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The Effect of Temperature and Oxygen Flow Rate on the Morphology of ZnO Nanostructures

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Abstract: Three different morphologies of ZnO nanostructures were prepared by vapor transport on Au coated silicon substrates. Randomly oriented nanowires (NWs) mixed with few nanoflakes were obtained at furnace temperature of 750 °C and oxygen flow rate of 20 sccm. While thicker, longer and denser NWs were obtained at furnace temperature of 900 °C with the same oxygen flow rate of 20 sccm. Keeping the furnace temperature at 750 °C and lowering the oxygen flow rate to 5 sccm, changed the morphology of the NWs to unspecified features with few NWs in between. Both the growth temperature and the oxygen flow rate have proven to have great influence on stoichiometry. The control of the growth and stoichiometry of ZnO may have an impact in optoelectronic applications.

Keywords: ZnO NWs; Vapor transport; growth; temperature; oxygen flow.

1 Introduction

ZnO nanostructures have emerged as promising candidates for being used as photoanodes in photoelectrochemical cells[1], gas sensors [2], solar cells [3], UV photodetector[4], field-effect transistors [5] and in many other electronic and optoelectronic devices [5,6].

The growth of ZnO nanowires (NWs) has been demonstrated by various methods [7]. The most famous method is the vapor transport, including vapor-solid (VS) and vapor-liquid-solid (VLS) growth mechanisms [7-17]. In the VS mechanism, the vaporized precursor condensates directly along the growing nanowire. In the VLS mechanism, the melted catalyst forms a liquid droplet by itself or by alloying with the growth material, and acts as preferential condensation site for the vaporized precursor; when a supersaturated solution is reached, growth material precipitates resulting in one dimensional growth [11].

There are many factors which affect the final form of ZnO NWs grown by vapor transport. The most relevant factors are catalyst type and thickness, substrate temperatures, argon and oxygen flow rates, the diameter of the tubular furnace, the chamber pressure, the type and geometrical shape of the substrate, the kind of the source material, the time of deposition and the addition of other gasses such hydrogen [12-17]. Although, these factors affect the morphology and thereby the physical and chemical properties of the resulting ZnO nanostructures, less attention has been focused on them. Therefore in this work the effects of temperature and oxygen flow rate on the morphology of ZnO nanostructures are examined.

2 Experimental Procedure

ZnO nanostructures were synthesized by the thermal evaporation method with vapor-liquid-solid (VLS) growth technique where Zn metal granules, ~2 mm diameter (Aldrich chemicals; 99.95%), was placed in an alumina boat at the center of the quartz tube furnace (internal diameter 36 mm and length of 60 cm). The synthesis was carried out on Au coated (~ 25-30 nm) Si (100) wafers (cut into 1 cm × 1 cm and ultrasonically cleaned). The Au coating of Si was done using AC Ion sputtering device (JFC-1100E). The Au-coated Si substrates were put approximately 5 cm and up to 13 cm away from the alumina boat. Three different deposition experiments were carried out. The first one was carried out at furnace temperature of 750 °C and oxygen flow rate of 20 sccm. The second was carried out at furnace temperature of 900 °C and oxygen flow rate of 20 sccm. The third was carried out at furnace temperature of 750 °C and oxygen flow rate of 5 sccm. The argon flow rate and deposition time, in all the experiments, were fixed to 200 sccm and 30 min, respectively. After deposition, the furnace was cooled down to room temperature.

The surface morphology of the synthesized ZnO nanostructured samples was examined by scanning electron microscope (SEM) type JOEL model JSM-6380 LA. The

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chemical composition of the synthesized nanostructures was analyzed using energy dispersive analysis of X-ray (EDAX) unit attached with the SEM.

3 Results and Discussion

The typical morphology of the ZnO nanostructures formed on Au-coated Si(100) substrate at furnace temperature of 750 °C and oxygen flow rate of 20 sccm is shown in Fig.(1a,b).

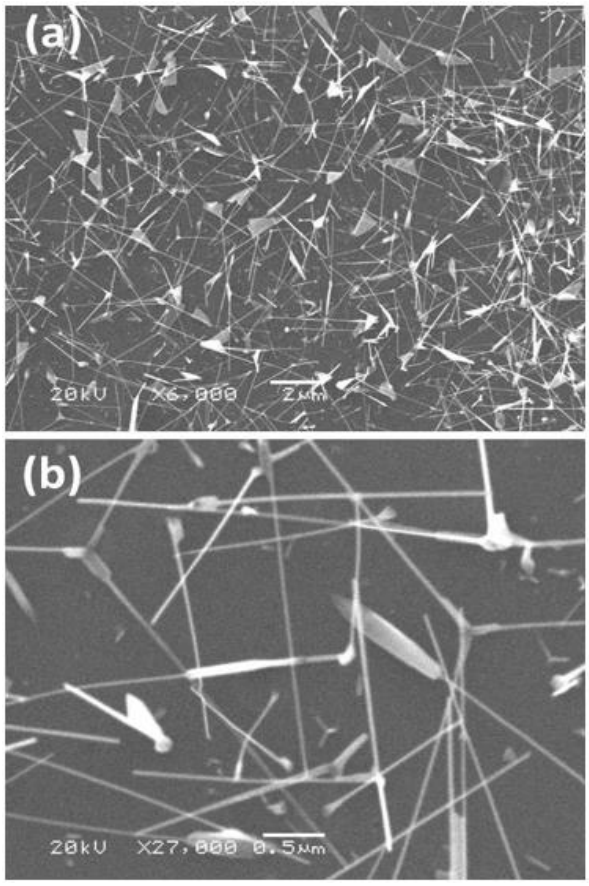

Fig. 1: (a) low and (b) high magnifications SEM images of ZnO nanowires, prepared J

It is observed that the morphology is mainly NWs mixed with few of nanoflakes. The NWs are randomly distributed on the substrate. The diameters of the NWs and nanoflakesare ranged from 29.6 - 44.4 nm and 150 - 200 nm, respectively, and the NWs lengths are longer than 4 μm. The presence of some droplets on the ends of some nanowires indicates the growth by the VLS mechanism. EDAX analysis revealed that the nanowires contain dominant zinc and reasonable level of oxygen. Within a precision of 2 at.%, the zinc and oxygen atomic percentages are found to be 56.08 at.% and 43.92 at.%, respectively. Thus, the predicted stoichiometry is $ZnO_{0.78}$.

Raising the furnace temperature to 900 °C and keeping the oxygen flow rate at 20 sccm, led to the formation of thicker, longer and denser NWs as shown in Fig.(2a,b). The typical NWs diameters are in the range 90-400 nm and the lengths extends to 6 μm. Clearly, the temperature play a crucial role in defining the morphology of the nanostructure by the thermal evaporation on to the Au coated Si substrate. At low temperature, the little population density of vapors species decreases the absorption and precipitation surrounding the Au droplets, leading to the formation of a thin NWs.

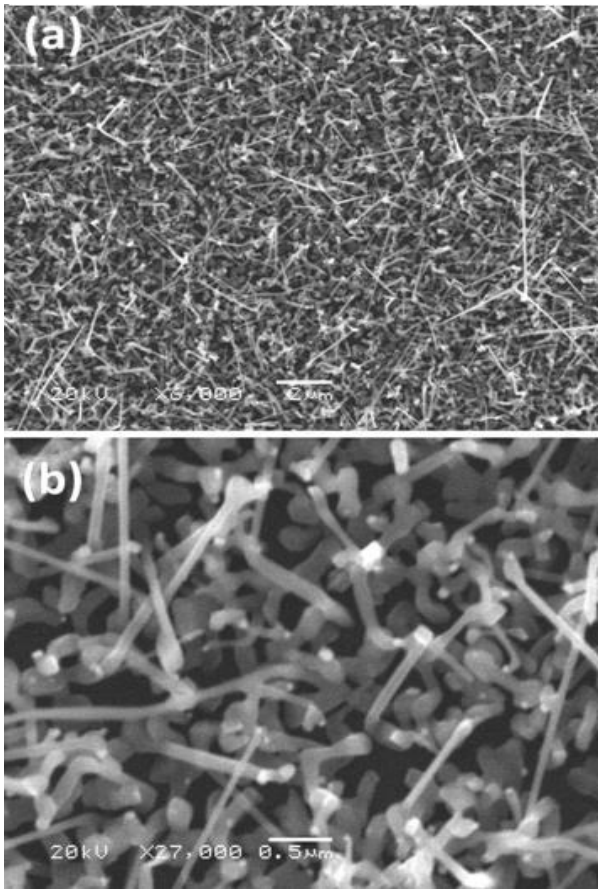

Fig. 2: (a) low and (b) high magnifications SEM images of ZnO nanowires, prepared at furnace temperature of 900 °C and oxygen flow rate of 20 sccm.

Table 1: Elemental ratios of oxygen and zinc for ZnO nanostructures prepared at different conditions.

T (°C)	O_2 flow rate (sccm)	Chemical composition (at.%)		
		Zn	O	ZnO_x
750	20	56.08	43.92	$ZnO_{0.78}$
750	5	59.74	40.26	$ZnO_{0.67}$
900	20	52.12	47.78	$ZnO_{0.92}$

At higher temperature the increase of population density of vapor species as well as the coalescence of Au droplets leads to the formation of thicker NWs. Thus, the morphology change can be ascribed to the change in the degree of supersaturation which is determined by the vapor pressure of the growing materials and the temperature of the substrate [16,17]. The presence of some droplets on the ends of some nanowires indicates the growth by the VLS

mechanism. The EDAX analysis of ZnO NWs grown at 900 °C revealed the presence of Zn and O with atomic percentages of 52.12 at.% and 47.78 at.%, respectively, indicating the formation of zinc oxide with stoichiometry of $ZnO_{0.92}$ (within a precision of 2 at.%). It is worth mentioning that zinc oxide is generally containing excess zinc metal in the intestinal positions of the oxide and cannot strictly reach the stoichiometry in normal conditions [18].

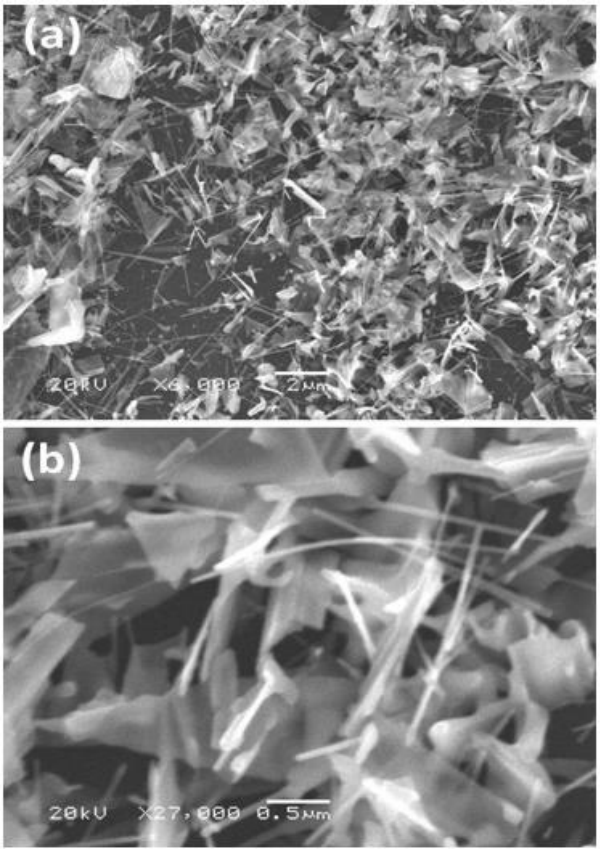

Fig. 3: (a) low and (b) high magnifications SEM images of ZnO nanostructures, prepared at furnace temperature of 750 °C and oxygen flow rate of 5 sccm.

Fig. (3a,b) shows SEM images of ZnO nanostructures prepared at furnace temperature of 750 °C and oxygen flow rate of 5 sccm. Clearly the deficient of oxygen change the morphology of the nanowires to unspecified features with few NWs in between. An appropriate interpretation for the change of the morphology with changing the oxygen content is related to the nature of gas phase in the ambient of the reaction. The gas phase supersaturation with different oxygen ratios change the growth rate and the morphology of the structure as well as the surface energy of the growing planes[15]. According to Wang [7] oxygen influences not only the product morphology but also the volatility of the source material and the stoichiometry of the vapor phase. The zinc and oxygen atomic ratios, as revealed by EDAX analysis, are 59.74 at.% and 40.26 at.%, respectively. This kind of sub-stoichiometric $ZnO_{0.67}$ nanostructures may show some promising properties [8].

4 Conclusions

ZnO nanostructurs were grown on Au coated Si(100) by using vapor transport from Zn metal granules at different furnace temperatures and oxygen flow rates. Variation of the temperature and oxygen flow rate during the reaction has significant effect on the stoichiometry and shape of the nanowires. To be specific, at furnace temperature of 750 °C and oxygen flow rate of 20 sccm, randomly oriented NWs mixed with few nanoflakes were obtained, while thicker, longer and more dense NWs were obtained at furnace temperature of 900 °C. Besides, decrease of the oxygen content leads to deformation of the NWs morphology. The control of the growth and stoichiometry of ZnO may have an impact in optoelectronic applications.

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