Structural, optical and electrical characterization of ITO, ITO/Ag and ITO/Ni transparent conductive electrodes

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1. Introduction

Indium tin oxides (ITO) are widely used in optoelectronic applications as transparent conductive electrodes (TCE) for light emitting and light detecting devices such as light emitting diodes (LED) and solar cells. This is due to its unique properties of highly transparent over the visible spectrum (>80%), very low resistivity (~10^-4 Ω cm), high carrier concentration (~10^21 cm^-3) with mobility around 10–30 cm²/Vs, wide optical band gap (~3.6–3.9 eV) and high work functions (~4.20 eV) [1–3]. ITO thin films can be prepared by electron beam evaporation [4], thermal evaporation [5], pulsed laser deposition [6], DC sputtering [7] and RF sputtering [8]. Among them, sputtering technique is mainly used to deposit the ITO thin films as it provides high deposition rates, easy to control sputtering parameter and able to deposit on a large area of substrates with good thin films quality. This highly degenerate n-type transparent conductive oxides (TCO) have been deposited on several substrates such as Si [9], glass [10], PET [11] and GaN [12,13] for studies on its structural, optical and electrical properties for optoelectronic device applications.

The fabrication of transparent conductive electrodes with high optical transparency and low electrical resistivity is of great importance for optoelectronic device applications. However, deposition of ITO single layer contact at room temperature resulted in high electrical resistivity due to the amorphous nature characteristics of the ITO. Therefore, the insertion of thin metal films intermediate layer with high electrical conductivity can improve the electrical resistivity of the TCE. But this scheme yielded a low optical transmittance due to the opaque characteristics of the metal films. Some research groups reported on the insertion of Ag inter-layer (ITO/Ag/ITO) and Ni inter-layer (ITO/Ni/ITO) with different structural, optical and electrical characteristics depending on the deposition techniques and parameter [14–17]. The insertion of the metal inter-layer improved the electrical conductivity, whereas the ITO TCE layer assists in suppressing light reflection in the visible spectrum [15,18].

Since ITO thin films deposited at room temperature are mainly amorphous with low electrical conductivity and relatively poor optical transmittance in visible spectrum, heating the substrates during deposition or performing post deposition annealing can improved the structural, optical and electrical properties of the ITO. A group of researcher reported on the properties of ITO deposited at different substrate temperature of 200–500 °C [3], whereas other groups reported on post annealing of ITO thin films at temperature variation of 150–450 °C [19], 350–550 °C [4] and 200–600 °C [20]. For the Ag inserted multilayer, some groups of researcher reported on the post annealing of ITO/Ag/ITO at temperature variations of 150–200 °C [21] and 300–540 °C [22]. Besides that, another groups
reported on Ni/ITO ohmic contacts with post annealing temperature of 250 °C [23] and 400–800 °C [24]. In addition to the annealing temperature, they also performed the annealing process under different annealing time and pressure as well as in various gases ambient such as air, O₂, Ar and N₂.

In this work, we investigated the effect of post-annealing on the properties of ITO, ITO/Ag and ITO/Ni thin transparent conducting electrodes for the application of optoelectronic devices. The structural, optical and electrical properties were examined at different moderate annealing temperature. It is suggested that the crystalline quality of the ITO thin films could be enhanced after the post annealing process.

2. Experimental setup

ITO and ITO/metal TCE thin films were deposited onto Si and glass substrate at room temperature. The glass was used in conjunction with the silicon substrate in order to examine the optical transmittance of the ITO and ITO/metal thin films. Prior to the ITO deposition, Ag and Ni intermediate metal layer were individually deposited on the Si and glass substrates by thermal evaporator. The thin metal layer evaporation process was performed under vacuum pressure of 4 × 10⁻⁵ mbar at room temperature. Subsequently, ITO thin top layer was sputter deposited on the thin metal intermediate layer by RF magnetron sputtering. An ITO target (99.99% purity) with In₂O₃ and SnO₂ with weight ratio of 90:10 was used under argon ambient. During sputtering, the plasma vacuum pressure was set at 6.6 × 10⁻³ mbar with sputtering rate of ~0.2 nm/s. After deposition, the ITO, ITO/Ag and ITO/Ni samples were post annealed at moderate temperature of 500 °C and 600 °C in air. The thickness of the samples determined by optical reflectometer model Filmetrics F20 are 125 nm, 125 nm/24 nm and 125 nm/24 nm for ITO, ITO/Ag and ITO/Ni, respectively.

Structural properties of the ITO, ITO/Ag and ITO/Ni TCE were determined by phase analysis X-ray diffraction (XRD) with Cu Kα₁ (λ = 1.540598 Å) radiation as the excitation source at working voltage of 40 kV and filament current of 30 mA. Optical transmittance of the films on the substrates was examined by UV–Vis spectrophotometer within visible ranges of 400–700 nm. Electrical characteristics in term of resistivity, carrier concentration and mobility were investigated by Hall Effect measurement system using Van der Pauw test configuration. Surface morphology of the TCE thin films were scanned and analyzed by atomic force microscope (AFM) operated at tapping mode.

3. Results and discussion

Phase analysis XRD was used to determine the crystal orientations and grain sizes of the samples, as shown in Fig. 1. The as-deposited TCE films were found to be an amorphous in all three types of samples as in Fig. 1(a–c). After post-annealing in air at 500 °C and 600 °C, the samples show polycrystalline structure revealing a cubic bixbyte of indium oxide. The annealed samples show a well-defined ITO peak at ~30.7° oriented along (2 2 2) direction and a weak ITO peak of (4 0 0) orientated at ~35.6° which is almost similar to the results obtained by Diniz [25] and Wan [4]. This strong (2 2 2) preferred orientations after post annealing is mainly due to the effect of thermal energy on ITO films. The post deposition thermal treatment seems to relief the stress present on ITO thin films and consequently forming polycrystalline structure. In addition, a strong Si (1 1 1) orientation is observed at ~28.4° in all samples. A strong Ag peak at (1 1 1) directions is also noted at ~38.1°, showing that the Ag thin films with protective ITO layers was crystallized after post annealing especially at 600 °C. Jung et al. also reported on the significant Ag (1 1 1) orientation after thermal treatment at 350 °C [26]. By using Scherrer’s equation, the grain sizes of ITO, ITO/Ag and ITO/Ni at 500 °C was calculated as 54 nm, 34 nm and 34 nm, respectively, whereas 54 nm, 41 nm and 41 nm for 600 °C annealed samples, respectively.

The optical quality of the ITO and bi-layer ITO/metal thin films based on its transparency were examined with the aid of UV–Vis spectrophotometer. Fig. 2 shows the optical transmittance at visible spectrum of the ITO and ITO/metal bi-layer TCE thin films. ITO single layer shows the highest transmittance of more than 80% for the as-deposited and post-annealed samples. Accordingly, the ITO/Ag bi-layer shows lower transmittance characteristics as compared to the ITO single layer. But after post annealing process, the ITO/Ag shows an increasing transmittance of more than 70% especially at 600 °C. ITO/Ni at the other hand shows relatively lower transmittance characteristics as compared to the ITO and ITO/Ag sample. But the post annealing process at 600 °C increases the transmittance characteristics of the ITO/Ni to ~40%, which shows similar trend.

![Fig. 1. XRD spectra of TCE thin films for the as-deposited and post annealed of (a) ITO (b) ITO/Ag and (c) ITO/Ni.](image-url)
with the ITO and ITO/Ag thin films. These transmittance characteristics are comparable with the results reported by Elhalawaty [27] for single ITO, Guilèn [15] for ITO/Ag/ITO and Kim [16] for ITO/Ni/ITO. The improvement in transmittance characteristics of the samples after post annealing is mainly due to the improved crystalline quality of the films as shown in XRD spectra. Furthermore, the post annealing in air results in further oxidation of the partially oxidized indium atoms which consequently improve the transmittance characteristics with improved stoichiometry [25]. In addition, the lower transmittance of the ITO/Ag and ITO/Ni were also resulted from the opaque characteristics of the metal under layer.

To form a low resistivity ohmic contact requires not only highly conductive contact layer but also low interface resistance between the substrate and the contact layer. Fig. 3 shows the resistivity of ITO, ITO/Ag and ITO/Ni at different post annealing temperature. It is clearly noted that the ITO/Ag shows the lowest resistivity as compared to the ITO and ITO/Ni. The resistivity after post annealing is relatively lower than the as deposited sample. The lowest resistivity for ITO, ITO/Ag and ITO/Ni is $4.4 \times 10^{-4}$ Ω cm, $4.0 \times 10^{-5}$ Ω cm and $7.0 \times 10^{-5}$ Ω cm, respectively after post annealing process. Strong crystallization of the thin films contact layer after post annealing at moderate temperature helps in reducing the resistivity. The relatively low resistivity of the ITO/Ag as compared to ITO/Ni resulted from the relatively lower electrical resistivity of bulk Ag as compared to bulk Ni.

Fig. 2. Transmittance characteristics at visible spectrum of (A) ITO as deposited (B) ITO annealed at 500 °C (C) ITO annealed at 600 °C (D) ITO/Ag as deposited (E) ITO/Ag annealed at 500 °C (F) ITO/Ag annealed at 600 °C (G) ITO/Ni as deposited (H) ITO/Ni annealed at 500 °C (I) ITO/Ni annealed at 600 °C.

Fig. 3. Electrical resistivity of transparent conductive electrode of the ITO, ITO/Ag and ITO/Ni.

Fig. 4. Electrical properties of ITO, ITO/Ag and ITO/Ni thin films (a) carrier concentration (b) mobility at different post annealing temperature.

Fig. 5. RMS surface roughness of the ITO, ITO/Ag and ITO/Ni scanned by AFM.
Figure of merit, FOM ($\phi_{TC}$) is used as an importance criterion for evaluating the overall performance of the TCO films. FOM can be determined from [17]

$$\text{FOM, } \phi_{TC} = \frac{T^{10}}{R_s}$$

where $T$ is the optical transmittance and $R_s$ is sheet resistance. FOM for ITO, ITO/Ag and ITO/Ni is $5.5 \times 10^{-3}$ $\Omega^{-1}$, $8.4 \times 10^{-3}$ $\Omega^{-1}$ and $3.0 \times 10^{-3}$ $\Omega^{-1}$, respectively, at wavelength of 470 nm and post annealing temperature of 500 °C. The ITO/Ag shows the highest FOM as compared to the ITO and ITO/Ni. The higher FOM indicates that the ITO/Ag offers better optoelectronic properties than ITO and ITO/Ni thin films. These results show that there are compromise between the optical transparency and the electrical resistance in ITO and ITO/metal thin films. Higher quality of TCE can be characterized by high optical transmittance with a very low electrical resistance, resulting in high FOM.

Fig. 4 shows the electrical properties in term of carrier concentration and mobility of the TCE thin films at different post annealing temperature. Carrier concentration of the as deposited ITO layer is relatively higher than the ITO/metal bi-layer as shown in Fig. 4a. The high carrier concentration of all samples after deposition could be attributed to the oxygen vacancies which donate two electrons for each vacancy as well as the substitution of Sn$^{4+}$ ions into In$^{3+}$ ions sites. After post annealing, the carrier concentrations decreases with ITO/Ag bi-layer show the lowest concentration as compared

![Image of figure 6](image_url)

Fig. 6. Surface morphology of (a) ITO (b) ITO/Ag and (c) ITO/Ni scanned by AFM over 1.0 x 1.0 $\mu$m$^2$. 
to the ITO and ITO/Ni. The carrier concentration for the ITO/Ag is $\sim 10^{20} \text{ cm}^{-3}$ whereas the ITO and ITO/Ni show almost similar concentration of $\sim 10^{21} \text{ cm}^{-3}$. The decreasing of carrier concentration is mainly due to the oxygen deficiency after post annealing. Further investigations on Hall mobility of the TCE layers as a function of post annealing temperature are shown in Fig. 4b. The post annealed ITO and ITO/Ag shows almost similar mobility of $\sim 10^{-13} \text{ cm}^2/\text{V} \cdot \text{s}$. The existence of thin Ni layer between the substrate and ITO resulted in higher carrier mobility as compared to the ITO and ITO/Ag. The mobility of the as deposited ITO/Ni bi-layer is 114 cm$^2$/Vs and reducing to 52 cm$^2$/Vs after post annealed at 600 °C.

Further examinations on the ITO and ITO/metal TCE were performed to determine the surface effects on the electrical and optical properties. Fig. 5 shows the root-mean-square (RMS) surface roughness for ITO, ITO/Ag and ITO/Ni thin films scanned by AFM using tapping mode. Post-annealed samples show an increasing RMS surface roughness as the temperature were increased from 500 °C to 600 °C. Although the as deposited samples especially ITO shows relatively higher RMS value as compared to the post annealed, but the roughness can be considered low (<1 nm) for the TCE films. The surface roughness of post annealed ITO, ITO/Ag and ITO/Ni at 500 °C is 0.28 nm, 0.68 nm and 0.34 nm, respectively, whereas at 600 °C, the values are 0.54 nm, 0.73 nm and 0.54 nm, respectively. As a comparison, Yang [28] reported the RMS surface roughness of ITO and ITO/Ag of 2.30 nm and 1.67 nm, respectively.

Fig. 6 shows surface morphology of the ITO, ITO/Ag and ITO/Ni for the as deposited and post annealed samples scanned over 1.0 × 1.0 μm$^2$ by AFM. The measured average grain sizes of ITO thin films by Bruker NanoScope Analysis is ~24 nm, ~100 nm and ~38 nm for the as deposited, 500 °C and 600 °C, respectively. The insertion of Ag under-layer changes the top ITO grain sizes to ~32 nm for the as deposited and 500 °C, whereas a bit larger for 600 °C of ~36 nm. This ITO grain sizes is almost comparable with the calculated value from XRD analysis of 34 nm and 41 nm for the 500 °C and 600 °C post annealed samples. More identical changes on the top ITO surface morphology were observed when a thin Ni layer was deposited under the ITO layer, as shown in Fig. 6c. The ITO grains were almost combined after deposition. After post annealing at 500 °C, the surface grains were completely combined with a few porous-like structure. But as the post-annealed temperature was increased to 600 °C, the structure were completely combined with a few peaks emerged from the scanned area. This surface morphology affects the transmittance of the visible light through the TCE thin films. Separated grain morphology increases the light transmittance as compared to the continuous and combined grain morphology.

4. Conclusion

ITO, ITO/Ag and ITO/Ni were deposited on Si and glass at room temperature. The as-deposited samples were amorphous in nature with poor optical and electrical characteristics. Post annealing at moderate temperature improves the crystalline quality of the TCE and consequently improves the optical and electrical characteristics of the samples. Higher FOM of the ITO/Ag as compared to ITO and ITO/Ni makes it the best choice as a TCE for optoelectronics device applications. Moreover, separated grain morphology of ITO and ITO/Ag assists in lights transmittance through the TCE thin layer as compared to the combined grains of ITO/Ni bi-layer.

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