

On the correlation of morphology and growth parameters in ZnO nanowires

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Abstract

The growth of ZnO nanowires as a function of the thickness of Au thin layers, deposition temperature and surface properties through simple carbothermal evaporation method is studied. Investigations by X-ray diffraction (XRD) revealed the (002) plane as the preferred plane for the growth of ZnO nanowires. Our experiments indicated that the temperature range of 800-900 °C under flow of 100 sccm N₂ gas with Au catalyst layer, is the suitable condition for producing the most aligned nanowires. The Vapour – Liquid - Solid (VLS) mechanism more than other mechanisms is dominant for growth process.

PACs: 81.07.Bc; 81.16.Pr; 62.23.Hg; 81.07.Gf

Keyword: ZnO nanowires; Nanostructures; Growth conditions; Growth mechanism; Au catalyst; Silicon substrate

1. Introduction

Zinc oxide, as a direct band gap (~3.37eV) semiconductor is the focus of much research for its potential in fabricating light emitting diode (LED) [1], light and gas sensors [2], and UV laser diodes [3]. The reason could be due to its large exciton binding energy (~60 meV) which is two times higher than the thermal energy at room temperature. It has been used as a piezoelectric [4], transparent conducting materials [5], and antibacterial activities [6]. Various methods such as physical vapor deposition [7], chemical vapor deposition [8], laser-assisted vapor-liquid-solid growth [9], sol-gel [10], and electrochemical deposition [11] have been developed to prepare 1D and quasi-1D ZnO nanostructures. So far, different ZnO nanostructures such as nanowires [12], nanobelts (nanoribbons) [13], comb-like nanowires arrays [14], nanoneedles arrays [15], and nanorings [16] have been successfully synthesized.

In this work controlled growth of vertical ZnO nano/microwires, using a simple physical vapor deposition is reported. Source material was a mixture of ZnO and graphite powders. Au layer on the silicon substrate as the metal catalyst and N₂ as the carrier gas, were used. The effect of catalyst layer thickness, deposition temperature, and surface roughness of the substrate on diameter and density of nanowires were studied.

2. Experimental details

p-type silicon wafer with (111) orientation, and 1.5 Ω-cm resistivity was used as substrate. Si wafers were ultrasonically cleaned in acetone then ethanol for 10 min. A thin layer of Au (10-30 nm) was sputtered on the silicon wafers as catalyst. Samples were annealed at 700 °C for 1h. A mixture of ZnO and graphite powder with 1:1 ratio, as the source material was placed in a quartz boat located in the centre of a horizontal tube furnace. The tube was heated at 1050 °C for 1h under flow of N₂ (100 sccm/s) as carrier gas. This experiment was repeated by placing silicon substrate at different distance from the source material. It was found that the desired deposition temperature region for the growth of ZnO nanowires is 800-900 °C. The fabricated nanowires were characterized by scanning electron microscopy (SEM, JEOL JXA-840) micrographs and x-ray diffraction (XRD, Philips X'pert pro x-Ray diffractometer, $\lambda = 1.78897 \text{ \AA}$) spectrum. The effect of deposition temperature, surface parameters, catalyst layer and catalyst thickness on the density and diameter of ZnO wires in order to achieve desirable ZnO nanowires, have been discussed in details.

3. Results and discussion

3.1. Effect of deposition temperature

The temperature affects the growth procedure in three ways: 1) size and density of catalyst droplet on substrate surface, 2) it determines diffusion length of adsorbed vapour species, 3) it determines the tendency of the vapor for condensation [17].

At high temperature (~850 °C) with N₂ gas flow (~100 sccm/s), the grown wires become dense, nor-

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mal to the substrate surface and well-aligned with hexagonal shape on top .

When substrate temperature increases to more than 900°C , the nanowires become shorter, thicker, less dense and disordered.

We found an intermediate temperature range ($800\text{--}900^{\circ}\text{C}$), which produces the best condition for growing the ZnO nanowires.

Fig. 1. shows the typical SEM images of different morphologies due to the different deposition temperatures. It can be seen that when temperature is more than 900°C (Fig. 1(a)), the vapour of material is very energetic so the rate of reevaporation is high which leads to short and, disordered nanowires covering all the substrate surface. When the substrate temperature decreases about 850°C (Fig 1(b)), the nanowires become dense, hexagonal, prenormal to the surface and small in diameter compared to wires grown at temperatures less than 800°C (Fig. 1(c)).

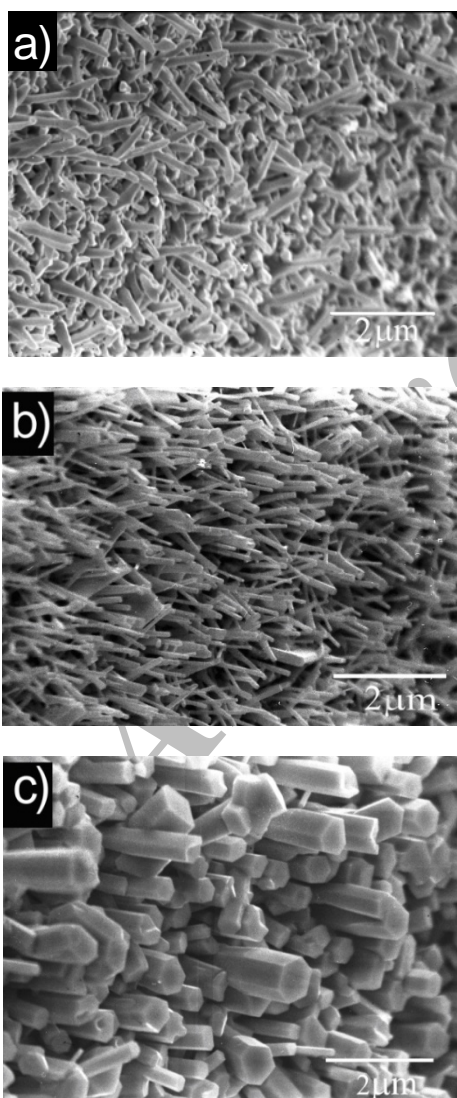


Fig. 1. SEM images of three Si substrates with 10 nm Au catalyst at different temperatures. a) $T = 950^{\circ}\text{C}$; b) $T = 850^{\circ}\text{C}$; c) $T = 750^{\circ}\text{C}$

3. 2. Effect of catalyst layer thickness

We chose thin layer Au as the catalyst because; a) it is physically active but chemically inert at all temperatures used in our experiments, b) Au particles relative to other metal catalyst particles result in the thinnest and longest nanowires, c) Au layer forms particles with homogeneous size distributions at all annealing temperatures concurring with the prevalent usage of Au as catalyst for nanowire growth [18].

In order to investigate the effect of catalyst layer on the growth of ZnO, wires, ZnO was deposited on bare Si substrate. When substrate is not covered with catalyst layer, the eutectic does not form and ZnO wires just grow in some places randomly. The grown wires have larger diameter (especially at tips) when compared with samples grown with Au catalyst. Then, catalyst layer plays a major role in the growth of ZnO microstructures on substrate. These structures do not have any preferred orientation and also they are not normal to the surface. The hexagonal cross section of ZnO structures is clear in Fig. 2. This kind of morphology is called needle-like rods [19].

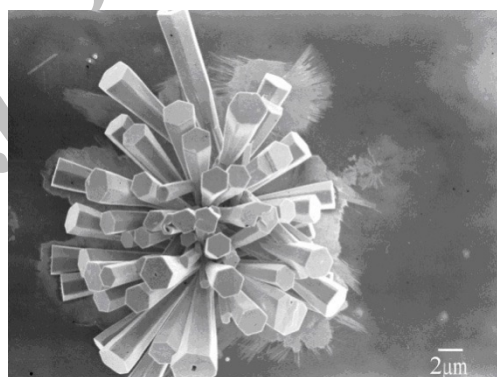


Fig. 2. SEM images of ZnO microstructures grown on bare silicon.

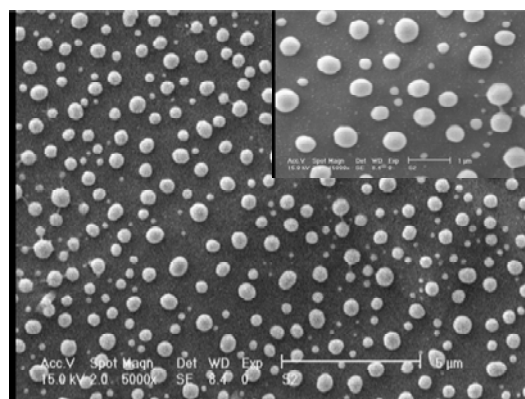


Fig. 3. SEM image of Au catalyst droplets on Si substrate after annealing.

The distribution and diameter of grown wires depend on the distribution, diameter and thickness of the Au catalyst islands formed during annealing of the

sample annealing. The thickness of the initial Au film has a major effect on the size distribution and density of Au particles. Thinner Au film results in a smaller average island size, narrower distribution and larger island density as compared to thicker ones. After annealing, the discontinuity in Au thin layer (≈ 10 nm) forms compressed islands which are nuclei of ZnO wires. When Au layer is thicker (>10 nm) the discontinuity disappears then the effect of Au nucleations for growth of ZnO wires decreases. Fig. 3. shows SEM image of the 10 nm Au layer after annealing at 600 °C for 1 hour. It can be observed that Au droplets are formed in hemispherical shape, while some of them are almost coalesced (connected with a bridge).

Fig. 1(b) shows the growth pattern of almost aligned nanowires with 10 nm Au catalyst, which are denser, thinner and normal to the surface compared to the samples with 20 nm Au layer (Fig. 4(a)) and 30 nm Au layer (Fig. 4(b)).

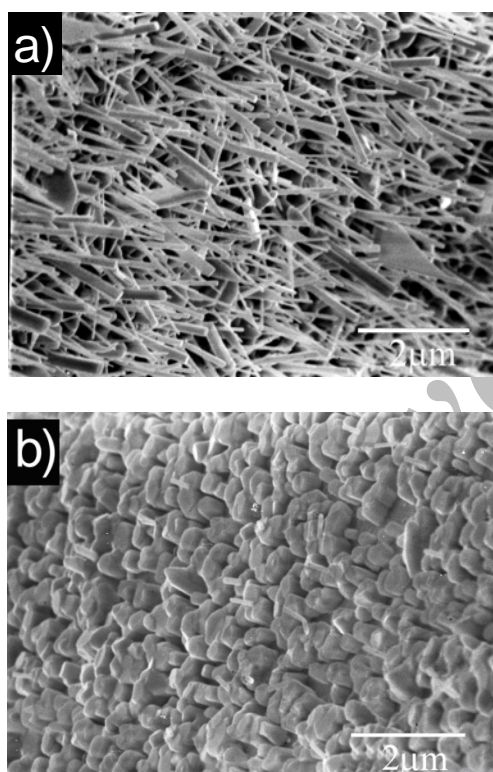


Fig. 4. SEM images of ZnO nanostructures with different Au thickness at 850 °C. a) $t = 20$ nm, b) $t = 30$ nm. Other conditions are held unchanged.

3.3. Effect of substrate surface roughness on growth of ZnO nanostructures

Fig. 1(b) shows regular and condensed nanostructures on rough silicon substrate which were coated with about 10 nm Au thin layer. Fig. 5 shows random ZnO nanostructures on smooth silicon substrate with the same Au thickness as that on rough silicon substrate surface. It has been shown that the roughness of the surface has a major role on nucleation and also on

the formation of regular nanostructures. As a result, the binding energy of ZnO atoms to the smooth surface is weaker than its value to the rough surface which have been coated by thin Au layer [20]. Fig. 5 does not show regular nanostructures on smooth surface of silicon. Their shapes are of different types such as nanowires, comb-like nanostructures and nanolayers.

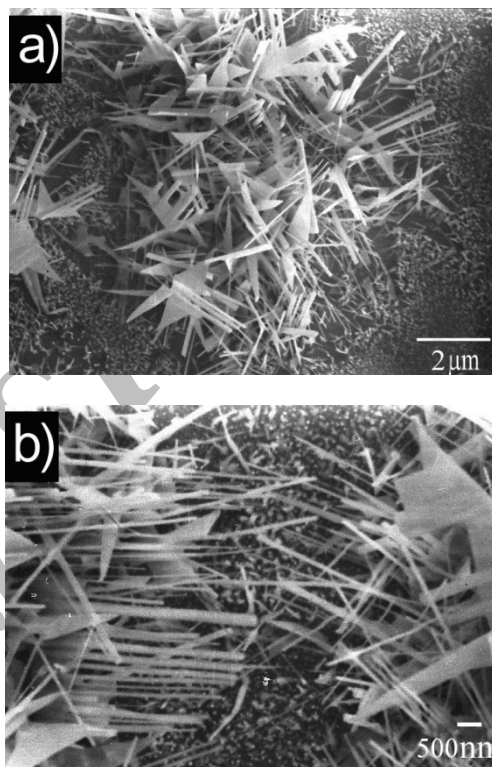


Fig. 5. SEM images of ZnO nanostructures grown on the smooth surface of silicon in 850 °C.

3.4. Crystalline structure of the nanowires

XRD measurements were made on the fabricated products to assess the structure and phase purity. The X-ray spectrum of the fabricated product is shown in Fig. 6. The investigations show that all the deposited materials on the silicon substrate are pure ZnO with the wurtzite structure. All of the diffraction peaks can be well-indexed to the ZnO wurtzite-type [hexagonal phase with calculated cell Parameters $a = 0.325$ nm and $c = 0.520$ nm, consistent with the standard values reported previously for bulk ZnO (PCPDF, Cardfile No.79-0206, wavelength = 1.78897 Å).

3.5. Growth mechanism

In the popular vapor transport method the ZnO nanowire growth usually takes place on silicon, sapphire, or nitride substrates coated with Au catalytic nanoparticles. In most cases, the vapor-liquid-solid (VLS) process is claimed as the growth mechanism [18].

Some studies have reported an alternate mechanism of aligned ZnO nanowires on the single-crystal Al_2O_3 covered with a layer of AlN followed by AlGaIn as the substrate with a solid catalyst particle during growth, called the vapor-solid-solid (VSS) mechanism [21]. Another mechanism which is proposed for growth of ZnO nanowires without any catalyst is vapor-solid (VS) process. Due to the role of Au droplets in growth, the VLS mechanism seldom leads to the formation of complex structures. In general, VS mechanism is dominant in the synthesis of many kind of ZnO architectures and hierarchical nanostructures such as nanoneedles, nanocombs and so forth [18].

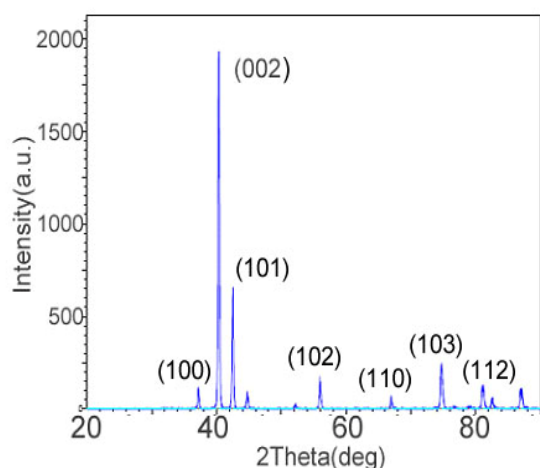


Fig. 6. The x-ray diffraction pattern of ZnO nanowires on silicon substrate.

Type of substrate, growth temperature, source material and use of catalyst are essential parameters in the determination of the reaction kinetics which lead to the formation of ZnO nanostructures. The state of the catalyst particles during growth is of vital importance since the existence of liquid metal droplets is a prerequisite for the VLS process to occur but it is not enough. It was found that at 500 °C the VS process plays a dominating role even when the liquid-phase catalytic nanoparticles are present. When VS mechanism becomes important Au particles merely provide a low energy interface to collect precursor materials [18]. The state of Au catalyst is substrate-dependent. Si from the substrate is necessary for the catalyst to liquefy [22]. In fact, melting of the gold requires a eutectic interaction. The Au-Si eutectic temperature, 366 °C, is below the growth temperature [23], and lower than either Au (1063 °C) or Si independently. Then this eutectic melts and forms the nucleation sites in low surface energy points, defects and disorders of the substrate surface. The effect of decreasing particle size which can also lower the melting temperature of Au particles at 700-950 °C, is negligible [21]. We have used Si as the substrate since VLS growth of ZnO nanowires relies on the eutectic formed at the interface between the Au catalyst and the Si substrate.

In the carbothermal evaporation process at high

temperature condition, Zn or Zn suboxides are produced by the following reactions [19]:



Zn and ZnO_x ($x < 1$) vapors diffuse into the catalyst particle until it becomes supersaturated. The growth species have similar bonding type of the liquid droplet. Then, these species more likely diffuse into the catalyst particle where Zn reacting with O atoms precipitate towards the substrate to form ZnO nanowires. In the other words, the nanowire growth results from the difference of sticking coefficients of liquid droplets and nanowires, namely, sticking coefficients of nanowires are orders of magnitude smaller than that of liquid droplets. As a result, the droplet and solid nanowire can capture and reject nearly all the constituents of the growing material from the vapor phase, respectively [24].

With attention to our experimental conditions for growth of nanowires including type of substrate, temperature range, type of source material which produce low Zn pressure, we believe that the role of the VLS mechanism is more than other mechanisms for synthesis.

In ZnO wire growth without catalyst, at the temperature range 750-800 °C (lower than 907 °C, i.e., the boiling point of Zn [19]) Zn vapor should condense on the minimum surface energy sites of Si substrate to form liquid droplets which are nuclei of ZnO wires. Yao et al believed that these liquid droplets are ideal nuclei of ZnO nanowires for the VLS reaction [19]. Other group [18] say that such a self-catalyzed growth resembles the VS process except the existence of liquid Zn droplets.

4. Conclusion

Different ZnO wires including nanowires and micro-wires were fabricated by a simple carbothermal evaporation method. The influence of deposition temperature, catalyst layer thickness and surface roughness of the substrate in the ZnO structures were studied. It was found that the convenient conditions for growth of vertical and almost aligned nanowires on a silicon substrate, are 100 sccm N_2 gas flow at approximately 850 °C with 10 nm Au catalyst layer. We showed maximum thickness of Au catalyst layer is 10nm, Although Most of researchers [25, 26] have used Au catalyst layer with thinner thickness (<10 nm) to produce these structures. Our experimental results showed that the VLS mechanism in comparison with other mechanisms is more dominant.

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