Effects of Oxygen Annealing on Kaolin-Doped Zinc Oxide Discs

To cite this article: F Azhari et al 2018 J. Phys.: Conf. Ser. 1083 012006

View the article online for updates and enhancements.

You may also like
- UV Irradiation Enhanced In-Vitro Cytotoxic Effects of ZnO Nanoparticle on Human Breast Cancer
  U Lestari, N Mufti, D A Lutfiyah et al.
- Nonvolatile Memory Thin Film Transistors Using Spin-Coated Amorphous Zinc Indium Oxide Channel and Ferroelectric Copolymer
  Sung-Min Yoon, Soon-Won Jung, Shin-Hyuk Yang et al.
- Spatial separation of electrons and holes for enhancing the gas-sensing property of a semiconductor: ZnO/ZnSnO$_3$ nanorod arrays prepared by a hetero-epitaxial growth
  Ying Wang, Peng Gao, Linna Sha et al.
Effects of Oxygen Annealing on Kaolin-Doped Zinc Oxide Discs

F Azhari¹, S Mahmud¹, S K Mohd Bakhouri¹, M F Che Pa¹, N S Mohd Latiff¹ and A F Omar¹

¹ School of Physics, Universiti Sains Malaysia, 11800, USM, Pulau Pinang, Malaysia

fahimy_azhari@hotmail.com

Abstract. ZnO nanostructures were used to prepare sintered ZnO discs that were pure ZnO discs (ZnO-100) and kaolin-doped ZnO discs (ZnO-97) containing 3 weight % of kaolin. The ZnO powder was mixed via ball milling process, pressed into discs and sintered at 1000 °C followed by annealing at 700 °C under oxygen ambient. The annealed discs were labeled as ZnO-100/O₂ and ZnO-97/O₂. Optical, structural and electrical properties were characterized using Raman scattering, XRD and current-voltage measurement. The crystallite size of ZnO was calculated using XRD data in that pure ZnO-100 had crystallite size of 33.034 nm and ZnO-100/O₂ oxygen annealed had 41.972 nm. The XRD data also showed oxygen annealed kaolin-doped ZnO-97/O₂ had a smaller crystallite size of 13.054 nm while unannealed kaolin-doped ZnO-97 had 14.285 nm. Kaolin doping and oxygen annealing on ZnO discs appeared to affect crystallite size. The resistance measured on the ZnO disc surface revealed that doped ZnO-97 had lower resistance (2 MΩ) compared to ZnO-100 (6 MΩ). On the other hand, annealed ZnO-97 O₂ had a lower resistance (0.8 MΩ) compared to annealed ZnO-100 O₂ (30 MΩ). The aluminum element in kaolin could have served as a dopant that lowered the potential barrier for electrical conduction to take place.

1. Introduction
Over the years, ZnO has been used widely in optoelectronics for many applications. Such as LED’s, sensors, solar cells and electronic devices. ZnO exhibit versatile characteristics, such as chemical sensitivity to numerous gases, high chemical stability, low cost, radiation hardness, high temperature resistance and flexibility for fabrication [1,2]. ZnO has been recognized to have many advantages. Firstly, it is a semiconductor that has direct and wide bandgap of 3.37 eV and it has large excitation binding energy (60 meV). These properties make ZnO an important and useful metal oxide which exhibits near-ultraviolet emission and photonics [3]. Secondly, ZnO is piezoelectric and can be used as electromechanically coupled sensors and transducers. Lastly, ZnO is biosafe, biocompatible and low in toxicity, which can be used for various biomedical purposes [4]. ZnO is zinc compounds which are generally known as safe product by U.S Food and Drug Administration [5].

Al and Si doped ZnO show reasonable sensor responses through lowering resistance values than undoped ZnO. Lowering the resistance make this device suitable for sensory and metal oxide varistor application. Structural, optical and electrical properties that had been studied were discussed in order to obtain the relationship how these properties are related to doping, sintering and annealing. In this study, 100 % ZnO disc and 97% ZnO disc doped with 3% kaolin were fabricated. The samples were annealed with oxygen for 700 °C for an hour.
2. Methodology
ZnO powder was synthesized by using French process as described by Mahmud [6]. The powder was divided into four groups and pressed into disc form. Subsequently, the discs were sintered at 1000 °C for 1 hour soaking time. Then, the crystalline structure of the discs was confirmed by using XRD PanAnalytical X’Pert Pro at 20-80 degree of 2θ. The optical properties of ZnO were studied using Raman spectroscopy by Horiba Jobin Yvon at room temperature. The current voltage response was characterized using Keithly to evaluate the resistance properties of the sample.

3. Results and Discussions
Figure 1 shows XRD spectra for all ZnO. It confirmed that all ZnO is a wurtzite structure with no impurities. From the XRD data, crystalline size of ZnO was calculated using Scherrer’s equation [7]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

Where \( k \) is plank constant and \( \lambda \) is wavelength of Kα of x-ray tube at 1.542 Å, \( \beta \) is full width at half maximum (FWHM) and \( \theta \) is Bragg angle. The calculation considering an average of highest peak at (100), (002) and (101) for all ZnO. From the calculation, the crystallite size for all ZnO is as shown in table 1.

![XRD patterns](image)

Figure 1. XRD patterns for (a) ZnO-100 and ZnO-100/O2 ; (b) ZnO-97 and ZnO-97/O2.

| Sample       | Crystallite size (nm) |
|--------------|-----------------------|
| ZnO-100      | 33.034                |
| ZnO-100/O2   | 41.972                |
| ZnO-97       | 14.285                |
| ZnO-97/O2    | 13.054                |
The crystallite sizes of ZnO-100 and ZnO-100/O₂ discs were 33.0.34 nm and 41.972 nm respectively, showing increment in crystallite size. This result implies that oxygen annealing at 700°C did not alter the structural orientation of the sample but may modify the surface condition of the ZnO discs. Meanwhile, the crystallite size for ZnO-97 and ZnO/O₂ discs were 14.285 nm and 13.054 nm. It shows that by adding kaolin to ZnO can decrease the crystallite size of ZnO disc. Although XRD patterns in all ZnO are similar, but the calculated average crystallite size of all ZnO types showed some changes. This result implies that FWHM of peaks (100), (002) and (101) are significantly change.

Figure 2 shows the Raman spectra of all ZnO. It shows phonon modes of A₁ (TO), E₁ (TO), E₂ (high), E₁ (LO) is viable. Other than that, the raman mode is silent and could not be detected. The Raman shift for each ZnO is shown in Table 2 below. For A₁(TO) the slightly blueshift of wavenumber occurred after doped with kaolin. On the other hand, E₂ (high) for all ZnO are similar. Yoshikawa et al describe the decreased of E₂ (high) phonon frequency is attribute to better crystallinity and particle size dependent [8]. This statement is contradicted with E₂ (high) in Table 2, whereby the values are similar for all ZnO. This condition may attribute to insignificant effects of oxygen annealed on doped kaolin. Nevertheless, XRD calculation showed significant different in crystallite size, and Raman spectrum should be decreasing in E₂(high) frequency according to Yoshikawa et al. But in this report, the E₂(high) is not dependent on crystallite size. It may have influenced by the adsorption of oxygen molecules on ZnO surface by which it did not affect the phonon vibration.

![Figure 2. Raman spectra of (a) ZnO-100 and ZnO-100/O₂; (b) ZnO-97 and ZnO-97/O₂.](image-url)
Table 2. Raman shift for all ZnO.

| Sample      | $\text{A}_1$ (TO) | $\text{E}_1$ (TO) | $\text{E}_2$ (high) | $\text{E}_1$ (LO) |
|-------------|-------------------|-------------------|---------------------|-------------------|
| ZnO-100     | 332.907           | 379.010           | 437.293             | 583.249           |
| ZnO-100 O$_2$ | 332.355           | 378.462           | 437.293             | 584.481           |
| ZnO-97      | 330.152           | 380.102           | 437.293             | 584.310           |
| ZnO-97 O$_2$ | 330.704           | 379.557           | 436.751             | 584.841           |

Figure 3 shows the current-voltage curve of all ZnO. The resistance measured on the ZnO disc surface revealed that ZnO-97 had lower resistance (2 MΩ) compared to ZnO-100 (6 MΩ). On the other hand, annealed ZnO-97/O$_2$ had a lower resistance (0.8 MΩ) compared to annealed ZnO-100/O$_2$ (30 MΩ). The Kaolin doped ZnO showed lower resistance because kaolin contained Al and Si elements and caused atomic substitution [9]. Doping with Al and Si (in Kaolin) into ZnO crystal lattice increases free charge carriers (electrons) thereby reducing resistivity. According to Maldonado et.al, by computer simulation, the electron jump produced free electron in conduction band thus increase the conductivity and decreased the resistance. [9]. Moreover, the oxygen annealing at 700 °C effects has lower the oxygen vacancies concentration by oxygen adsorption [10] on the ZnO disc surfaces.

Figure 3. Current-voltage response for all ZnO dics.

4. Conclusion
In conclusion, the ZnO disc doped with kaolin have affected the physical and electrical properties. The changes are beneficial as it provides lower resistance to the ZnO disc. This advantage can be used in sensory application such as UV sensor or as dopant in metal oxide varistor as it can alter the breakdown voltage according to desired application.
Acknowledgement

The authors would like to acknowledge the FRGS grant [203/PFIZIK/6711605] and grant [304/PFIZIK/6313209] for financial support. Moreover, the author is grateful to Solid State Laboratory, School of Physics and Institute of Nano-optoelectronics Research and Technology (INOR).

References

[1] J Sun, F Juan, H Huang, J Zhao, Z Hu, X Zhang and Y Wang 2010 Fast response ultraviolet photoconductive detectors based on Ga-doped ZnO films grown by radio-frequency magnetron sputtering Appl. Surf. Sci. 257 921-24

[2] O Lupan, L Chow, G Chai, L Chernyak and O Lopatiuk 2008 Focused ion beam fabrication of ZnO nanorod-based UV photodetector using in-situ lift-out technique Phys. Stat. Sol. (a) 205 2673-78.

[3] D C Reynolds, D C Look, B Jogai, C W Litton, T C Collins, W Harsh and G Cantwell 1998 Neutral donor bound excitation complexes in ZnO crystals Physical Rev. 57 12151-55

[4] S K Sahoo, S Parveen and J J Panda 2007 The present and future of nanotechnology in human health care Nanomedicine 3 20-31

[5] M Premanathan, K Karthikeyan, K Jeyasubramaniam and G Manivannan 2011 Selective toxicity of ZnO nanoparticles towards gram-positive bacteria and cancer cell by apoptosis through lipid peroxidation Nanomedicine 7 184-192

[6] S Mahmud 2011 One-dimensional growth of ZnO nanostructures from large micro-particles in a highly rapid synthesis J. Alloys Compd. 509 4035-40

[7] B M Han, S Chang and S Y Kim 1999 Chopping effect on the crystallinity of ZnO prepared by r.f. planar magnetron sputtering method Thin Solid Films 338 265-68

[8] M Yoshikawa, K Inoue, T Nakagawa, H Ishida and N Hasuiker 2008 Characterization of ZnO nanoparticles by resonant Raman scattering and cathodoluminescence spectroscopies Appl. Phys. Lett. 92 113115

[9] F Maldonado and A Stashans 2010 Al-doped ZnO: electronic, electrical and structural properties, J. Phys. Chem. Solids 71 784-87

[10] D Chakraborti1, G R Trichy1, J T Prater and J Narayan 2007 The effect of oxygen annealing on ZnO: Cu and ZnO: (Cu,Al) diluted magnetic semiconductors J. Phys. D Appl. Phys. 40 24