
<td>8.64</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.32</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>7.42</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.12</td>
<td>14</td>
</tr>
<tr>
<td>PEN</td>
<td>2</td>
<td>9.89</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>8.75</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>8.45</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.68</td>
<td>2</td>
</tr>
</tbody>
</table>

Variations of grain size and surface roughness with different thickness of Cu in Glass and PEN substrate are shown in Table 2. Among other properties surface roughness is one of the important properties for many opto-electronic and flexible display applications. Smooth surface is appropriate for OLED and display application where as rough surface is preferable for solar cell. Rough surface increases the scattering the light as a result optical transmission increases and finally it enhance the efficiency of the Cell. [40-45]

4. Conclusion
Multilayer films of ZnO/Cu/ZnO structure show high transmission in visible range of solar spectrum with low sheet resistance of 12 Ω/cm² by RF magnetron sputtering techniques. The good electrical resistivity (8.6 × 10⁻⁵ Ω-cm) and optical transmission (86%) of the multilayer films on glass are achieved by the optimization of growth condition. Also the 4 nm thick copper layer in the structure shows carrier concentration 5.32 × 10²¹ cm⁻³ and 1.36 × 10²¹ cm⁻³, figure of merit 1.84 × 10¹⁸ and 1.09 × 10¹⁸ glass and PEN substrate respectively. Electrical conduction and optical transmission were interdependent properties among others mainly affected by film structure. Improved electrical and optical properties also depends on preparation process parameters. Due to this advantage, RF magnetron sputtering is found to be most favorable deposition method. The properties such as electrical and optical of the multilayer films, depended dominantly on the characteristics of the metal interlayer. To achieve the low resistivity and high optical transmission, optimum thickness of the copper layer plays a crucial role with minimal loss in transmission due to absorption, reflection and scattering. The morphology and structure of very thin metal layer was also sensitive to the deposition condition. Room temperature deposited films shows excellent conductivity and optical transmission compare to those commercial indium tin oxides. The result makes the ZnO/Cu/ZnO multilayer is appropriate candidates for optoelectronic device and flexible display applications.

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Conflict of interest
There are no conflicts to declare.

Supporting information
Not applicable

References
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