EFFECT OF ANNEALING TIME ON RESISTIVITY OF KENAF FIBER MODIFIED INDIUM ZINC OXIDE PREPARED VIA DIP COATING PROCESS

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ABSTRACT: This paper reviewed the annealing time effect on resistivity of kenaf fiber modified indium zinc oxide (KF-IZO) as a functional material. Firstly, kenaf fiber (KF) had undergone alkaline surface treatment using Sodium Hydroxide (NaOH) solution with 5 % concentration. Dip coating process was applied in order to deposit amorphous IZO (In/Zn : 6.0 %) solution at room temperatures, 27^{o}C at 5 mm/s dipping rate. The thin film built up was annealed at 150^{o}C for 2, 4, 8 and 16 hours. Electrical resistivity was tested by Four Probe Method with copper attachment to determine the resistance of KF-IZO. As a result, KF-IZO with 4 hours annealing time showed the lowest resistivity with 0.12 Ω.mm while the highest resistivity 12.62 Ω.mm was shown by 16 hours annealing time. Surface morphology was observed under optical microscope, Scanning Electron Microscope (SEM) and SEM-EDX to reveal coating distribution, elemental analysis and imperfection of KF-IZO. Moreover, the entire KF-IZO samples image illustrated revealed no significant fiber damages.

KEYWORDS: *IZO, KF, resistivity, surface treatment, dip coating process*

1.0 INTRODUCTION

Transparent conducting oxides (TCOs) are well known conductive coating material according to their capabilities of transporting electrical charge and transmitting visible photon for various applications such as solar cell and liquid crystal displays [1]. Among them, doping of ZnO film by Indium (IZO) is the best option due to high electrical conductivity, high chemical stability against environment and high transparency in the visible region [2]. Previous studies also mention that, indium zinc oxide (IZO) is one of the best materials that exhibit good transparency in the visible range, low resistivity, and high mobility [3-5]. Indium has been selected as dopant material and it targeted to be used in low percentage because of high cost and scarcity [6]. In other aspects, IZO are non-toxicity material and easy to handle, low cost, highly durable and wide material availability as compare to Indium Tin Oxide (ITO) that makes it suitable for manufacturing point of view [7-8]. The IZO was selected because it could be processed in low temperature as to adapt with the natural fiber substrate. Researchers have successfully analyzed the amorphous structure and electrical performance of low-temperature annealed (100 - 200^{o}C) amorphous IZO transparent thin film transistors [9]. In general, sputtering, chemical vapour deposition (CVD) and pulsed laser deposition (PLD) known as utmost method to create the highest quality of ZnO based TCO films [10], however dip coating is primarily selected as low cost, wide area productivity and also good film quality [2].

In recent year, natural fibres coated with conductor material have been prominently used for various applications in manufacturing process. In addition, natural fibers are highly available, low cost, renewable, non-irritate, non-abrasive and reduce energy consumption [11-12]. Kenaf (hibiscus cannabinus) is one of the popular natural fibers that has been widely applied as particleboard, growth media, and animal bedding material [13-17]. Furthermore, tailoring new material within the perspective of sustainable development is seriously taken into consideration in kenaf fiber modified indium zinc oxide development. The newly development of IZO deposited onto natural fiber has promised the challenge as it is not much studied yet by previous researchers [18]. The annealing process is one of the important segments that need to be studied especially when being adapted to natural fibers. One of the disadvantages of natural fibers is their low thermal stability [19]. Therefore, the process conditions of TCOs need to be adjusted to allow coating of such heat-sensitive substrates. Moreover, temperature and time during annealing process are the parameters that affect the natural fiber accordingly. The effects of annealing on the properties of ZnO thin films have been reported by many groups [20-23]. However, the annealing conditions, such as ambient gas species, annealing temperature and time, are different for the different groups, and results are still under debate, especially for the effect of annealing time [24]. Therefore, the aim of this study was to investigate the effect of annealing time on the KF with IZO thin layer. As a result, the newly developed KF-IZO would be applied in the area of composite technology, solar panel, electronic and semiconductors.

2.0 METHODOLOGY

Initially, kenaf bast fiber non-woven mat with surface density of 800 g/m^2 used in this study was supplied by Innovative Pultrusion Sdn Bhd. The kenaf fiber size of 1′ x 1′ underwent surface treatment using Sodium Hydroxide (NaOH) solution with 5 % concentration and then immersed for 48 hours at 25°C. This treatment was to eliminate the impurities associated with untreated KF fibers. After that, it was rinsed accordingly for 5 times with deionized water. This process continued with drying process wat 80°C for 24 hours in vacuum furnace to ensure that the surfaces were dry and was free from any contamination.

The IZO solution was prepared with an In/Zn ratio of 6.0 %. In order to prepare the IZO solution, zinc acetate dehydrate was dissolved in ethanol (precursor) at 25°C. The mixture was then magnetically stirred for about 1 hour at this temperature. During the process, deionized water, which acted as a stabilizer, was dropped into the mixture by a syringe. Once the dissolution was complete, indium (III) chloride (dopant) was added to the solution. The resulting mixture was then stirred for 1 hour at 75°C. In the end, a clear and homogenous solution of IZO was obtained. IZO was deposited to KFs using a dip-coating method at 25°C with dipping rate of 1–30 mm/sec (Figure 1). After the deposit, KF-IZO was dried at 120°C and followed by annealing process at 120°C for 2, 4, 8 and 16 hours in vacuum furnace. Electrical measurements test was performed using Four Probe Method (Hewlett Packard 34401A multimeter with Advantest R6144 voltmeter) together with copper attachment to determine electrical resistivity of KF-IZO (Figure 2). TGA with operating temperature, 30 - 1000°C was carried out for KF thermal analysis. Focused Ioned Beam (FIB) system of type JEOL (JEM-9320FIB) with acceleration voltage 30 kV was carried out for cross section cutting single fiber. Lastly, optical microscope by MORITEX Scopemen series (magnification 166x) and SEM EDX (JEOL, JSM-6510A) with acceleration voltage 30 kV was used to reveal the coating condition as well as to provide elemental identification and quantitative compositional information.

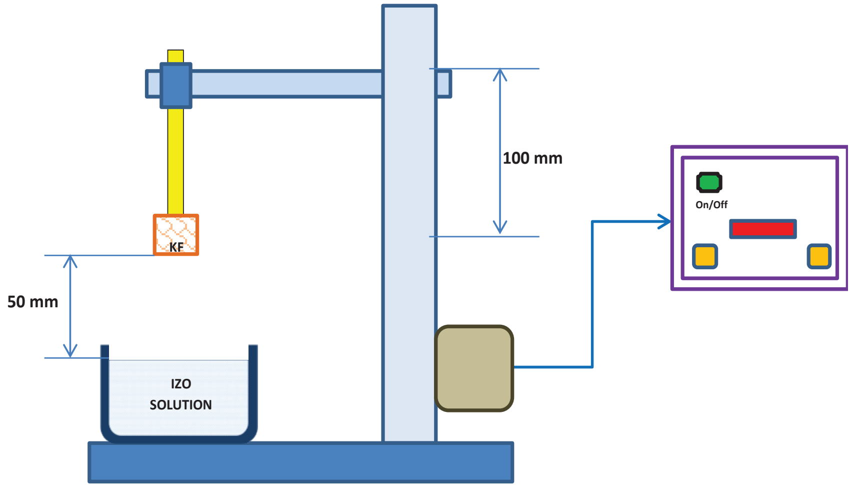

Figure 1: Schematic diagram of dip coater set up

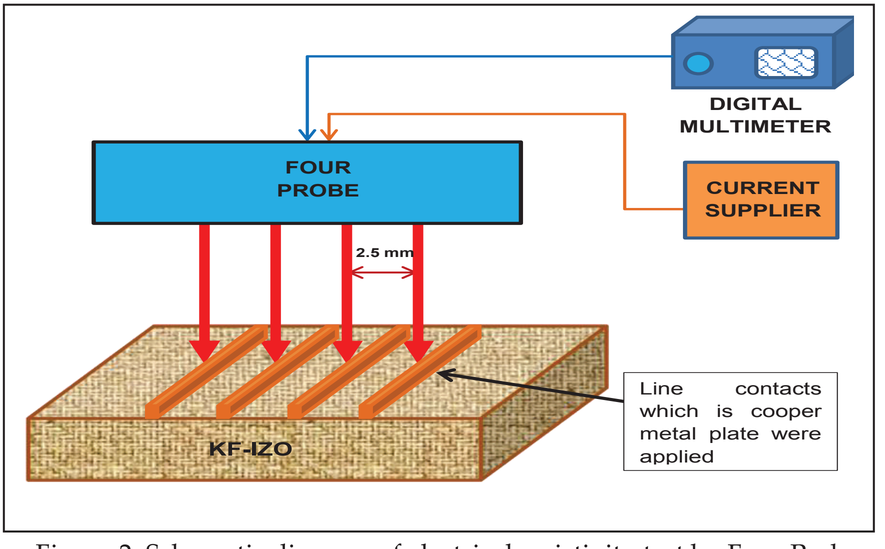

Figure 2: Schematic diagram of electrical resistivity test by Four Probe Method

3.0 RESULTS AND DISCUSSION

3.1 Kenaf fiber modified indium zinc oxide characterization

Thermogravimetric (TGA) analysis showed that the entire KF-IZO samples started to decompose at 200°C and about 80-90 % of remaining KF weight (Figure 3). From the observation, at 150°C with annealing time of 2, 4, 8 and 16 hours, a different loss weight (%) was shown by the KF-IZO sample. The details in values of loss weight are shown in Table 1. The loss weight is most probably due to moisture evaporation during the annealing process.

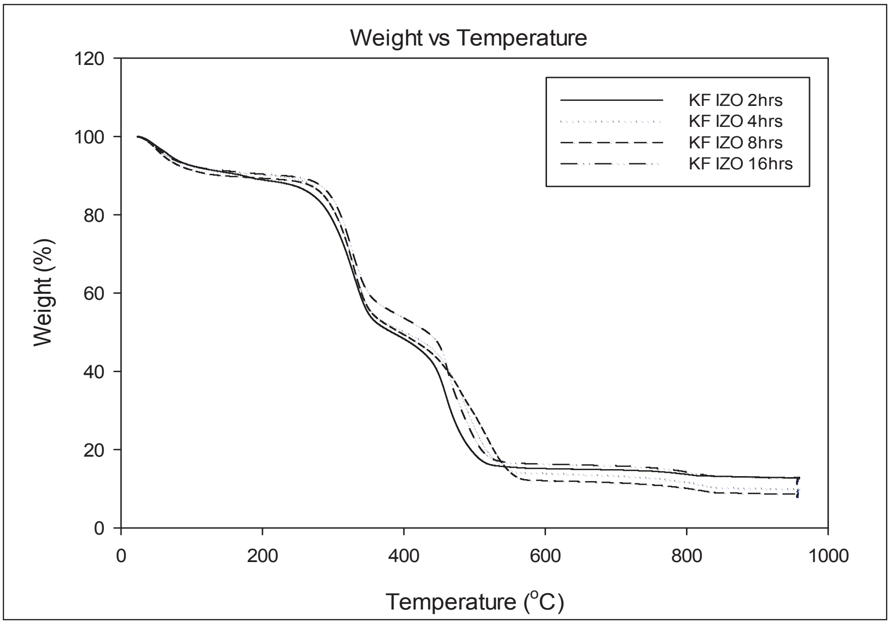

Figure 3: KF-IZO thermogravimetric analysis for different annealing time; 2, 4, 8 and 16 hours

3.2 Electrical resistivity

Low annealing temperature and time are strictly required for natural fibre because they are known as low temperature application resources. TGA results revealed that KF must be operated in low temperature (≤200°C). As seen in Table 1, the optimum annealing time for a conducting thin film was 4 hours with minimum resistivity value of 0.0853 Ω.mm, while the maximum resistivity value was recorded at 16 hours annealing time, 12.6154 Ω.mm. The same results was also reported by Seng et.al (2016) stating that the optimum annealing time for a conducting thin film (Aluminium doped tin oxide, (SnO_2: Al) is approximately 4 hours, while the sheet resistance and resistivity reaches the minimum value of 6.7757×10^6 (Ohm/sq) and 0.212 k (Ohm-cm) [24]. Based on Figure 4, resistivity performance of KF-IZO increased with the increase of annealing time. It was assumed that annealing time had directly affected the electrical properties of KF-IZO. These results could be attributed to the decomposition of KF especially during annealed process. According to Ishak et al. (2012), natural fibre significance mass loss (up to 70 %) can be found from its basic constituent; cellulose, hemicellulose and lignin where they can occur starting from temperature $100-140^{o}$C and above [25]. In this study, TGA results for KF-IZO with different annealing time showed that temperature range between 150 to 200^{o}C, KF loss about 4-6 % in a total weight as shown in Table 1.

Table 1: KF-IZO sample for different annealing time at temperature of 150^{o}C

Annealed Time (hr)	**Resistivity (Ω.mm)**	**Loss weight of KF (%)**	**% Carbon (Diamond form)**
2	0.6370	4.27	3.8
4	0.0853	5.32	3.9
8	5.2678	6.03	12.5
16	12.6154	6.38	17.0

Moreover, amount of % carbon also increased caused by the built up of carbon concentration on KF-IZO (Table 1). It could be seen on the color changing of KF-IZO samples with annealing time increase (Figure 5). It showed that within 16 hours annealing time at 150 °C, KF-IZO turned to black in colour and looked burnt as compared to other samples. These scenario occured because KF was burning and forming carbon coal/diamond. Carbon in a form of diamond/coal is known as non-conductor material. As a consequence, the amount of carbon formed introduced a barrier towards IZO coating. In addition, percentage of carbon increased with the increase of annealing time. It was drastically increased at 8 to 16 h annealing time. It is also observed that KF-IZO looked more brittle and had low strength as compared with raw KF.

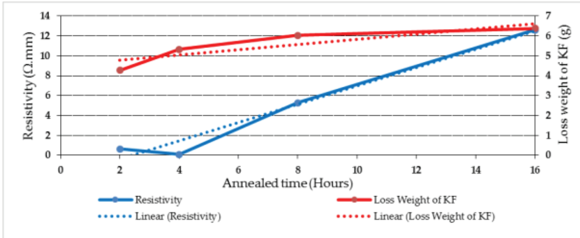

Figure 4: Dependence of resistivity and loss weight on the annealing time at 150°C annealing temperature

Figure 5: KF-IZO changing color for 4 different annealing time (MORITEX – Scopemen series with Magnification166x)

3.3 KF-IZO thin layer

To ensure the homogeneity of IZO distribution on KF, surface and cross sectional analysis of KF-IZO samples was carried out. The samples were prepared using focused ioned beam (FIB) system. FIB revealed the coating thickness condition as well as distribution of IZO thin layer. Then, SEM-EDX analysis of the cross sectional and surface area of KF-IZO was carried out to determine the presence of Zn^{2+} as shown in Figure 6. A good condition of coating was observed for the annealing time of 4 and 8 hours as referred to Figure 6 (A1 and B1). KF-IZO samples shows that IZO thin layer was uniformly coated and well distributed on the fiber surfaces. Also, it was revealed that IZO thin layer thickness grew about 5μm on the surfaces which contained In^{3+} and Zn^{2+} ions accordingly.

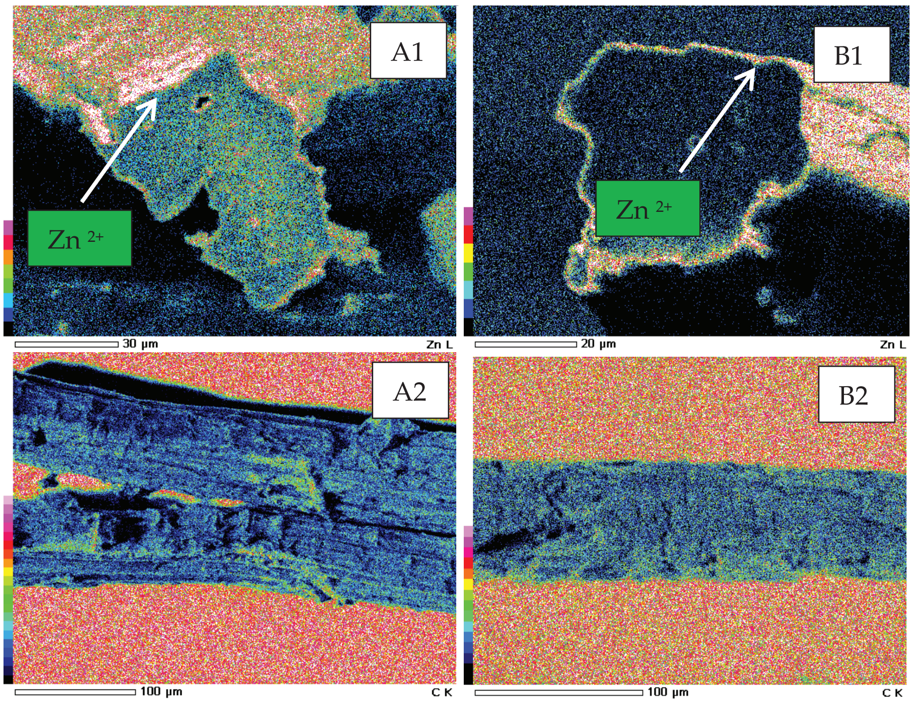

Figure 6: SEM-EDX analysis for Zn L and C K on cross sectional and surface area of KF-IZO samples; A1 and A2: 4 hours, B1 and B2: 8 hours annealing time

Figure 6 (A2 and B2) showed that C elements existed on the KF IZO surfaces. C elements were detected more clearly in Figure 6 (B2) which represented 8 hours annealing time. It is predicted that C elements formed with the increase of annealing time. As a consequence, it will create obstacles for electrical conduction. Meanwhile, SEM-EDX elemental analysis results showed that In/Zn ratio were about 5.5 % to 6.5 % which was close as to the prepared solution. However, El Yamny and Abdel (2012) reported that within the range of 2 – 5 % of In/Zn, the lowest electrical resistivity was obtained [2,26]. ZnO thin layer with In dopant were successfully detected on the KF surfaces which indicated possibility of conductive properties of KF-IZO (Figure 7). According to Liu, the conductive properties of ZnO thin films is primarily dominated by electrons generated vacancies and charge donations [18]. Other elements such as C, O and Cl existed on the KF-IZO where C and O are from natural fiber content, while Cl+ ion existed because the doping used was Indium (III) Cloride.

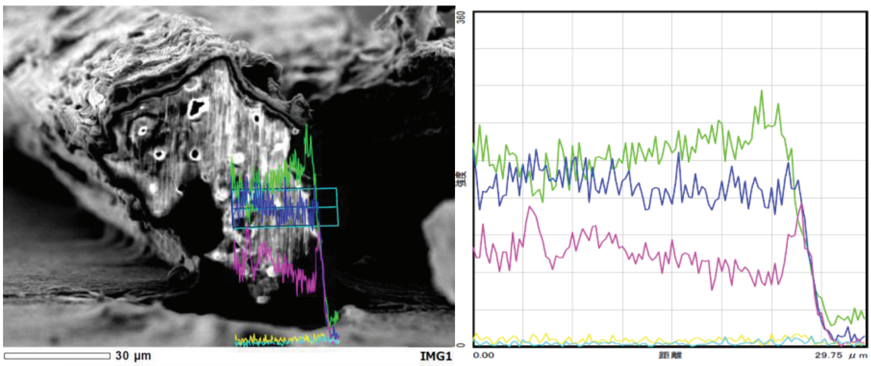

Figure 7: SEM-EDX scanned analysis on cross sectional area of KF-IZO (4 hours annealing time)

4.0 CONCLUSION

KF has successfully coated IZO using dip coating method. ZnO as precursor and Indium as dopant material for IZO-TCO are the best combination because it could be processed in low temperature as to adapt with KF. The lowest resistivity is shown by KF-IZO for 4 hours annealing time, 0.12 Ω.mm while the highest is 12.62 Ω.mm for 16 hours annealing time. SEM-EDX elemental analysis claims In/Zn ratio is about 5.5 % to 6.5 % which is closely similar to the prepared solution. FIB reveals good coating condition of KF-IZO as well as IZO thin layer thickness growth of 5μm. In this work, time of annealing is found to influence the electrical resistivity of KF-IZO because of the carbon formation element contributed by KF. In a nutshell, these outcomes could provide information and ideas on newly developed KF-IZO especially on the effect of annealing time.

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