The effects of post heat treatment on ITO/AgAl/ITO/p-Si multilayer films

Aliyu Kabiru Isiyaku1,2*, Ahmad Hadi Ali1, Nafarizal Nayan3

1 Optical Fiber Laser Technology Focus Group, Department of Physics and Chemistry, Faculty of Applied Sciences and Technology Pagoh Educational Hub, KM 1 Jalan Panchor, 86400 Muar, Johor, Malaysia.
2 Department of Physics, Faculty of Science, Kaduna State University, Tafawa Balewa Way P.M.B 2339, Kaduna State, Nigeria.
3 Microelectronic and Nanotechnology Shamsuddin Research Centre (MiNT-SRC), Universiti Tun Hussein Onn Malaysia.

*kiakasu@gmail.com

Abstract For the past few decades, the quest for an improve indium tin oxide (ITO) films have attracted a lot of interest by scientists and industries for application in advanced optoelectronic devices. ITO/AgAl/ITO multilayer films were deposited on p-silicon (Si) substrates at room temperature by radio frequency (RF) and direct current (DC) magnetron sputtering respectively. The effects of post-heat (annealing) treatment on the structural, optical and electrical properties of the ITO/AgAl/ITO multilayer films were investigated at different temperature of 200 ºC, 300 ºC, 400 ºC and 500 ºC respectively. X-ray diffraction (XRD) results reveal an amorphous structure for the as-deposited film whereas the post annealed films show a polycrystalline and cubic bixbyte structure with preferential peaks orientation along ITO (222), Ag (111), and ITO (440) crystalline directions. Atomic force microscopy (AFM) analysis indicates a smoother surface morphology and improved grain size after post heat treatment. Ultraviolet-visible spectrophotometer measurements show a significant increase in optical transmittance spectra as the annealing temperature increases. Maximum transmittance peak of 87.2 % was obtained by film annealed at 500 ºC. Four-point probe measurements exhibit a substantial decrease in sheet resistance with respect to increasing post-annealing temperature. The sheet resistance of the as-deposited film is about 7.85 Ω/sq and falls down to 3.23 Ω/sq as the post-heat temperature is increased to 500 ºC. Compared to as-deposited film, the post annealed multilayer films optical and electrical properties have been successfully enhanced, fine turned and favourable for Si solar cell application.

1. Introduction
Transparent conducting oxides (TCO) thin films have been used for decades in several optoelectronic applications as transparent conductor due to their high optical transmittance and electrical conductivity. Each TCO material exhibits different optical and electrical properties that determine the performance of the devices. The high transparency and work function couple with low resistivity properties of indium tin oxide (ITO) film has generated a lot of interest for this material and so it is widely considered for industrial and laboratory research applications [1,2]. ITO thin films are incorporated in several optical and electronic applications as a transparent and conductive contact or electrode including solar cells, LED, laser diodes and flat panel displays [3–5]. In2O3:SnO2 (ITO) is a degenerate semiconductor with
a direct and wide band gap (3.7-4.3 eV) energy. The ITO band gap is responsible for the high optical transmittance in the visible light region [6]. The arising intrinsic oxygen vacancies and extrinsic Sn\textsuperscript{4+} doping in ITO formation are attributed for the high electrical conductivity of the material [6]. ITO films optoelectronic properties depend heavily on the preparation method used for the films deposition. Different types of deposition techniques have been applied, from low pressure to high vacuum [7]: thermal evaporation method [8], electron beam deposition [9], chemical vapour deposition [10] and direct DC and radio frequency RF magnetron sputtering method [11]. Good adhesion and uniform films deposition over a large area with high transmittance and low resistivity have been obtained by magnetron sputtering [7].

Obtaining ITO films with an enhance optoelectronics properties and a reduce market cost has been a challenge for the researchers nowadays due to cost-effectiveness of indium metal. Moreover, the domination of indium metal (a scarce metal) in ITO couple with the increasing demand for this material has clearly affected the market value of the ITO contact [6]. Hence, finding a way to minimize the consumption of indium metal as well as improve the ITO contact properties is necessary to balance the market value. Besides, the reduction of ITO films to less than 100 nm increases the electrical resistivity, even though transparency improved. Therefore, ITO/metal/ITO multilayer films structure has been explored in order to enhance the optoelectronic properties and lessen the use of indium metal [6]. The insertion of thin metal layer in-between the ITO layers drastically improved the conductivity but transparency reduces due to the reflection from the metal [12]. The reflection from the thin metal films can be minimized by selecting an optimum thickness of the films which also allows one to set the required transparency in the visible region [13]. Several metals as interlayer in TCO multilayer structures have been used; ITO/Al/ITO [14], ITO/Ag/ITO [15] and ITO/Ag(cr)/ITO [16]. Each metal plays different roles with respect to its properties and films thickness selected [17].

Mostly, the deposited ITO films at room temperature resulted in the amorphous structure. Post annealing (heat) treatment of the as-deposited ITO films has been reported to have improved the crystalline quality of the films [18]. This process enhances the films crystallite growth and electronic mobility which in effect improved the optoelectronic properties [12,19]. Balasundaraprabhu et al. [19] investigated the effect of post-annealing treatments from 100-400 °C on ITO/p-Si heterostructures deposited by DC magnetron sputtering. The results indicated gradual enhancement in both the film and the ITO/Si interface properties as the temperature increases up to 300 °C. Degradation of the films electrical and interface properties were observed at 400 °C. Ali et al. [11] conducted post-annealing treatment on ITO films at 500-700 °C deposited by RF sputtering. Strong crystallization, high transmittance of more than 90% in the visible range and lowest electrical resistivity of $6.68 \times 10^{-4}$ were achieved at 700 °C.

In this work, post heat treatment effects on ITO/AgAl/ITO/p-Si multilayer films have been analysed. The films were characterized based on the structural, optical and electrical properties.

2. Methodology

ITO ceramic (In\textsubscript{2}O\textsubscript{3} 90 % weight : SnO\textsubscript{2} 10 % weight), Ag (99.999 % purity) and Al (99.999 % purity) targets were used. P-type Si (111) and Soda-lime glass (for optical characterization) were also used as substrates in this work. Bottom ITO thin layer was deposited on the substrates by RF magnetron sputtering at room temperature followed by Al metal thin layer and then Ag metal thin layer using DC magnetron sputtering respectively. Top ITO thin layer was after that, deposited on AgAl/ITO/p-Si structure using RF sputtering completing the ITO (45 nm)/Ag (4) Al (6 nm)/ITO (45 nm) multilayer structure. At the end of the preparation, the as-deposited ITO/AgAl/ITO multilayer films were then undergone post heat treatment (furnace annealing) at different temperature in a range of 200-500 °C for 5 minutes in air.
The individual film thicknesses were measured by a Filmetrics F20 system. The multilayer films structural properties were examined by X-ray diffraction (XRD) method, while the surface morphologies of the films were analysed using atomic force microscopic (AFM). Optical transmittance measurements were conducted using Ultraviolet-visible (UV-vis) spectrophotometer in a range of 250-850 nm wavelengths. Finally, the electrical characteristics were determined using a four-point probe method.

3. Results and Discussion

Figure 1 shows the as-deposited and annealed XRD pattern of ITO/AgAl/ITO multilayer films. It can be seen that only a very narrow peak was observed from as-deposited film indicating an amorphous structure. However, enhanced peaks were identified after post-heat treatment confirming the crystallization of the films and indium oxide cubic bixbyite structure. Al peak of (200) reflection appears after annealing at 400 °C and 500 °C with the strong peaks intensities at ITO (222), Ag (111) and ITO (440) demonstrating an improvement in both ITO, Ag and Al crystallinity at these temperatures which is also inconsistent with the work of Cho et al. [14]. The general enhancement in the annealed films is attributed to the reduction of grain boundary scattering due to the increase in grain size with respect to increasing temperature annealing [6, 20].

![Figure 1. XRD pattern for as-deposited and annealed ITO/AgAl/ITO multilayer films.](image)

The influence of the post-heat treatment on the surface morphology of the ITO/AgAl/ITO multilayer films was studied by AFM technique. Figure 2 displayed the AFM images of as-deposited and annealed ITO/AgAl/ITO films scanned over an area 1000 nm × 1000 nm. Smooth surface morphology is observed with the annealed 400 °C, and 500 °C films showing the smoothest surface morphology. The AFM values of grain size and surface roughness as a function of post-heat temperature is shown in Figure 3. As seen from Figure 2 and Figure 3 more uniform and larger grain size, as well as increase in average roughness Ra and root mean square RMS roughness were obtained as the temperature is increased from
200 °C- 500 °C. The enhanced surface profile reduces the grain boundary scattering effect which helps in enhancing optical and electrical properties of the films.

Figure 2. AFM images of (a) as-deposited ITO/AgAl/ITO film and post annealed (b) 200 °C (c) 300 °C (d) 400 °C (e) 500 °C films respectively.

Figure 3. ITO/AgAl/ITO multilayer films AFM surface profile as a function of temperature.

Optical transmittance characteristics for the as-deposited and post annealed ITO/AgAl/ITO films are shown in Figure 4. It can be seen that the post-annealing treatment clearly improves the optical
transmission in the visible region. Minimum transmittance of 81.4% was obtained by as-deposited film at 450 nm wavelength and increases to 83% after annealed at 200 °C. Significant enhancement of optical transmittance was observed at high temperature with film annealed at 500 °C exhibiting maximum transmittance of 87.2% in the visible light region. The improvement in crystallinity of both the ITO and metals films as well as the films surface morphologies are attributed for the enhancement in transmittance spectra [11]. Figure 5 displayed changes in ITO/AgAl/ITO films sheet resistance and transmittance with respect to post-annealing temperature. Decreased in sheet resistance as well as increased in optical transmittance were observed as the annealing temperature increases. The lowest sheet resistance of 3.23 ohms/sq by film annealed at 500 °C was obtained.

![Transmittance spectra of the ITO/AgAl/ITO multilayer films.](image1)

**Figure 4.** Transmittance spectra of the ITO/AgAl/ITO multilayer films.

![Changes in electrical sheet resistance and transmittance with respect to temperature annealing.](image2)

**Figure 5.** Changes in electrical sheet resistance and transmittance with respect to temperature annealing.

### 4. Conclusion

ITO/AgAl/ITO multilayer films have been grown on p-type Si substrates by RF and DC magnetron sputtering technique at room temperature. The as-deposited multilayer films were subjected to post-heat treatment at different temperature of 200 °C, 300 °C, 400 °C and 500 °C respectively. Structural, optical and electrical properties of the multilayer films were optimised after heat treatment. XRD analyses
reveal enhanced crystalline films with increasing temperature annealing. Strong peaks intensity for ITO (222), ITO (440), and Ag (111) crystallite directions were obtained by the annealed films. AFM results indicate that the increase of the post-annealing temperature increases the surface roughness and squarely improves the surface morphologies especially at 400 °C and 500 °C respectively. Compared with 81.4 % of the as-deposited film, significant enhancement of optical transmittance was observed with maximum transmittance of 87.2 % at 450 nm wavelength achieved by film annealed at 500 °C. The sheet resistance of the as-deposited film is about 7.8 Ω/sq and falls down to 3.23 Ω/sq as the post-heat temperature is increased to 500 °C. The optoelectronic properties of the ITO/AgAl/ITO multilayer films were successfully enhanced and fine-tuned and can be suitable for application as contact in Si solar cells devices.

References
[1] Hu Y, Diao X, Wang C, Hao W and Wang T 2004 Vacuum 75 18
[2] Bhopal M F, Won Lee D, Rehman A ur and Lee S H 2016 Vacuum 133 108
[3] Feng T, Ghosh A K and Fishman C 1979 J. Appl. Phys. 50 4972
[4] Zhou S, Cao B, Liu S and Ding H 2012 Opt. Laser Technol. 44 2302
[5] Gulen M, Yildirim G, Bal S, Varilci A, Belenli I and Oz M 2013 J. Mater. Sci. Mater. Electron. 24 467
[6] Guillén C and Herrero J 2011 Thin Solid Films 520 1
[7] Joshi R N, Singh V P and Mcclure J C 1995 Thin Solid Films 257 32
[8] Jan S W and Lee S C. 1987 J. Electrochem. Soc. 134 2056
[9] Kobayashi H, Ishida T, Nakamura K, Nakato Y and Tsubomura H 1992 J. Appl. Phys. 72 5288
[10] Maruyama T and Fukui K 1991 Thin Solid Films 203 297
[11] Ali A H, Hassan Z and Shuhaimi A 2018 Appl. Surf. Sci. 443 544
[12] Ren N, Zhu J and Ban S 2017 AIP Adv. 7 5
[13] Kumar M D, Park Y C and Kim J 2015 Superlattices Microstruct. 82 499
[14] Cho E N, Moon P, Kim C E and Yun I 2012 Expert Syst. Appl. 39 8885
[15] Park Y S, Choi K H and Kim H K 2009 J. Phys. D. Appl. Phys. 42 235109
[16] Meshram N, Loka C, Park K R and Lee K S 2015 Mater. Lett. 145 120
[17] Isiyaku A K, Ali A H and Fauziyyah R N 2019 Mater. Today Proc. 7 692
[18] Yun J H, Kumar M D, Park Y C and Kim J 2015 Mater. Sci. Semicond. Process. 31 334
[19] Balasundaraprabhu R, Monakhov E V, Muthukumarasamy N, Nilsen O and Svensson B G 2009 Mater. Chem. Phys. 114 425
[20] Isiyaku A K, Ali A H, Nayan N 2019 Beilstein Arch 104