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Effect of post annealing treatment on electrical and structural properties of zinc oxide nanostructures

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Abstract

This paper work presents the effect of post annealing treatment on electrical and structural properties of nanostructured Zinc Oxide (ZnO) which was fabricated by hydrothermal process. I-V measurement shown the nanostructured ZnO exhibit Schottky conductive mechanism. The resistance of nanostructured ZnO was reduced as respected to the annealing temperature. XRD and EDX analysis confirmed the presence of ZnO element of Si substrate. Finally, FESEM analysis indicated a small nanoparticle growth on Si surface have 28.64 nm of average diameter size. These experiment results revealed, annealing treatment might be used to assist the formation of nanostructured ZnO on bare substrate.

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Keywords: Annealing treatment; Zinc oxide; Hydrothermal process; Schottky; Nanoparticle

1. Introduction

ZnO thin film is widely used in various fields of device making technologies such as ultraviolet laser [1], light emitting diodes [2], field emission devices [3], biosensor and solar cells [4]. There were several methods have been utilized to grow ZnO nanostructures, which are spray pyrolysis deposition [5], chemical vapour deposition [6], RF sputtering [7] and hydrothermal method [8]. Among of them, hydrothermal method is the simplest, cost effective and environmental friendly [9]. However, this method required severe condition such as a seed layer for

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nanostructured growth [10]. Literature survey found, that non-homogeneous thin film formed as a bare substrate (SiO_2/Si) was used due to poor nucleation process [11]. In this work, post-annealing treatment have been used to assist the nanostructured ZnO growth on bare Si substrate. Next, to investigate the effect of post annealing treatment, different annealing temperature (0°C , 300°C and 600°C for one hour) were used. Annealing treatment is executed in ambient environment. The change in surface morphology, structural and electrical properties of nanostructured ZnO prepared with different annealing temperature were examined by using field emission scanning electron microscopy (FESEM), X-Ray Diffractometer (XRD) and D1500 measurement respectively.

2. Experimental

Nanostructured ZnO films were deposited on p-type Si substrate (2 cm x 1 cm) by hydrothermal process. Si substrate had etched dilute HCl (37%) solution in 10 min before immersed in tin sensitizer solution for 30 s to enhance the surface wettability. Then, the substrate dried under Nitrogen flux. While zinc nitrate (Alfa aesar 99+%) was stirred in DI water by adding hexamethylenetetramine (Alfa aesar 99+%) for one hour. Both solutions have 0.1 M in 100 mL final stock solution. The stock solution be poured gently into autoclave. The substrate was place on top of stage inside the autoclave. Hydrothermal process had done under 90°C for 30 minutes. After hydrothermal process, samples were annealed in ambient atmospheric pressure with different temperature of 0°C , 300°C and 600°C for one hour. The experiment procedure and illustration of sample in autoclave can be refer to Fig. 1(a) and (b) respectively.

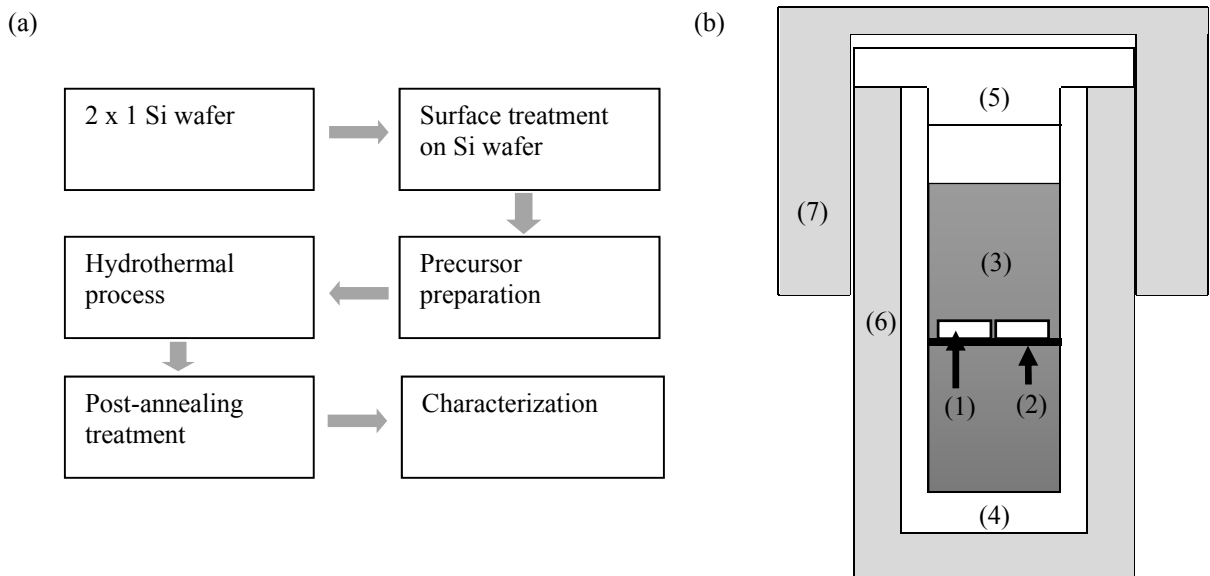


Fig. 1. (a) Flow chart of experiment process; (b) Schematic diagram of autoclave: (1) Si wafer substrate, (2) stage, (3) precursor solution, (4) Teflon, (5) Teflon cover, (6) stainless steel, (7) stainless steel cover.

The electrical properties were measured by means of semiconductor analyzer (D1500). To perform the I-V measurement, the nanostructured ZnO was attached gold contact using sputter as a metal contact. Crystal structure was measured by x-ray diffraction (XRD PANanalytical X-Pert³ Powder). The system was operated in 40kV tube voltage and 40mA tube current. Field emission scanning electron microscopy (FESEM Hitachi SU8020) was used for morphological observation and element composition analysis using energy dispersive x-ray spectroscopy (EDX) that attached in FESEM system.

3. Results and discussions

3.1. Electrical properties

To explore the electrical properties of fabricated nanostructured ZnO, the I-V measurement was carried out using semiconductor analyzer (two probes methods) using adhesive gold as a metal contact. The voltage varied between -1V and 1V. The variation of current has been plotted for 300 °C and 600 °C of annealed temperature samples as showed in Fig. 2. It was found that both samples have non-linear I-V curve, indicating that conduction mechanism is Schottky. The graph shown increased of current as respected to the annealed temperature. There are two ways to enhance the conductivity which are by increasing their concentration of carrier and grain size. In this work, it was believed that the grain size of nanostructured ZnO increase substantially as respond toward annealed temperature thus reduce the grain boundary as same with reported previously [12, 13]. The grain boundary is responsible to suppress the mobility of electron transfer because by formation of space charge region between interfacial grain [14]. Presence of space charge region act as a sanction for the electron transfer. Reducing the grain boundary, suppressed the formation of charge space region. Furthermore, measurement from each slope showed as increasing of temperature the resistance of layer is decreased as $40.01 \times 10^{-5} \Omega$ and $7.15 \times 10^{-5} \Omega$ for 300 °C and 600 °C respectively. Another study by Anuradha et. al stated that, the zinc interstitials and oxygen vacancies in the ZnO system were increased with the annealing temperature and presumably attributed to the increase of free carrier [15]. There was no response (not conductive) for the sample prepared without annealing treatment (0 °C).

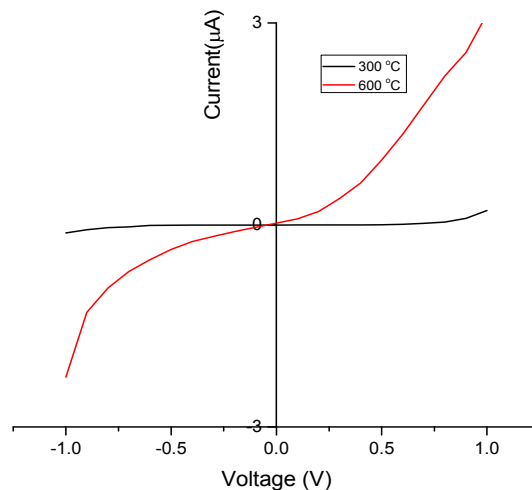


Fig. 2: I-V graph of nanostructured ZnO films prepared with different annealing temperature

3.2. Structural analysis

To further the study in their structural analysis, two different samples that annealed at 0 °C and 300 °C have examined using PANalytical X-Pert³ Powder. The system was operated in 40kV tube voltage and 40mA tube current. Fig. 3 shown an XRD spectrum for both sample. The sample that annealed at 0 °C shown no peak observed. Different situation happened for sample prepared at 300 °C, XRD spectra note the peak at (110) plane orientation can be indexed to hexagonal wurtzite structure of ZnO with JCPDS no 36-1451 [16]. This indicated an improvement in the crystallinity structural of the film after annealing treatment. Similar phenomena occurred have been found previously [17]. The annealing treatment was believed could be increased the surface diffusion by reducing the activation energy [18, 19]. Besides that, EDX analysis revealed the presence of main element which are zinc and oxygen without impurity on the substrate. However, the atomic percentage of Zn and O were found to be 1.1 % and

4.3% respectively indicated an excess of oxygen value in nanostructured ZnO. The EDX pattern also embrace Si peak energy cause by Si substrate as refer to Fig. 3 (b).

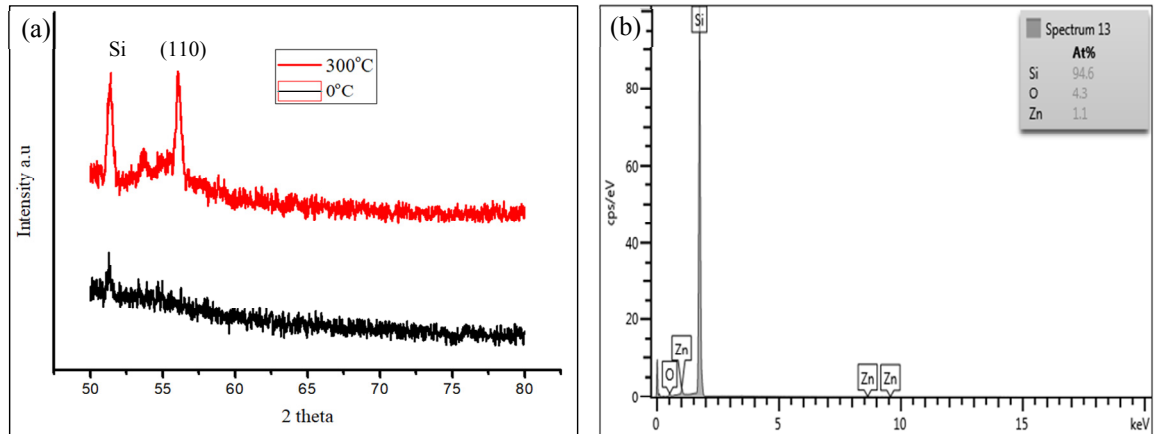


Fig. 3: (a) XRD spectrum of sample annealed at 0 °C and 300 °C (b) EDX spectrum of nanostructured ZnO prepared at 300 °C

3.3. Surface morphology

Fig. 4 shown the surface morphology of sample prepared at 0 °C and 300 °C. Fig. 4 (a) and (b) for 20k and 100k magnification of top view for sample prepared without annealing treatment (0°C). Then, Fig. 4 (c) and (d) for 20k and 100k magnification of top view for sample prepared with annealing treatment (300°C). Fig 4(a) and (b) indicated existence of structure. However, result from XRD revealed there was no ZnO peak for that sample. Furthermore, there was not conductive behaviour responded during I-V measurement. Different situation happened when the sample was annealed after hydrothermal process. An agglomeration of nanoparticles were observed. Each of nanoparticle size was in the range of 28.64 nm. In this case, a few portion of island deposited on Si surface (non-homogenous layer).

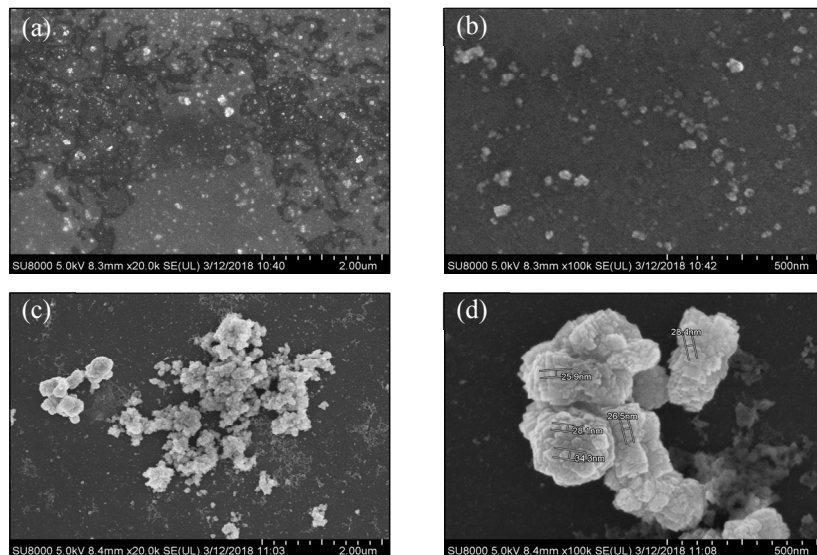


Fig. 4: FESEM image of sample without annealing treatment (a) at 20k magnification (b) 100k magnification and with annealing treatment of 300 °C (c) at 20k magnification (d) 100k magnification

4. Conclusion

In summary, nanostructured ZnO was deposited by the hydrothermal process assisted post annealing treatment. Schottky behavior was observed by I-V measurement. As annealing temperature increased, it reduced its resistance thus had enhanced the conductivity. XRD and EDX result confirm the existence of nanostructured ZnO. Meanwhile surface morphology observation indicated the nanostructured after annealing treatment at 300 °C has average grain size of 28.64 nm. As a result, post annealing treatment could provide useful technique for the fabrication of nanostructured ZnO on bare substrate without seed layer.

Acknowledgements

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