Improved optoelectronics properties of ITO-based transparent conductive electrodes with the insertion of Ag/Ni under-layer

Ahmad Hadi Ali a,b,*, Ahmad Shuhaimi Abu Bakar c, Zainuriah Hassan b

a Science Department, Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn Malaysia, Johor, Malaysia.

b Nano Optoelectronics Research and Technology Laboratory, School of Physics, Universiti Sains Malaysia, Penang, Malaysia.

c Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, Universiti Malaya, Kuala Lumpur, Malaysia

A R T I C L E   I N F O

Article history:
Received 17 April 2014
Received in revised form 16 June 2014
Accepted 25 July 2014
Available online 2 August 2014

Keywords:
ITO
Ag/Ni
Sputtering
Transparent conductive electrode
Annealing

A B S T R A C T

ITO-based transparent conductive oxides (TCE) with Ag/Ni thin metal under-layer were deposited on Si and glass substrates by thermal evaporator and RF magnetron sputtering system. Ceramic ITO with purity of 99.99% and In2O3:SnO2 weight ratio of 90:10 was used as a target at room temperature. Post-deposition annealing was performed on the TCE at moderate temperature of 500–600 °C and 700 °C under N2 ambient. It was observed that the structural properties, optical transmittance, electrical characteristics and surface morphology were improved significantly after the post-annealing process. Post-annealed ITO/Ag/Ni at 600 °C shows the best quality of TCE with figure-of-merit (FOM) of 1.5 × 10−2 Ω−1 and high optical transmittance of 83% at 470 nm as well as very low electrical resistivity of 4.3 × 10−5 Ω−cm. The crystalline quality and surface morphological plays an important role in determining the quality of the TCE multilayer thin films properties.

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1. Introduction

Indium tin oxides (ITO) is preferred as a contact layer on optoelectronic semiconductor devices as it offers good electrical conductivity and highly transparent to visible light [1]. This transparent conducting oxides (TCO) serves as a good current spreading layer when connected to the external potential for application in visible light-emitting diode (LED). Electrical current from the external potential is spread uniformly by the TCO layer to the active region through the p-type semiconductor layer consequently producing photon in term of visible light. This visible light is transmitted out through the transparent TCO contact layer without losing much of its intensity and optical spectrum to the contact layer.

This wide band gap (~3.7–4.5 eV) [2] and high work function (~4.20 eV) [3] TCO can be prepared by RF magnetron sputtering system due to its ability of producing high quality thin films with high purity target material, almost contamination free under very low vacuum pressure and easy control of sputtering parameter. However, most of the sputtered single layer ITO thin films were amorphous in nature which results in relatively higher electrical resistivity of ~10−3 Ω−cm as compared to the crystalline ITO of ~10−4 Ω−cm [4]. Therefore, metal thin films are used as an intermediate layer in order to improve the electrical resistivity of the ITO. Kim reported his work on ITO/Ni/ITO multilayer films by RF magnetron sputtering with optical transmittance at blue spectrum of ~75% and electrical resistivity of 3.2 × 10−4 Ω−cm [5]. Guillén and Herrero investigated ITO/Ag/ITO multilayer electrodes with optical transmittance at blue spectrum of ~60–70% and sheet resistance of 6 Ω/sq [6]. Due to the opaque properties of the metal layer, the light transmittance through the ITO/metal/ITO contact layer decreases as compared to the single ITO thin films of ~85% [7,8]. These electrical and optical challenges can be overcome by performing substrate heating during sputtering or post-deposition annealing at specific heat treatment conditions [9–11]. Post-deposition annealing at certain temperature can transform the as grown amorphous ITO into polycrystalline ITO with superior optoelectronics functionality [12]. Some researchers observed an improvement in both the ITO thin films and the ITO/Si interface properties with the increasing of annealing temperature up to 300 °C [13], whereas other group of researchers reported on the improved optoelectronics properties of ITO-based transparent conductive electrodes after post-deposition annealing at temperature of 500–600 °C [14].

In this report, we discussed on the multilayer transparent conductive electrode (TCE) based on ITO with the insertion of Ni and Ag.
metal thin films to improve the electrical properties of the contact layer. The effect of post-deposition annealing at moderate temperature of 500 °C, 600 °C and 700 °C were investigated based on the TCE structural, optical, electrical and morphological characteristics.

2. Experimental setup

Si and glass were used as a substrate to deposit the ITO/Ag/Ni TCE multilayer. Glass was used in conjunction with Si in order to determine the optical transmittance of the TCE multilayer. Initially, thin Ni layer was deposited on Si and glass substrates by thermal evaporator followed by second metal thin films of Ag. The base vacuum pressure of the evaporator was set at $3.4 \times 10^{-5}$ mbar. Then ITO thin films were deposited on the Ag/Ni thin metal layer by RF magnetron sputtering. ITO with purity of 99.99% and In$_2$O$_3$:SnO$_2$ weight ratio of 90:10 was used as a target under Ar gas ambient at room temperature. Plasma vacuum pressure was set at 6.61 $\times 10^{-3}$ mbar with sputtering rate of $\sim 0.05$ nm/s. The TCE multilayer thicknesses measured by optical reflectometer model Filmetrics F20 are 70 nm, 5 nm and 3 nm for the ITO, Ag and Ni, respectively. The samples then were post-annealed at moderate temperature of 500 °C, 600 °C and 700 °C under consistent flowing of N$_2$ gas.

The crystalline quality of the ITO/Ag/Ni TCE multilayer was determined by 2Theta phase analysis X-Ray diffraction (PAXRD) with Cu $K_{\alpha 1}$ ($\lambda = 1.540598$ Å) as a radiation source at working voltage of 40 kV and filament current of 30 mA. Optical transmittance was examined by using UV–vis spectrophotometer over the spectrum ranges of 350–800 nm. The electrical resistivity, carrier concentration and mobility were investigated by means of Hall Effect measurement system. Surface morphological analysis in terms of surface roughness root-mean-square, $R_q$ and crystallite sizes were determined using atomic force microscope (AFM) operating under tapping mode and Nanoscope Analysis software, respectively.

3. Results

The structural properties of the ITO/Ag/Ni multilayer TCE inspected by PAXRD are shown in Fig. 1. No significant ITO peaks for the as deposited sample shows that the sample was amorphous. However, after post-annealed at 500 °C, 600 °C and 700 °C, a significant peak of ITO (2 2 2) and (4 0 0) corresponding to cubic bixbyite structure were identified at around 30.6° and 35.4°. An Ag (1 1 1) peak is also observed at $\sim 38.1°$ after undergone post-annealing process. Strongest ITO and Ag peaks were observed for a sample post-annealed at 600 °C as compared to other samples.

None of the spectrum indicated any characteristics peak of Ni due to the very thin layer of Ni. After post-annealing, the ITO structures were re-oriented and turned into crystalline from the as deposited amorphous nature. Thermal energy from the heat treatment process helps in improving the orientations and crystallizations of the ITO and Ag TCE multilayer. Guillén and Herrero have also reported the diffraction peak of ITO (2 2 2) and Ag (1 1 1) after post-annealing process [15]. A Si (1 1 1) peak also was noted at around 28.4° corresponding to the Si (1 1 1) substrate. From Scherrer’s equation, the calculated grain sizes of the ITO (1 1 1) is 34 nm, 33 nm and 36 nm corresponding to the post-annealed TCE of 500 °C, 600 °C and 700 °C, respectively.

The optical transmittance of the ITO/Ag/Ni TCE on glass was characterized by using UV–vis spectrophotometer along the wavelength ranges of 350–800 nm, as shown in Fig. 2. Post-annealed TCE at 600 °C demonstrate highest transmittance as compared to the other samples. At 470 nm, the 600 °C post-annealed TCE transmit almost $\sim 83%$ of lights as compared to the 500 °C ($\sim 76%$) and 700 °C ($\sim 74%$). The optical transmittance characteristics of the post-annealed samples were almost consistent throughout the visible spectrum ranges. The as deposited sample shows lower transmittance characteristics as compared to the post-annealed samples with $\sim 61%$ light transmittance at 470 nm. In addition, the optical transmittance characteristics of the as deposited TCE also do not consistent throughout the 350–800 nm spectrum ranges. The transmittance was gradually decreasing towards the ultraviolet region due to the light absorption by the TCE, whereas steadily decreasing towards the infrared wavelength region due to the light reflectance from the TCE multilayer. This results in less optical efficiency especially for the devices that transmitting light along the UV, visible and infrared region through the TCE multilayer. In general, post-annealing not only improving the optical transmittance characteristics of the TCE but the optical efficiency as well by consistently maintains the almost same amount of optical transmittance throughout the spectrum ranges. Moreover, the low transmittance characteristics of the as deposited amorphous TCE is mainly due to the disordered structure that causes light trapping and light scattering as well as light reflectance between the glass–Ni, Ni–Ag and Ag–ITO interfaces. In the other hand, the post-annealed TCE are more crystalline with highly ordered structure thus have higher and almost consistent transmittance characteristics.

Electrical properties of the TCE multilayer in term of resistivity, carrier concentration and mobility are shown in Fig. 3a–c. The resistivity of the 600 °C post-annealed TCE is the lowest of $4.3 \times 10^{-5}$ $\Omega$·cm as compared to the other post-annealed TCE, as in Fig. 3a. This resistivity is lower than as reported by Kim [5] of...
$3.2 \times 10^{-4} \, \Omega \cdot \text{cm}$ for ITO/Ni/ITO and Jeong [16] of $1.49 \times 10^{-3} \, \Omega \cdot \text{cm}$ for ITO/Ag/ITO multilayer thin films. From the relation of $\rho = 1/ne\mu$ where $\rho$ is the resistivity, $n$ is the carrier concentration, $e$ is the charge of the carriers and $\mu$ is the mobility, the resistivity is lower when the carrier concentration and mobility is higher [17]. This is confirmed from the results obtained as in Fig. 3b and c where the carrier concentration and mobility of the $600^\circ\text{C}$ post-annealed TCE is higher than the other post-annealed TCE. The measured carrier concentration and mobility of the $600^\circ\text{C}$ post-annealed sample is $1.43 \times 10^{22} \, \text{cm}^{-3}$ and $69.3 \, \text{cm}^2/\text{V} \cdot \text{s}$, respectively. The high carrier mobility and low resistivity results in higher conductivity of the TCE. Electrical current is easier to spread uniformly across the TCE multilayer into the optoelectronic devices. In the other hand, the higher resistivity and lower carrier concentration of the $700^\circ\text{C}$ post-annealed TCE as compared to the as deposited TCE are mainly due to the oxidation of the Ag/Ni metal intermediate layer during the post-annealing process.

It is important to evaluate the efficiency of the TCE multilayer based on their transmittance and electrical properties for appropriate application in optoelectronic devices. Figure of merit (FOM) allow to evaluate the performance of transparent conductive electrodes [18]

$$\text{FOM, } \varphi_{\text{TCE}} = \frac{T_{10}}{R_{\text{sh}}}$$

where $T_{10}$ is the transmittance and $R_{\text{sh}}$ is the sheet resistance. FOM for the as deposited, $500^\circ\text{C}$, $600^\circ\text{C}$ and $700^\circ\text{C}$ at $470\,\text{nm}$ wavelength are $5.4 \times 10^{-4} \, \Omega^{-1}$, $4.9 \times 10^{-3} \, \Omega^{-1}$, $1.5 \times 10^{-2} \, \Omega^{-1}$ and $9.2 \times 10^{-4} \, \Omega^{-1}$, respectively. FOM of the $600^\circ\text{C}$ TCE is the highest as compared to other TCE samples. Therefore, the $600^\circ\text{C}$ post-annealed TCE shows the best efficiency and consequently helps in improving the performance of optoelectronic devices. For comparison, a group of researchers have also reported the FOM for ITO/Ni/ITO of $4.9 \times 10^{-3} \, \Omega^{-1}$ [19] and ITO/Ag/ITO of $2.3 \times 10^{-3} \, \Omega^{-1}$ [20].

![Fig. 3. Electrical properties in term of (a) resistivity; (b) carrier concentration; (c) mobility of the TCE multilayer.](image)

![Fig. 4. Surface roughness root-mean-square of the TCE at different post-annealed temperature.](image)
Surface morphology also plays an important role in determining the efficiency of the TCE, especially for high optical transmittance and good electrical contact purposes. Surface roughness root-mean-square is generally used to describe the surface characteristics of the TCE layer. Fig. 4 shows the surface roughness $R_q$ of the TCE at different post-annealing temperature. The surface roughness $R_q$ decreases as the post-annealing temperature increased to 600 $^\circ$C and increases as the post-annealed temperature gets higher. The 600 $^\circ$C post-annealed TCE shows the smoothest surface morphology with measured surface roughness $R_q$ value of 1.4 nm, whereas the 700 $^\circ$C TCE shows the roughest surface with $R_q$ of 2.2 nm.

The surface roughness can be interrelated with the crystallites properties of the TCE multilayer. The crystallites orientation on the surface of the TCE multilayer are shown in Fig. 5a–d, scanned by AFM over an area of 1.0 $\mu$m $\times$ 1.0 $\mu$m. Identical sharp peaks were observed emerging from the TCE surfaces of the as-deposited sample. After post-annealing, the crystallite re-oriented forming different orientations as shown in Fig. 5b–d. The crystallites diffuse and interconnect with each other forming larger and elongated crystallites. These combinations results in porous-like surfaces which in turn assist in improving the light transmittance through the TCE layer. Measurement by Nanoscope Analysis software revealed the average crystallites sizes for the as deposited, 500 $^\circ$C, 600 $^\circ$C and 700 $^\circ$C are 25 nm, 36 nm, 35 nm and 37 nm, respectively. This post-annealed sample trend of result is in good agreement with the surface roughness $R_q$. The measured crystallite sizes are almost similar with the calculated value from the PAXRD results. As a comparison, Indluru also reported the measured grain sizes by AFM in the ranges of 35–50 nm [21].

4. Conclusion

ITO/Ag/Ni transparent conductive electrode multilayer was deposited by thermal evaporator and RF magnetron sputtering at room temperature. Post-annealing at moderate temperature improved the structural, optical and electrical properties of the TCE thin films significantly. The highest FOM of $1.5 \times 10^{-2}$ $\Omega^{-1}$ was achieved for the post-annealed TCE at 600 $^\circ$C with high optical transmittance of 83% and very low electrical resistivity of $4.3 \times 10^{-5}$ $\Omega$ cm. Crystallization of the TCE after post-deposition annealing assists in improving the optoelectronic properties of the TCE layer. Moreover, surface roughness and crystallite orientations...
with the formation of porous–like structure also assists in improving the optical and electrical properties of the TCE multilayer thin films.

Acknowledgments

The support from Universiti Sains Malaysia, Universiti Tun Hussein Onn Malaysia, Universiti Malaya and Ministry of Higher Education Malaysia are gratefully acknowledged. This research was partially funded by USM RU Postgraduate Research Grant Scheme (RU-PRGS), USM RU Grant, Exploratory Research Grant Scheme (ERGS) ER012-2011A, High Impact Research and University of Malaya Research Grant (UMRG) RG141-11AFR.

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