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ZnO NANOSTRUCTURE HYDROTHERMAL SYNTHESIS: MORPHOLOGY CONTROL BY O_2 PLASMA CONDITIONING

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ABSTRACT

This study investigates the effect of oxygen plasma conditioning to the final morphology of nanostructure prepared via facile hydrothermal synthesis. Two parameters; plasma temperature and flow rate of oxygen gas were varied while plasma time and power were kept constant. Scanning Electron Microscopy (SEM) analysis reveals that lower plasma temperature has bigger influence on diameter and length of the ZnO nanorods compared to high temperature setting. For both setting, lower oxygen flow rate will produce tighter distribution of diameter at ~ 10 nm and length of ~ 1.1 micron while higher oxygen flow rate produced nanorods with diameter of ~ 35 nm and ~ 2.2 micron in length. These results demonstrated that oxygen plasma process is one of the possible alternatives that can be used to manipulate the final morphology of ZnO nanostructure growth in facile hydrothermal growth method.

Keywords: oxygen plasma, zinc oxide, hydrothermal, nanostructure array.

INTRODUCTION

Hydrothermal process was considered as facile approach to synthesis ZnO due to its simplicity. This method which was classified under aqueous chemical process requires lower process temperature and less sophisticated equipment if compared to other technique such as chemical vapour deposition (CVD) or thermal evaporation synthesis [1]. Other than that, hydrothermal synthesis will result in wide variety of ZnO crystal structures such as disk like, pencil like, flower like, rod like and so on. [2-3].

There are a few different hydrothermal growth procedures that have been studied [4-6]. This includes investigation on plasma treatment which has shown to produce further improvement to optical and structures properties of ZnO. Nevertheless, the outcome of the morphology will highly depend on the condition of the precursor. On the same note, there are quite number of research conducted to investigate the effect of growth parameters such as temperature [7], reactant molar ration and precursor concentration [8-9], and annealing time and annealing temperature [10] but investigation on plasma precondition effect to the final morphology is relatively new.

In order to study the effect of plasma parameters to the final morphology of the nanostructure, design of experiment (DOE) approach was used. DOE has widely used proven to systematically identify both the significant factors which influence the response of the process as well as the interaction among them [11].

METHODOLOGY

ZnO nanostructures were synthesized by hydrothermal growth on oxidized silicon (SiO_2) substrates. The seeding precursor solution was prepared by mixing 0.2 M zinc acetate dehydrate with diethalonamine in ethanol. The seed layer was then coated onto the SiO2 substrates by spin coating at 3000 rpm for 30 seconds. The samples were soft baked in an oven at 100° C for 1 hour to promote nucleation on the SiO_2 surface prior to the final annealing.

To study the effect of O2 plasma, the samples were divided into four different groups according to a Design of Experiment (DOE) metric generated from Minitab Statistical software shown in Table-1. The samples then undergo O2 plasma treatment using PECVD (Oxford Instruments, Plasma-Lab System). All the samples were then vertically immersed in a nutrient solution consisting of 0.04 M zinc nitrate hexahydrate and hexamethylenetetramine inside a sealable glass beaker and heated up to 80° C for 4 hours.

Table-1. Fix and variable plasma process parameters.

Fix Parameter	Variable Parameter
Duration - 60 min	Temperature - 45°C and 90 °C
Plasma Power - 200 W	O2 Flow - 100 and 200 sccm

Table-2. DOE experimental metric generated from minitab software.

Run Sequence	Temperature Setting (°C)	O2 Flow (sccm)	Group ID
1	45	200	1
2	45	100	2
3	90	200	3
4	90	100	4

At the end of the growth process, the samples were rinsed with de-ionized water, followed with post-heat treatment at 90°C for 5 min. A scanning electron microscope (JEOL JSM 7500) was used to characterize

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the morphology and size of the grown ZnO nanorods. Raman spectrometry was performed using NT-MDT system equipped with 20mH He-Ne laser emitting at 473nm. All measurements were collected at room temperature with no special sample preparation.

RESULT AND DISCUSSIONS

The cross sectional SEM images of the grown nanorods as shown in Figure-1. ZnO nanorods produced on the substrate have vertical orientation. Figure-1 (b) and (c) indicates that groups with lower O_2 flowrate seem to be more consistences in the orientation direction. On top of that, they were also denser and less variation in diameter and length as opposed to group with higher O_2 flow rate (Figure-1(a) and (d).

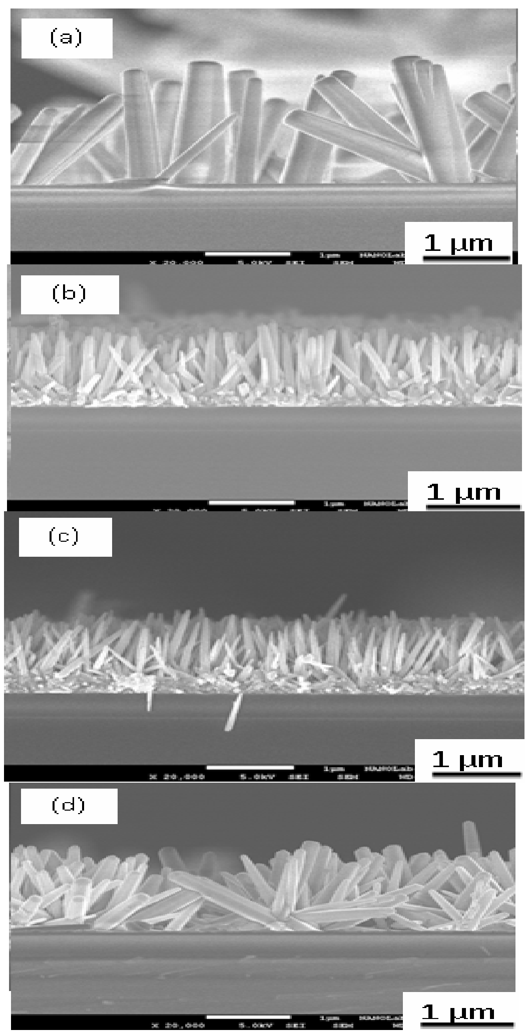

Figure-1. SEM image of ZnO nanostructure undergone pre-condition with different temperature and gas flow setting of 45°C, 200 sccm (a), 45°C, 100 sccm (b), 90°C, 100 sccm (c) and 90°C, 200 sccm (d) at same scale of 1 µm.

Base on the histogram graph in Figure-2, distribution of diameter and length of the grown nanostructures is much tighter when using lower level O_2 flow rate during plasma which is consistence with the previous observation. Group 1 shows wide distribution of diameter as well as length. This suggests high variance of nanostructure was produced from this plasma process and not suitable for application requires high uniformity of nanostructure.

In contrast, group 3 shows relatively narrow distribution for both diameter and length dimension which indicates the homogeneity of the nanostructure produced by this pre-condition treatment. Basically, a gas flow rate of 100 sccm is more dominant in producing low variance of ZnO nanostructure for this hydrothermal process.

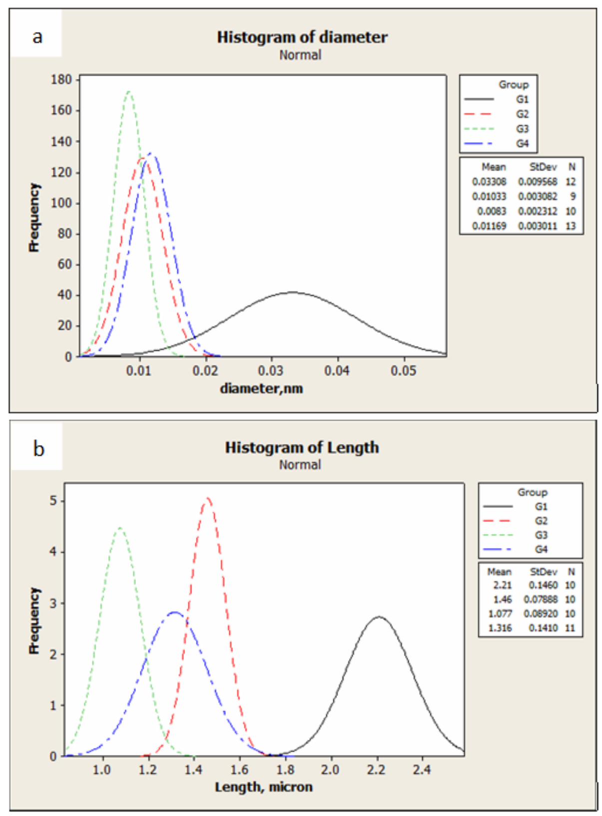

Figure-2. Analysis of diameter distributions (a) and length distributions (b) for different groups.

As far as the interaction is concerned, there was no trend observed. Figure-3 shows that both temperature and gas flow rate have parallel effect to nanorods diameter and length. Nevertheless, the steepness of the line suggests that temperature setting of 45°C have bigger influence to both diameter and length. Increasing the flow rate at 45°C will greatly increase diameter and length while this effect is less significant for 90°C. In both cases, flow rate of 100 sccm will produce smaller mean value for both dimensions regardless of the temperature setting.

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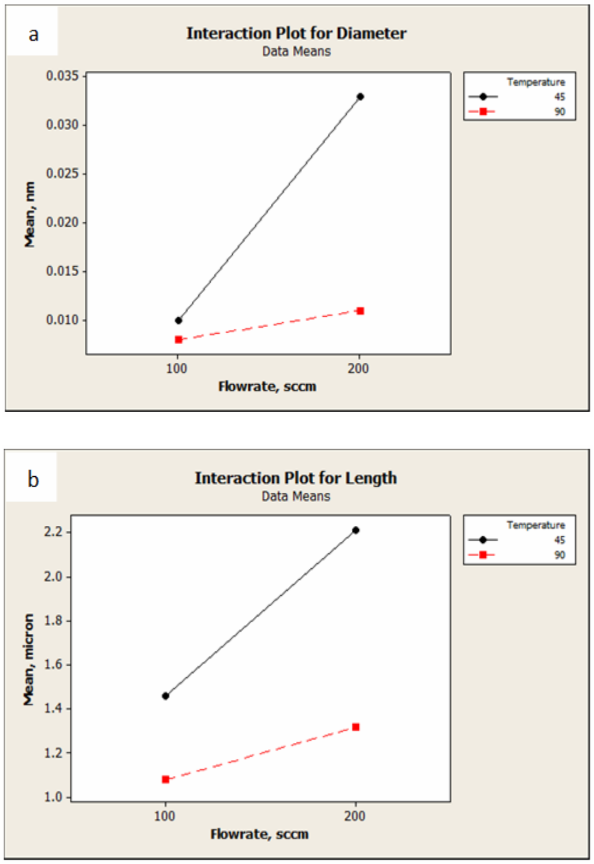

Figure-3. Interaction plot of gas flow rate versus temperature in O_2 plasma process.

Figure-4 shows the Raman spectra of ZnO nanorods on silicon substrate from 200 cm¯¹ to 800 cm¯¹ under four groups condition as Table-1. The Raman spectra are sensitive to crystallization, structural disorder and defects in micro and nanostructures. ZnO crystal is the hexagonal wurtzite structure, which belongs to the group C46v and has two formulas per unit primitive cell [12].

According to the group theory, single-crystallined ZnO has eight sets of optical phonon modes at A1 and E1 modes are polar which split into transverse optical (A1T and E1T) and longitudinal-optical (A1L and E1L) phonons, while E2 mode consists of two modes of low and high-frequency phonon (E2L and E2H) which are Raman active.

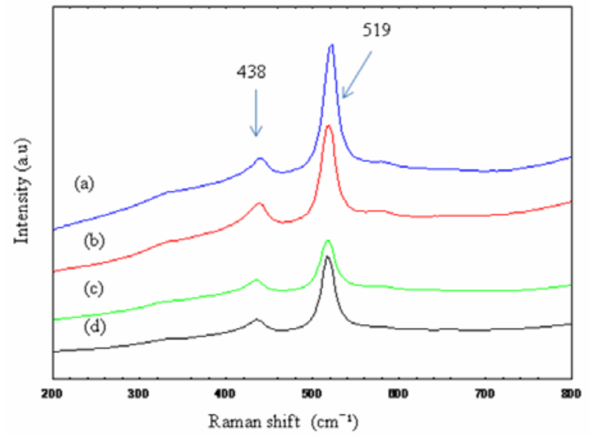

Figure-4. Raman spectrum on ZnO nanorods grown from different O2 plasma pre-condition setting; 45°C, 200 sccm (a), 45°C, 100 sccm (b), 90°C, 200 sccm (c) and 90°C, 100 sccm (d).

As shown in Figure-4, the presence of E2H is observed at 438 cm¯¹ which is an intrinsic characteristic of the Raman- active mode of wurtzite hexagonal ZnO and nonpolar optical phonons. The peak located at 519 cm¯¹ attributed to the Si-substrate vibration mode. The Raman spectra obtained in this study agrees with that Li. *et al.*, [13].

CONCLUSIONS

This paper reports the impact of conditioning ZnO seed layer using oxygen plasma prior to the hydrothermal growth process. Through design of experiments method, the effect of temperature and oxygen flowrate was investigated. The result shows that plasma temperature has a bigger influence to the diameter and length distribution of the nanorods. In summry, the diameter and length distribution of ZnO nanorods grown by hydrothermal method is possible to be controlled by oxygen plasma precondition process.

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REFERENCES

Rashid Amirul Abd, *et al*. 2013. Preliminary Study of WO3 Nanostructures Produced via Facile Hydrothermal Synthesis Process for CO2 Sensing. Applied Mechanics and Materials. 431: 37-41.

Zhang Hui, *et al*. 2005. Controllable growth of ZnO nanostructures by citric acid assisted hydrothermal process. Materials Letters. 59.13: 1696-1700.

Baruah *et al*. 2009. Hydrothermal growth of ZnO nanostructures. Science and Technology of Advanced Materials. 10.1: 013001.

Abd Rashid Amirul *et al*. 2014. Selective ZnO nanowire growth through resist pattern method. Applied Mechanics and Materials. 606: 51.

Rashid Amirul Abd, *et al*. 2014. PH Tester Gauge Repeatability and Reproducibility Study for WO3 Nanostructure Hydrothermal Growth Process. IOP Conference Series: Materials Science and Engineering. 58(1). IOP Publishing.

Abd Rashid Amirul *et al*. 2014. Controlled dimensional type WO3 through DOE. Applied Mechanics and Materials. 607: 47.

Guo Min, *et al*. 2005. The effect of hydrothermal growth temperature on preparation and photoelectrochemical performance of ZnO nanorod array films. Journal of Solid State Chemistry 178.10 (2005): 3210-3215.

Le H. Q., *et al*. 2006. Systematic studies of the epitaxial growth of single-crystal ZnO nanorods on GaN using hydrothermal synthesis. Journal of crystal growth. 293.1: 36-42.

Guo *et al*. 2005. Hydrothermal growth of well-aligned ZnO nanorod arrays: Dependence of morphology and alignment ordering upon preparing conditions. Journal of Solid State Chemistry. 178.6: 1864-1873.

Rashid Amirul Abd, *et al*. 2014. Effect of Annealing Temperature and Time to Zinc Oxide (ZnO) Nanostructure in Hydrothermal Synthesis. Proceeding of International Symposium on Materials Characterisation and Testing 2014 (ISMCT).

Myers *et al*. 2009. Response surface methodology: process and product optimization using designed experiments. Vol. 705. John Wiley and Sons.

S.K. Mohanta *et al*. 2010. Optical properties of ZnO nanorods and hybrid structures grown on p-type GaN/sapphire and silicon-on-insulator substrates. Science of Advanced Materials. 2 64-68.

Li *et al*. 2010. Controllable growth of well aligned ZnO nanorods arrays by low temperature wet chemical bath deposition method. Applied Surface Science. 256: 1698-1702.