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Zinc Oxide Nanowires Synthesized using a Hot Tube Thermal Evaporation under Intermediate Heating Period

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ABSTRACT

Zinc oxide nanowires have been synthesized using a hot tube vacuum evaporation method. Essentially, ZnO powder and silicon substrate were placed in upper and lower streams of a horizontal quartz tube, respectively and heated via a furnace up to 960 °C for about 1 hour. During the heating process, evaporated ZnO vapour was transported to lower stream and deposited onto the substrate containing Au catalyst at constant pressure of 1 torr. The substrate tilt angles were chosen for 0° and 30° and argon flow rates between 1.1-5.0 sccm. Observation on FESEM/EDX and field emission results revealed the optimal growth of ZnO nanowires which occurred at an angle 30° and flow rate of 5 sccm. Parameters such as atom% of Zn and O and aspect ratio were measured and analysed.

| Hot-tube thermal evaporation | ZnO Nanowires | Vapour-liquid-solid mechanism |

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1. INTRODUCTION

ZnO is a semiconductor which possesses the characteristics of wide band gap of 3.37 eV, large exciton binding energy of 60 meV at room temperature, as well as high mechanical and thermal stabilities. In recent years, there has been increasing interest in ZnO nanostructures such as nanowires, nanorods, nanobelts and nanotubes due to their unique physical properties and potential applications in electronics, optics, photonics and sensing devices [1]. Various synthesizing methods of ZnO nanostructures were reported elsewhere [2-7], including thermal evaporation, CVDs and electro-deposition. The catalysts used in the thermal evaporation of ZnO nanostructure consisted of Au, Cu, Sn or other additives such as Ga and NiO [8-12] in order to assist and control the growth process. Additionally, a silicon substrate has an advantage over other choices due to its compatibility in the semiconductor integrated processing techniques. However, problem may arise in growing well-aligned ZnO nanowires on a Si substrate due to a rather large residual strain [13,14], developed when the large differences in the lattice constants and the thermal expansion characteristics between the ZnO nanowires and the Si occurs. This study is aimed at establishing the intermediate growth conditions for ZnO nanowire arrays on Si (100) substrates coated with Au catalyst, with a highlight on the substrate tilt angle and argon flow rate.

2. EXPERIMENTAL

Randomly oriented, catalytic growth of ZnO nanowire was fabricated by means of a hot tube thermal evaporation process in a horizontal-tube furnace reactor. Pure ZnO powders (purity 99.99%) were placed in an alumina boat and heated to 960 °C. The ZnO vapour was carried downstream by a 1.1 to 5.0 sccm Ar flow and condensed along the colder regions of the furnace tube where the Au-coated substrates were placed. Typical substrate tilt angles were set at 0° and 30°, with their temperatures expected to fall below 1000 °C. The Ar pressure was set to 10 mbar during growth and 0.1 bar during the temperature ramps, to provide pressure-based growth interruptions and avoid non-steady-state effects [15]. It is believed that the nanowires are generated directly from the vapour phase in the absence of a metal catalyst, and this process is often called vapour-solid (VS) growth. To generate the vapour phases of the source materials, vacuum conditions are sometimes needed. This is because some materials may not sublime in the normal atmosphere. An effective way to generate the vapour source materials in a normal atmosphere is to add additional materials to react with the source materials. For example, ZnO powder does not sublime in a normal atmosphere at 1000 °C. By adding carbon powder to react with the ZnO source, Zn or Zn-suboxide vapor phases can be easily generated at 1000 °C. Various forms of ZnO nanostructures grow in the low-temperature zone. In this case, vacuum conditions, carrying

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gases and catalysts are all unnecessary. Fig. 1 shows the experimental set up for synthesizing ZnO nanowires.

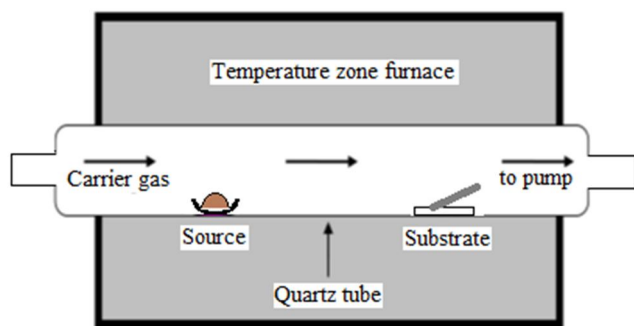
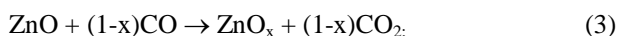


Fig. 1 Schematic of experimental setup

In the above experiment, Zn or Zn suboxide play a crucial role for the nucleation of ZnO nanostructures. This is because that at a high temperature condition ($T > 1100\text{ }^{\circ}\text{C}$), carbon reduced ZnO into Zn or Zn suboxides by the following reactions [15]:



In case of the sealed quartz tube the carbon powder might directly react with ZnO, whilst for the case of the open-end quartz tube carbon first react with oxygen to form CO. Zn and Zn suboxides have low melting temperatures (approximately $419\text{ }^{\circ}\text{C}$ for both Zn and ZnO_x , where $x < 1$) compared to that of ZnO ($1975\text{ }^{\circ}\text{C}$) and should be in vapour phases at $1100\text{ }^{\circ}\text{C}$. At the low temperature site, Zn vapour generated by reactions (2) and (3) will condense on the inner wall of the quartz tube forming liquid droplets, which are ideal catalysts for ZnO nanowire growth through the VLS mechanism. Carrying gases are not necessary for the formation of ZnO nanostructures. Temperature is the critical experimental parameter for the formation of different morphologies of ZnO nanostructures.

The addition of carbon during the reaction causes Zn vapour or droplets to partially oxidized and forming suboxides, which generally have low melting temperatures. This suboxides (ZnO_x) is formed because the amount of oxygen contributing to the reaction in the open-end quartz tube is limited. Such a condition is reasonable since Zn droplets co-exist with ZnO nanowire products in the early stage of the nanowire formation. Either Zn droplets or vaporized Zn suboxide droplets could be the nuclei for ZnO nanowires. Similar to the oxide-assisted growth mechanism Zn suboxides are more reactive than ZnO and may largely enhance the deposition of Zn oxides at the tips of ZnO nanowires during growth. Due to further oxidation of Zn or Zn suboxides, the concentration of oxygen in the droplets/tips increases, and thus ZnO deposits on the interface between the droplets and substrate, resulting in the growth ZnO nanowires.

The grown ZnO nanowires were characterized by a field emission scanning electron microscope (FESEM, JEOL JSM-6701F, Japan), combined with EDX for morphological and compositional analysis. Also, photoluminescence (LS55 Luminescence Spectrometer from Perkin Elmer) measurements performed using the 325 nm line of a He-Cd laser as the excitation source with a 350 nm filter to determine the field emission properties.

3. RESULTS & DISCUSSION

3.1 Structural Properties

3.1.1 Influence of Substrate Tilt Angle

In this study, substrate was placed at a fixed distance of 18 cm from the source and tilted 0° and 30° toward the horizontal. This make it different from the previous practice of placing substrate either above the source material [16] or next to the source material in the direction of carrier gas that makes zero degree (0°) with horizontal axis [17,18]. The effect of tilt angle on the structural properties of ZnO nanowires is discussed. Figs. 2 and 3 show the FESEM images of ZnO nanowires for the tilt angles of 0° and 30° , respectively. Generally, the nanowires appear to be randomly oriented with the aspect ratio of the former sample smaller (5.5) that that of latter one (7.7). However, in terms of density samples with tilt 0° has slightly higher value. Figs. 4 and 5 demonstrate the EDX spectra for both samples which comprised of a strong dominant peak of Si (substrate) and small peaks Zn and O (ZnO nanowires), as well as Au (catalyst).

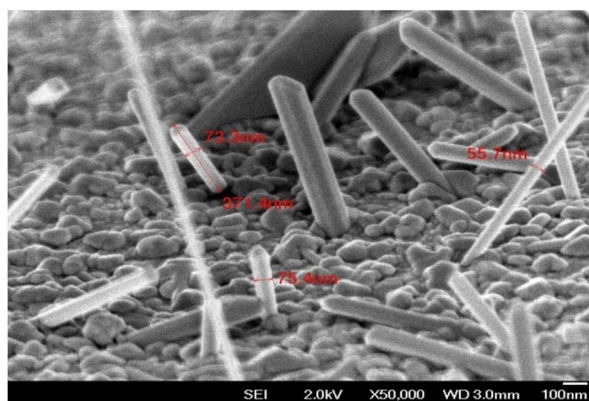


Fig. 2 FESEM images at angle 0°

Further analysis reveals the atomic percentage or amount of precursors (source atom) of the samples. Apparently, the atomic% of both Zn and O appears to be slightly changed, with the trend of reducing Zn and rich O content possibly due to more increased reaction at angle 30° . It may suggest that, chemical oxidation described in equations (2) and (3) is more likely to occur at this stage, thus producing more ZnO nanowires. is more actively Refer

to Table 1. Therefore, angle 30° was fixed for the preceding experiment.

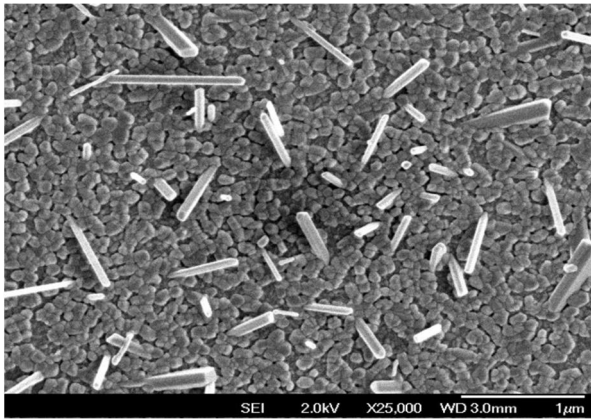


Fig. 3 FESEM images at angle 30°.

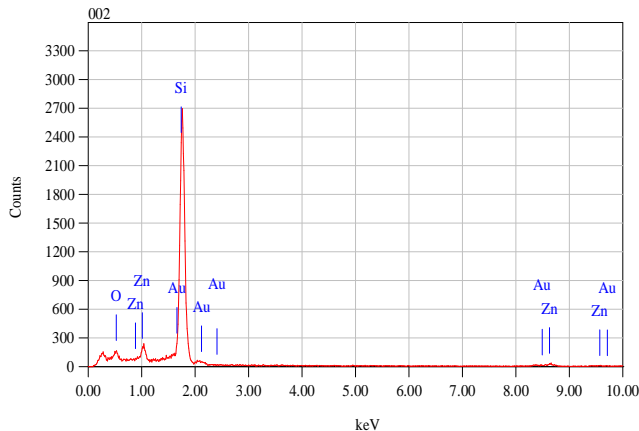


Fig. 4 EDX spectra at substrate tilt angle 0°.

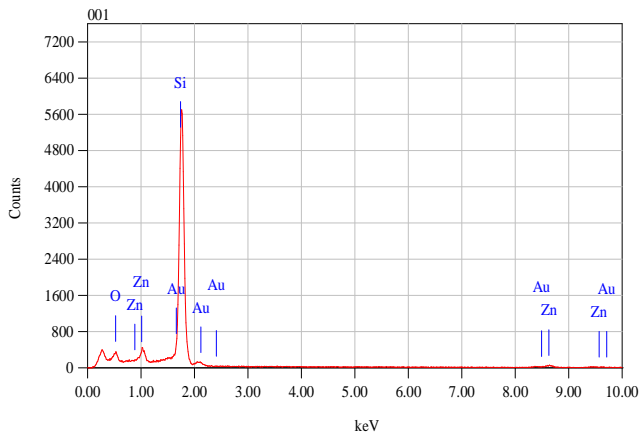


Fig. 5 EDX spectra at substrate tilt angle 30°

Table 1 Effect of substrate tilt angle

| Substrate angle, θ (°) | Zn (Atom%) | O (Atom%) | Aspect Ratio |
|-------------------------------|------------|-----------|--------------|
| 0 | 7.47 | 11.98 | 5.5 |
| 30 | 7.37 | 12.82 | 7.7 |

3.1.2 Influence of Flow Rate

The influence of argon flow rate is considered to be very significant in determining the nature of ZnO nanowires [19]. Essentially, three different concentrations; 1.1, 3.0 and 5.0 sccm were fixed, and the corresponding samples were analysed for each category. Other setting parameters were; tilt angle 30°, substrate-source distance 18 cm, furnace temperature 960 °C and heating duration 60 mins. Figs. 6, 7 and 8 show FESEM images which appear to be different in densities, sizes, and stability of the nanowires. This trend is in a good agreement with Meng et al. [19]. At flow rate 1.1sccm, the growth is limited to about 4 nanowires per area and average size of 83 nm (Fig. 6). Similar unstable nanowires are also observed in Fig. 7, but with increased density of 16 nanowires per area and size of 86 nm. A further increase of flow rate to 5 sccm results in more stable nanowires (Fig. 8), indicated by smooth background and high aspect ratio of 10.5. Analysis from EDX spectra are shown in Figs. 9, 10 and 11 which explain the possible growth mechanism of ZnO nanowires. Table 2 lists down the changes in atom% of the species involved, excluding the background contamination from Pt due to pre-cleaning procedures.

Table 2 Effect of argon gas flow rate

| Ar Flow Rate (sccm) | Zn (Atom%) | O (Atom%) | Aspect Ratio |
|---------------------|------------|-----------|--------------|
| 1.1 | 0.29 | 1.82 | 8.6 |
| 3.0 | 0.82 | 1.23 | 4.1 |
| 5.0 | 1.67 | 6.05 | 10.5 |

The above results indicate a significant influence of argon flow rate on the both atom% and aspect ratio. An increase of atom% is expected by the increased amount of precursor (ZnO vapour) transported onto the inclined substrate, thus allowing more oxidations at the tilted substrate to produce ZnO nanowires with improved densities and aspect ratios. Except for 3.0 sccm the discrepancy might be caused by the limited number of samples analysed at this stage. This result suggests a flow rate of 5.0 sccm and deposition time greater than 1 hour for producing better aspect ratio of ZnO nanowires.

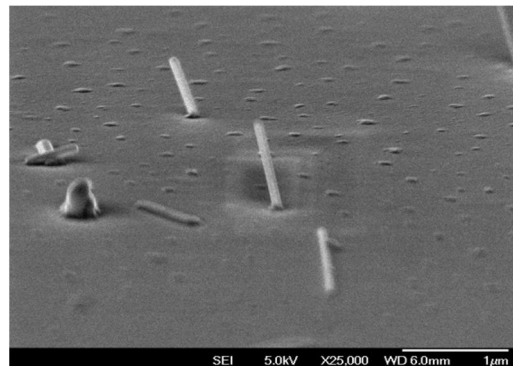


Fig. 6 FESEM images at flow rate of 1.1 sccm.

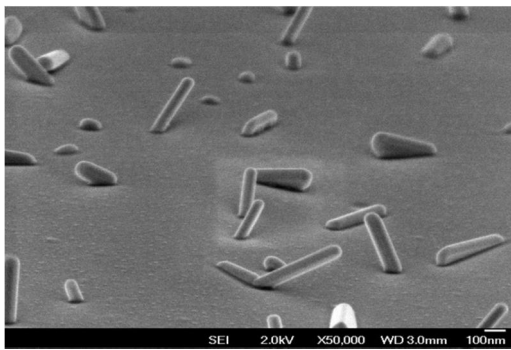


Fig. 7 FESEM images at flow rate of 3 sccm.

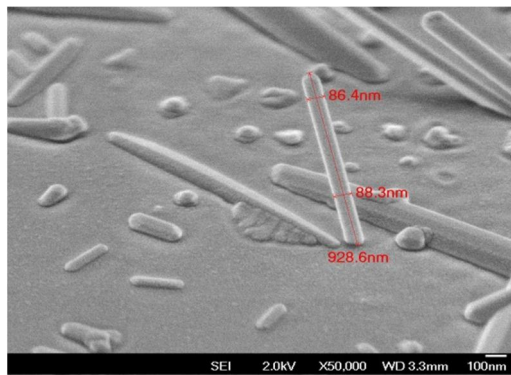


Fig. 8 FESEM images at flow rate of 5 sccm

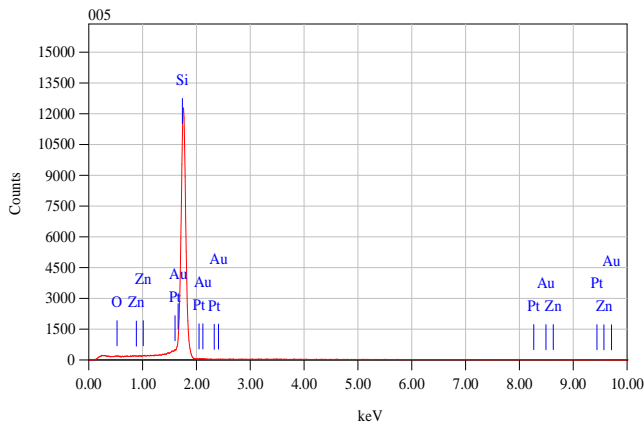


Fig. 9 EDX spectra at flow rate 3 sccm

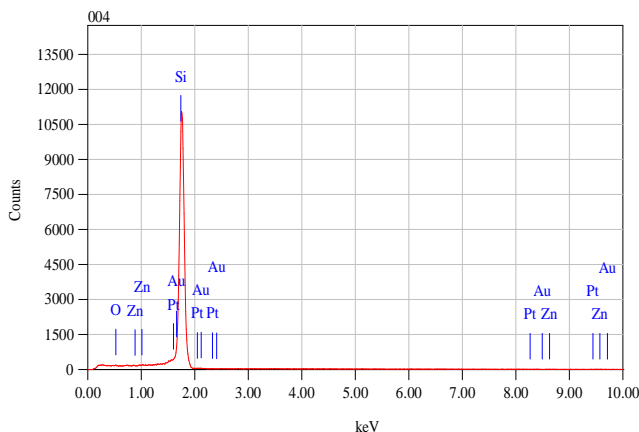


Figure 10 EDX spectra at flow rate 3 sccm

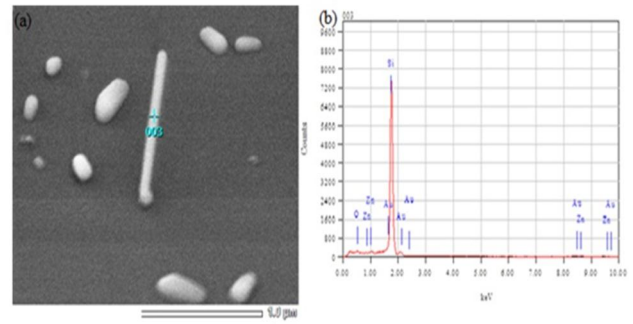


Fig. 11 EDX spectra at flow rate 5sccm, showing the measured position of ZnO nanowire

3.2 Field Emission Properties

3.2.1 Effect of Tilt Angle

The room temperature emission spectrum of ZnO nanowires shown in Fig.12 was obtained in the UV region and visible region (longer wave lengths of more than 400 nm for two samples). Samples A and B were placed inside the quartz tube at angles 0° and 30° , respectively. From the PL measurements sample A exhibits a broad emission from UV region to visible region and show two peaks at 375 and 430 nm (curve a). The peak emission at 375 nm ($E_g = 3.3$ eV) corresponds to the near band-band edge emission of ZnO [21] and the other peak at 430 nm ($E_g = 2.88$ eV) as evident for radiative recombination processes connected to defect or impurity present in the nanowires. In contrast, sample B exhibits a broad emission (blue emission) band extending approximately from 340 to 540 nm with a single peak at 440 nm (curve b). The peak represents a broad emission band of the nanowires in the visible spectral range $E_g = 2.81$ eV, and its origin is somewhat controversial. Nevertheless, there is increasing consensus that it arises from radiative recombination processes related to defects/impurity complexes [20].

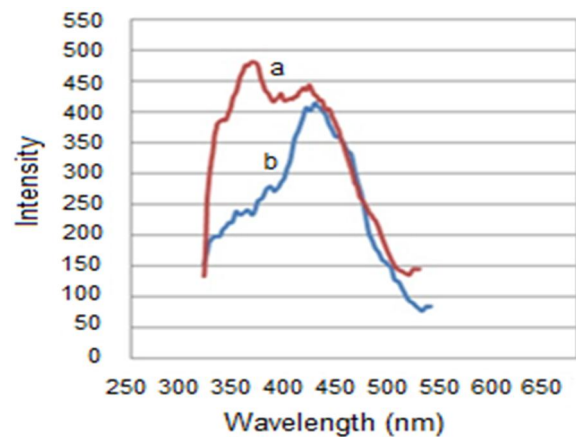


Fig. 12 Emission spectra at different substrate tilt angles: a) 0° and b) 30°

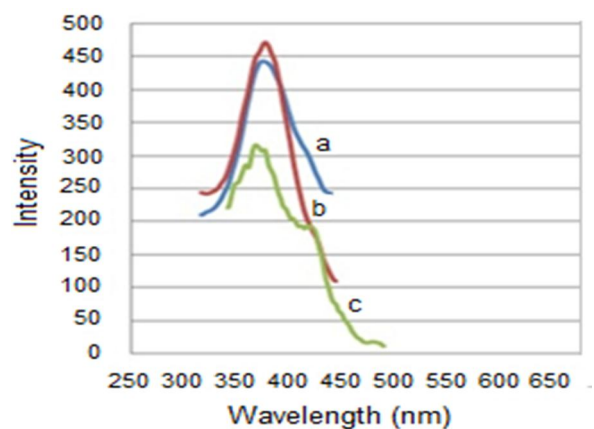


Fig. 13 Emission spectra at flow rates: (a) 1.1 sccm, (b) 3 sccm and (c) 5 sccm

3.2.2 Effect of Flow Rate

Field emission spectrums of the room temperature PL measurements were carried out to examine the effect of the flow rate on optical properties of ZnO nanowires and the results are shown in Fig.13. Three samples were synthesized at three different flow rates 1.1, 3, and 5 sccm and denoted a, b, and c, respectively. All three samples have the same ultraviolet emission peak at 374 nm ($E_g = 3.31$ eV) but with different intensities. The 374 nm emission is approximately corresponding to the recombination of free excitons between the conduction band and the valence band; this is called the near band-edge emission [20]. The band at the longer wave length could be attributed to the radial recombination of photon-generated holes with electrons belonging to the singly ionized oxygen vacancy in ZnO. The strong UV emission in the PL spectra indicates that they have good crystalline quality with disappearances of green emission [17]. Fig.14 shows the field emission spectra of an additional sample synthesized at 5 sccm flow rate and 90 min. growth time. The curve shows an ultraviolet emission peak shifting from 350 nm ($E_g = 3.54$ eV) to 380 nm, which may attribute to the presence of defect or impurity in the nanowires.

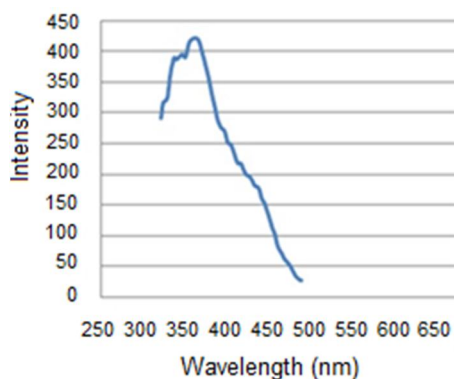


Fig. 14 Emission spectra at 5 sccm and longer growth time of 90 minutes

4. CONCLUSION

ZnO nanowires have been successfully grown on Si (100) substrate using a hot tube thermal evaporation under the optimal setting parameters of substrate tilt angle 30° and argon flow rate of 5 sccm. These resulted in ZnO nanowires with improved densities, sizes and most important was higher aspect ratio. Emission properties of nanowires: Peak at around 380 nm over the visible region, but could slightly shifted due to different processes and contaminations

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