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Annealing dependence on flexible p-$CuGaO_2$/n-ZnO heterojunction diode deposited by RF sputtering method

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Abstract. In this work, p-$CuGaO_2$/n-ZnO heterojunction diodes were deposited by RF powered sputtering method on polyethylene terephthalate (PETP, PET) substrates. Structural, morphology, optical and electrical properties of $CuGaO_2$/ZnO heterojunction was investigated as a function of annealing duration. The structural properties show the ZnO films (002) peak were stronger at the range of 34˚ while $CuGaO_2$ (015) peak is not visible at 44˚C. The surface morphology revealed that RMS roughness become smoother as the annealing duration increase to 30 minutes and become rougher as the annealing duration is increased to 60 minutes. The optical properties of $CuGaO_2$/ZnO heterojunction diode at 30 minutes exhibit approximately 75% optical transmittance in the invisible region. The diodes exhibited a rectifying characteristic and the maximum forward current was observed for the diode annealed for 30 minutes. The diodes show an ideality factor range from 43.69 to 71.29 and turn on voltage between 0.75 V and 1.05 V.

1 Introduction

Transparent conducting oxide (TCO) thin films have been extensively studied because it's have very interesting properties in various electrical and optical application such as gas sensor, light-emitting diodes, solar cells, thin-film transistors and varistor [1,2]. ZnO have become a promising TCO materials due to its non-toxic, inexpensive and abundant material compared to ITO that once was a commonly used materials [3-6]. Besides that, ZnO have a wide direct band gap of 3.3 eV, high electrical conductivity, high optical transmission and high excitation binding energy of 60 meV, which makes the $CuGaO_2$/ZnO heterojunction a demanding candidate in optoelectronic applications [7,8]. In order to fabricate p-n junction with n-ZnO, delafossite Copper Gallium Oxide ($CuGaO_2$) is proposed as p-type material, due to its smaller lattice mismatch with ZnO [9].

A flexible diode is the last missing jigsaw piece needed to achieve a lightweight, slim, flexible, high durability and cheaper devices. Therefore, plastic substrate is used in order to opens new application of $CuGaO_2$/ZnO heterojunction thin films as transparent films that utilize curved surfaces, which means the plastic device are flexible and bendable to a large angle [10,11]. Thin films diode on plastic or flexible substrates have many merits due to the fact that they can be lightweight, flexible, unbreakable, low cost and easily folded than other substrates like silicon and glass [12,13]. Contributions of annealing towards heterojunction thin films are to suppress or eliminate detrimental surface defects so that it is unable to trap carries again [14]. Annealing also can enhance device performance by the improvement of the active layer crystallinity, morphology and optical absorption [15,16]. However, the annealing duration effect the p-$CuGaO_2$/n-ZnO heterojunction diodes and has not been investigated yet.

This paper describes the deposition of p-$CuGaO_2$/n-ZnO heterojunction diodes by RF powered sputtering method on polyethylene terephthalate (PETP, PET) substrates. The motivation behind the present work is to clarify the dependence of annealing duration on the characteristics of p-$CuGaO_2$/n-ZnO heterojunction diodes. More specifically, the turn on voltage, saturation current and ideality factor of the p-$CuGaO_2$/n-ZnO heterojunction diodes were examined with respect to the annealing duration applied after the deposition.

2 Experiments

$CuGaO_2$/ZnO heterojunction thin films were prepared on commercially available indium tin oxide (ITO) coated polyethylene terephthalate (PETP) substrates by RF powered magnetron sputtering. The targets used are 3 inches diameter ceramic target of undoped ZnO and $CuGaO_2$ with 99.99 % purity. The substrates were ultrasonically cleaned for 5 minutes in distilled water, followed by ethanol and lastly acetone. After that, the substrates were rinsed again with distilled water and then dried with nitrogen gas.

A RF sputtering was used to prepare ZnO and $CuGaO_2$ layers, and a DC sputtering was used for the Cu contact. The deposition of the ZnO films was carried out at 200 ˚C and 9 mtorr with a thickness of 500 nm for 25

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minutes. The sputtering power was adjusted to maintain at 100 W and substrate rotation was 5 rpm, while the argon gas flow was kept at 25 sccm. The sputtering process of $CuGaO_2$ layer was performed in an argon atmosphere with flow rate 10 sccm at room temperature for 30 minute. The sputtering was carried out at RF power of 100 W and base pressure of 2.5 x 10^{-5} torr. Then, the films were annealed in a furnace at 250 ˚C and 5˚C/min at various annealing duration (10 minute to 60 minute) to investigate the effect of annealing duration to obtain the properties of $CuGaO_2$/ZnO heterojunction. After that, Cu electrode was sputtered on top of the $CuGaO_2$ layer through shadow masks. The sputtering process of Cu contact was performed in an argon atmosphere with 10 sccm flow rate at room temperature for 10 minutes.

The surface roughness was measured using a Nanolab 550 Profilometer. The structural and crystalline properties of the heterojunction diodes were characterized using X-Ray Diffraction Philips Expert Pro. The optical properties were analyzed by using UV-Vis Spectrometer Lambda EZ210 in the wavelength range from 340 nm to 840 nm and the electrical properties were investigated using a Keithley 2400 source meter.

3 Results and discussion

3.1. Structural and optical properties

Figure 1 shows XRD patterns of as-deposited and annealed $CuGaO_2$/ZnO/PETP films. The diffraction intensity peak of (002) plane at 34˚ are high indicated that the ZnO films were preferentially oriented in (002) direction, agreed with the results of Chang *et al*. and Sayago *et al* [17,18]. An obvious increment in the intensity of ZnO (002) peak noticed from 10, 20 and 30 minutes annealing duration indicating better crystallinity. An increase in the diffraction intensity observed with long annealing duration due to the enhanced films quality [19]. However, the intensity of ZnO (002) peak drops at 40 minutes and continues to decrease in longer annealing duration of 60 minutes indicate the films crystallinity deteriorates. Therefore, it is considered that the diffraction intensities of the ZnO films were strongly affected by the annealing duration for the films. From this analysis, it can be concluded that variations in the annealing durations are responsible for deviations in the crystallinity where there exists an optimum value of annealing time beyond which the film crystallinity deteriorates [20]. $CuGaO_2$ (015) peak is not visible at 44˚C due to insufficient thermal energy for the $CuGaO_2$ thin films to become crystalline. There is no $CuGaO_2$ (015) peak visible for thin film annealed at 250˚C probably because the thin films is still in amorphous state at this temperature [21].

Figure 2 shows the root mean square (RMS) roughness of $CuGaO_2$/ZnO heterojunctions diode in various annealing duration. The inset shows the profilometer 3D images for 30 minutes annealing duration. The RMS value of $CuGaO_2$/ZnO heterojunction diode surface with no annealing treatment was 4.08 nm. After undergoing annealing duration from 10, 20 and 30 minutes, the RMS roughness become smooth compared to without annealing treatment $CuGaO_2$/ZnO heterojunction diode with the value of RMS roughness are 3.58 nm, 3.39 nm and 3.20 nm, respectively. The RMS roughness values shows decreasing trend with increasing annealing duration [20]. The surface become rougher as the annealing duration is increased from 40, 50 and 60 minutes with RMS roughness of 4.70 nm, 5.39 nm and 5.44 nm, respectively. The inset 3D images for $CuGaO_2$/ZnO heterojunctions annealing for 30 minutes shows not only lower roughness compared to the other heterojunction thin films.

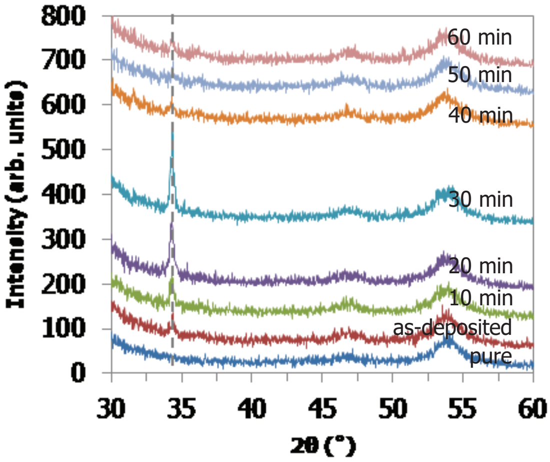

Fig. 1. (Black and White) XRD patterns of the $CuGaO_2$/ZnO/PETP films annealed for 0, 10, 20, 30, 40, 50 and 60 minutes in the furnace at 250 ˚C.

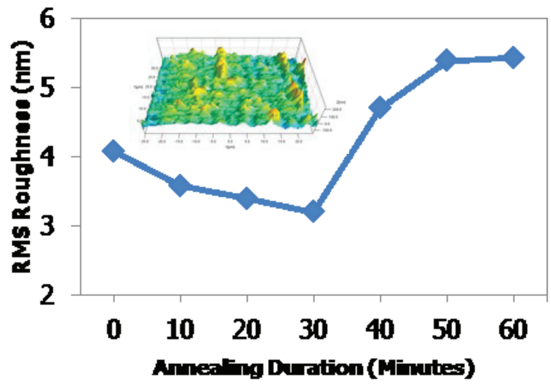

Fig. 2. (Black and White) The measured $CuGaO_2$/ZnO heterojunction diode RMS roughness for various annealing duration. The inset shows the profilometer 3D images for 30 minutes annealing duration.

Optical transmittance measurement has been done in order to investigate the transparency properties of the $CuGaO_2$/ZnO heterojunction diode. Figure 3 shows the optical transmittance versus wavelength spectra of the heterojunction thin film diode at 30 minutes annealing time that exhibit approximately 75% in the invisible region between 500 and 700nm. This result can be compared to an optical transmission in the visible that greater than 70% transmittance of thin film based p-

$CuCrO_2$:Mg/n-ZnO heterojunction and 80% transmittance of *p*-$CuCrO_2$:Mg/*n*-ZnO heterojunction in the visible region [22,23].

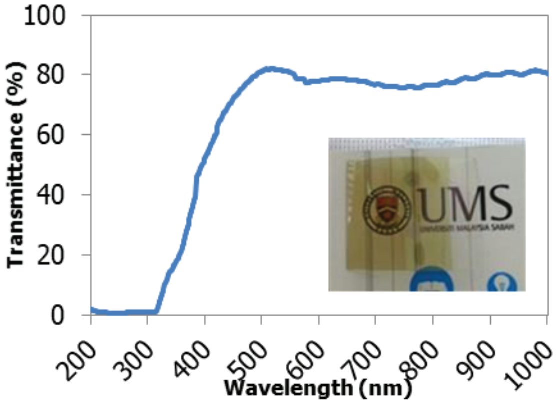

Fig. 3. (Black and White) Optical transmittance spectra of a typical p-$CuGaO_2$/n-ZnO heterojunction diode onto an ITO/PET substrate for 30 minutes annealing time. The inset shows a photograph of a $CuGaO_2$/ZnO/ITO/PET diode device to illustrate its level of transparency

3.2 Electrical diode characterization

Figure 4 illustrates the schematic diagram of the $CuGaO_2$/ZnO heterojunction structure and current-voltage (I-V) characteristics annealed at various times at 250 ˚C. The diodes exhibited a rectifying characteristic with turn on voltage, V_T between 0.75 V and 1.05 V. The maximum forward current was observed for the diode annealed for 30 minutes. This indicated that 30-minute annealing time was the suitable annealing duration to obtain a non-linear behavior of a diode. As shown in Figure 4, the saturation current (I_0), barrier height (φ_b) and series resistance ranging from $1.18x10^{-5}$ A to $3.51x10^{-7}$ A, 0.840 eV to 0.963 eV and 1693 Ω to 13560 Ω were obtained, respectively. In this region, an ideality factor range from 20.9 to 25.6 was extracted from the slope of the linear region of the forward bias I-V characteristics. The effect of annealing duration on the ideality factor calculated forward bias I-V characteristic was observed is in the range of those reported for ITO/ poly(3,4,ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/poly(2-methoxy-5-(2-ethlhexyloxy))-1,4-phenylenevinylene)(MEH-PPV)/Alq3/Lif/Au Schottky diode [24], and comparable to that those reported for ITO/MEH-PPV/A21 [28]. Large values of ideality factor were obtained due to the presence of recombination in the junction deposition or at junction interface [25], besides some structural defects and lattice mismatch between ZnO and $CuGaO_2$ [19]. The improvement of the device performance is attributed to the smoother surface [26]. One possible reason for this might be the rougher surface that provides better surface adsorption, resulting in degradation of electrical properties [27]. Besides that, smooth $CuGaO_2$/ZnO heterojunction interface would provide a more ideal interface for carrier exchange [28].

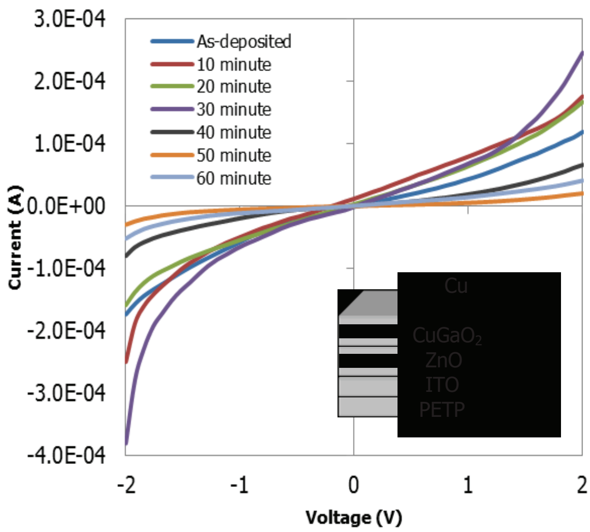

Fig. 4. (Black and White) The schematic diagram of the $CuGaO_2$/ZnO heterojunction and I-V characteristics annealed at various times at 250 ˚C.

In addition, as shown in Figure 4, the current for forward bias I-V characteristic annealed more than 30 minutes decreases due to coarsening of the morphology at longer annealing durations. These result consistent with the RMS value of p-n device that increase from 4.70 nm to 5.44 nm for 40 minute to 60 minute. The degradation of the rectification characteristics at longer annealing durations is due to the interfacial migration of carrier by the excessive heat treatment which usually increases the roughness of device surface [29,30]. For 10, 20 and 30 minute, the RMS roughness of the p-n device become smoother indicated the improvement on the flow of device current. RMS roughness of device decreased as annealing duration increased up to 30 minutes and its roughness increased as annealing time increased up to 60 minutes. 30 minutes is an optimum annealing duration for ideal $CuGaO_2$/ZnO heterojunction diode due to the maximum forward current found for that annealing durations. Besides that, the value of p-n device RMS roughness at that annealing duration also the smallest indicate that the device have the smoother surface morphology.

3 Conclusions

$CuGaO_2$/ZnO heterojunction diodes have been successfully fabricated on flexible substrate by using RF powered magnetron sputtering. The effect of annealing duration on the structural, morphology, optical and electrical properties of $CuGaO_2$/ZnO heterojunction diodes was investigated. The XRD pattern exhibits that ZnO films (002) peak were stronger at the range of 34˚ while $CuGaO_2$ (015) peak is not visible at 44˚C due to insufficient thermal energy. The surface RMS roughness become smoother as the annealing duration increase to 30 minutes and become rougher as the annealing duration is increased to 60 minutes. Optical transmittance of $CuGaO_2$/ZnO heterojunction diode annealed at 30 minutes approximately 75% in the invisible region. The diodes exhibited a rectifying characteristic with turn on voltage between 0.75 V and 1.05 V. The maximum forward current was observed for the diode annealed for 30 minutes. The diodes show an ideality factor range from 20.9 to 25.6 and barrier height (φ_b) range from 0.840 eV to 0.963 eV. This work has open up new opportunities for development in transparent and flexible optoelectronics device.

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