Synthesis of Zinc Oxide Nanowires on Seeded and Unseeded Gold Substrates: Role of Seed Nucleation and Precursor Concentration

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Abstract: ZnO nanowires were synthesized on gold-coated glass substrates using the hydrothermal method. The effects of precursor concentration, substrate annealing and seeding on the morphology, dimension, and distribution of resultant nanowires were investigated. We found that the density of nanowires on substrates pre-seeded with ZnO nanoparticles is about two orders of magnitude greater than unseeded ones, while the dimension of ZnO nanowires for pre-seeded samples is much smaller than unseeded samples. In addition, we found that the fraction of substrate area covered by nanowires for unseeded samples is proportional to the precursor concentration, and proposed a simple nucleation model to explain this behavior. For pre-seeded substrates, ZnO nanowire density first increases with concentration and decreases as concentration exceeds 20 mM. We attribute this behavior to the competition for ions among the dense wires of varying length as well as the fusion of neighboring wires into larger ones.

Keywords: ZnO nanowires; Hydrothermal growth; Nanoparticle seeds; Nucleation process

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1. Introduction

In recent years, zinc oxide (ZnO) nanomaterials have attracted the interest of many researchers due to their thermal and mechanical toughness, high luminescence efficiency, chemical stability, lowered lasing threshold, and transparency to visible light [1,2]. These properties make them ideal for a variety of applications such as light-emitting diodes [3,4], gas sensors [5-7], photosensors [8], field effect transistors [9], solar cells [10,11], anti-bacteria and UV-blocking coating on fabrics [12,13], room-temperature polariton lasers [14] and nanowire lasers [15-17], high efficiency quantum well structures [18], and efficient optical nanowaveguides [19,20].

ZnO nanowires can be synthesized using different methods: gas phase synthesis, sol-gel based synthesis, and solution phase synthesis [2,21]. Several processes have been used regularly to synthesize ZnO nanowire structures, but the hydrothermal growth method is especially attractive due to its simplicity and moderate growth conditions [22,23]. Vertically aligned ZnO nanowires have been grown using this process on a variety of substrates [24-26]. However, there have been few studies providing a systematic, quantitative comparison of the resultant nanowires synthesized on substrates with different pre-growth treatment and varying precursor concentrations. In this study, we report the synthesis of ZnO nanowires on gold-coated glass substrates using the hydrothermal method and investigate how the morphology, distribution, and dimension of nanowires are affected by the precursor concentrations and the annealing and pre-seeding of the gold substrates with ZnO nanoparticles.

2. Materials and methods

2.1. Preparation of substrates

ZnO nanowires were synthesized using a hydrothermal growth process on glass cover slips pre-coated with a 10-nm-thick gold film (Phasis, Geneva). Two different methods of substrate preparation were explored. In the first approach, the unseeded method, the substrate is prepared by sonicating in acetone, methanol, isopropyl alcohol, and deionized water consecutively for 10 min each, and then baking in air at 350 °C for 30 minutes. For this unseeded method, substrate pre-heating at temperatures ranging from 150 °C to 350 °C is conducted to study its effect on subsequent nanowire synthesis.

In the second approach, the pre-seeded method, we adapted the procedure established by Greene et al. [23,24]. The substrates are wetted with one 5 μ L droplet of 1 mM zinc acetate dihydrate (99.999%, Sigma Aldrich)

in ethanol after the same cleaning and pre-baking procedures are carried out as explained in the unseeded approach. Upon the drying of the seeding solution droplet, the sample is immediately rinsed with an ample amount of ethanol and blown dry with nitrogen gas. The sample is then baked in an air oven at 350 °C for 30 minutes to thermally decompose zinc acetate into ZnO nanoparticle seeds [24]. The morphology and size of the ZnO nanoparticle seeds are examined using high resolution transmission electron microscopy (TEM).

2.2. Hydrothermal synthesis of ZnO nanowires

Zinc oxide nanowires are then synthesized in a hydrothermal growth environment [22,23]. The growth solution used is a 400-mL equimolar aqueous solution of zinc nitrate hydrate (99.999%, Sigma Aldrich) and hexamethylenetetramine (HMTA) (99.5%, Sigma Aldrich) at various concentrations. The samples are placed to float on the solution surface with the gold coating side facing down in a sealed PYREX wide mouth media storage bottle inside a Yamato DKN-402C oven maintained at 95 °C. The growth time is set to be three hours. Upon completion of the growth process, the samples are taken out, rinsed in deionized water and blown dry with nitrogen gas, and are examined using scanning electron microscopy (SEM), TEM, and x-ray diffraction (XRD) analysis.

3. Results and discussion

3.1. Effect of substrate annealing

To investigate the dependence of nanowire alignment and morphology on the pre-growth annealing temperature, gold-coated glass substrates were prepared without seeding and annealed at different temperatures ranging from 150 °C to 350 °C in air for 30 minutes each. Zinc oxide nanowires were subsequently grown on the substrates in a 1:1 ratio aqueous solution of 10 mM HMTA and 10 mM zinc nitrate maintained at 95 °C for three hours.

The corresponding SEM images of the nanowires grown after annealing the substrate at different temperatures are shown in Fig. 1(a) - 1(c). The SEM images clearly show that the annealing temperature has a direct impact on the alignment and morphology of ZnO nanowires. At the low annealing temperature of 150 °C, there is a large variation in the structures produced including tripods, clusters of wires, horizontal wires, and a small number of vertically aligned wires. As the annealing temperature increases to 200 °C, although the number of clusters and

tripod structures decreases, horizontal wires are still present and have much larger sizes than vertical ones. However, a further increase of the annealing temperature to 350°C leads to nearly all nanowires being vertically aligned on the substrate and the uniformity in nanowire dimensions also improves. The alignment of the nanowires was also checked with XRD analysis. A large ZnO (002) peak was observed indicating that ZnO nanowires are oriented along the c-axis (data not shown here).

Fig. 1. SEM images of ZnO nanowires grown on unseeded substrates annealed at three different temperatures: (a) 150 °C, (b) 200 °C, and (c) 350 °C. The corresponding gold substrates are shown in images (d)-(f), respectively. 25° tilted view for image (b) and 20° tilted view for image (c), and plan view for all other images. Scale bar for (a)-(c): 10 μ m. Scale bar for (d)-(f): 200 nm.

These results indicate that both the nanowire morphology and alignment may be affected by the morphology of the gold film, which has been shown to influence the nucleation dynamics during nanowire synthesis [26]. As shown in Fig. 1(d), the gold film is granular at the low annealing temperature of 150 °C and consists of gold particles of 10~20 nm in size with surfaces orientated in various directions. At higher annealing temperatures, the gold particles can migrate and fuse together to form a continuous film with consistent thickness across the substrate as shown in Fig. 1(e) and 1(f). Although some large gold ‘nano-islands’ are also formed due to annealing, the flat surface in each localized area is large enough for a single nanowire to start its nucleation process and grow vertically. This is consistent with earlier findings, which demonstrate that vertical nanowires can grow on any substrate as long as the surface is flat [24,25]. Our study has shown that an annealing temperature of 350°C is sufficient to produce vertically aligned nanowires on gold substrates with good uniformity in nanowire dimensions. Therefore, 350°C was used as the constant annealing temperature to prepare substrates for the other experiments in this study.

3.2. Morphology of nanowires

In order to study the effect of pre-seeded ZnO nanoparticles on the dimension and morphology of ZnO nanowires synthesized using the hydrothermal method, a substrate was seeded using a 5 µL droplet of 1 mM zinc acetate dihydrate as described above. The sample was then processed using the hydrothermal method in precursor solutions of various concentrations at 95 °C for three hours. A second substrate without the pre-seeding step also underwent the hydrothermal process with the same settings. Once the growth process was completed, the samples were removed from the surface of the solution, rinsed with deionized water, blown dry with nitrogen gas, and examined under SEM and TEM.

Some typical SEM images of nanowires grown on pre-seeded (left panel) and unseeded (right panel) substrates in various precursor concentrations are shown in Fig. 2. The pre-seeded samples yield very dense nanowires of cylindrical shape, while the unseeded samples produce nanowires of tapered shape and a significantly smaller density.

Fig. 2. SEM images of ZnO nanowires grown on pre-seeded (a-d) and unseeded (e-h) substrates (Scale bar: 5 μ m). The precursor solution is 1:1 ratio of equimolar HMTA and zinc nitrate at various concentrations: (a) and (e) 1 mM, (b) and (f) 10 mM, (c) and (g) 50 mM, (d) and (h) 100 mM. 15° tilted view for image (c), 25° tilted view for image (d) and (e), and 20° tilted view for all other images. Insets in (b)-(d) show close-up views of the corresponding samples.

We attribute the tapered shape for unseeded samples to the high growth temperature of 95°C, which leads to a large growth rate of individual nanowires in both the axial and lateral directions [25]. The general mechanism of the hydrothermal process of growing ZnO nanowires is described by the following chemical reactions [27]:

The hydrolysis of HMTA at higher temperatures is much quicker than at low temperatures and causes HMTA to get exhausted within 1-2 hours [28]. As a result, this would lead to a depletion of hydroxide ions within the local vicinity of nanowires. Zinc ions are also being exhausted at a higher rate within the bulk solution to form zinc hydroxide compounds. Since the diameters of the nanowires grown on the unseeded substrates are much larger than on the pre-seeded substrates (see Fig 4.), there is an insufficient supply of ions for the nanowires to maintain a constant lateral size as they grow longer. As a result, the nanowires acquire a tapered morphology for unseeded substrates in comparison to pre-seeded substrates. An interesting phenomenon is noticed when pre-seeded substrates are grown in precursor concentrations of less than 5 mM. For these pre-seeded substrates, we have found that while a large fraction of nanowires exhibit the typical characteristics of pre-seeded substrates grown in precursor solutions of high concentrations, some wires display the same morphology features as those on unseeded substrates. This result suggests that the nanoparticle seeds have an impact on the growth of nanowires only when the precursor concentration is above the threshold value of 5 mM.

We have also analyzed ZnO seed nanoparticles and the resultant nanowires grown from the hydrothermal process with TEM. The results are shown in Fig. 3. We found the sizes of these nanoparticle crystals are in the range of 5 to 10 nm, in agreement with previous studies [24]. The nanowires grown on both unseeded and pre-seeded substrates were confirmed by TEM to be single ZnO crystals with the lattice constant c to be 5.2 Å.

Fig. 3. High resolution TEM images of (a) ZnO seed nanoparticles and (b) ZnO nanowires grown using the hydrothermal process.

In order to make a quantitative comparison between unseeded and pre-seeded samples and gain insight about the different growth mechanisms, we have analyzed the diameter, length, and density of nanowires grown on both substrates as a function of precursor concentration. The results are detailed below.

3.3. Diameter of nanowires

By extracting the sizes of 100-200 wires from SEM images taken at several locations across each sample, we can plot the histogram distribution of nanowire diameter and also obtain the average diameter. Fig. 4(a) and 4 (b) show the size distribution of nanowires synthesized in a precursor concentration of 20 mM on unseeded and pre-

seeded substrates respectively. For the unseeded substrate, the diameters are measured at the middle section of tapered nanowires and fall within a range from 200 nm to 400 nm with an average value of 305 nm, while the diameters of nanowires for the pre-seeded substrate are much smaller and range from 20 nm to 50 nm with an average value of 37 nm.

Fig. 4. Diameter distribution of nanowires synthesized on (a) unseeded and (b) pre-seeded substrates in a precursor concentration of 20 mM.

The average nanowire diameters at different precursor concentrations can also be obtained and are shown in Fig. 5. We can see that the average nanowire diameters increase slowly with precursor concentration for both unseeded and pre-seeded substrates despite their large difference in values. For the unseeded substrates, the diameter

increases from 200 nm to 440 nm as the concentration increases from 1 mM to 100 mM. On the other hand, the diameter for the pre-seeded samples increases from 28 nm to 65 nm as the concentration increases from 5 mM to 100 mM. This diameter range for pre-seeded substrates is in line with results obtained by R. Shabannia et al. [29].

Fig. 5. Nanowire diameter versus concentration for (a) unseeded and (b) pre-seeded substrates. Open circles are data, and the solid lines are best fits to the data using a power-law function. The concentration varied from 1 mM to 100 mM for unseeded substrates and from 5 mM to 100 mM for pre-seeded substrates.

We found that the dependence of nanowire diameter on concentration for both substrates can be fitted using a power-law function and the relationships between diameter D (in nm) and concentration C (in mM) for unseeded and pre-seeded substrates are found to be $D = 196C^{0.155}$ and $D = 18.6C^{0.248}$ respectively. The proportionality

constants of 196 nm and 18.6 nm for the unseeded and pre-seeded substrates are not surprising and probably reflect the fact that the zinc oxide nuclei are formed during the different stages of growth. For the pre-seeded samples, the nuclei are zinc oxide nanoparticles formed by the thermal decomposition of zinc acetate during the pre-seeding step and their sizes are on the order of 5-10 nm as shown in Fig. 3(a). While for unseeded samples, the nucleation sites are formed during the early stage of growth where zinc ions get attached to the substrate and nucleate to form nucleation sites. As discussed in section 3.4, the density for unseeded substrates is much smaller than that of pre-seeded substrates, which in turn lead to much larger nanowires.

It is well known that after the nucleation stage, ZnO nanowires grow slowly in the lateral direction than in the axial direction [24,25]. While the exact mechanism behind this is still a subject of debate [30-32], it is generally believed that the seemingly higher surface energy of the polar c-plane in comparison to that of the nonpolar sidewalls of the nanowire can result in preferential axial growth [31]. In our studies, we found the nanowire diameter increases slowly with concentration for both pre-seeded substrates and unseeded substrates. However the rate of increase is different. For unseeded substrates, an increase in the supply of precursor ions due to the increase of concentration is responsible for both producing more nuclei as well as increasing the size of an increasing number of nanowires. While for pre-seeded substrates, because a zinc oxide seed layer has been deposited prior to growth, nucleation on the substrate is not necessary, therefore the additional supply of ions is used to increase the nanowire size only. As a result, the nanowire diameter for pre-seeded substrates is more likely to increase with concentration at a faster rate than unseeded substrates, as reflected by the larger exponent in the power law dependence on concentration.

3.4. Density of nanowire and coverage ratio

The dependence of nanowire density on precursor concentration is shown in Fig. 6. We can see that the density for unseeded substrates increases with concentration and the dependence can be fitted using a power law function: $0.041C^{0.54}$ wires/ μm^2 . However, the density for pre-seeded substrates has a very different behavior. It first increases with concentration in the low concentration range below 10 mM, then levels off at 20 mM, and starts to decrease as the concentration further increases.

Fig. 6. Nanowire density versus concentration for (a) unseeded and (b) pre-seeded substrates. Open circles are data, and the solid line in (a) is a best fit to the data using a power-law function, and the solid line in (b) is for guiding the eyes. The concentration ranges are the same as Fig. 5.

For unseeded substrates, the nanowire density is controlled by the number of nuclei formed during the nucleation stage. After the nucleation stage, arriving ions have a higher probability of further aiding the growth of nuclei on the substrate than forming new nuclei [25], thus not changing the nanowire density. To quantitatively understand the relationship between the nanowire density and the precursor concentration, we propose a simple model based on the conservation of Zn ions during the nucleation process. As nucleation can only occur through the migration of the Zn^{2+} attached to the gold surface [25], we hypothesize that ions within a cylinder of radius r and length l will contribute to the initial formation of one ZnO nucleus (see Fig. 7), where l is the length at which ions

can strongly attach to the surface instead of being reabsorbed into the bulk solution. From Fig. 7, the density ρ_n of the ZnO nuclei can be expressed as:

$$\rho_n = \frac{1}{4r^2}, \quad (2)$$

Fig. 7. A schematic of the nucleation process. Ions within a cylinder of radius r and length l will contribute to the initial formation of one ZnO nucleus.

By employing the conservation of Zn ions before and after the nucleation process, we then have:

$$C \cdot \pi r^2 l = \frac{\pi d_0^2}{4} L_0 \frac{\rho_{\text{ZnO}}}{M_{\text{ZnO}}}, \quad (3)$$

where C is concentration of the Zn ions, d_0 and L_0 are the diameter and length of the ZnO nucleus at the end of the nucleation process respectively, ρ_{ZnO} is the density of ZnO, and M_{ZnO} is the molar mass of ZnO. It is known that during the nucleation stage, the nucleus grow mainly in the lateral direction, we thus assume that L_0 is independent of the precursor concentration, and d_0 depends on the precursor concentration and is related to the final diameter d of the nanowire by:

$$d_0 = \frac{d}{\alpha}, \quad (4)$$

where α is some constant that is independent of precursor concentration. Combining Eqs. (2)-(4), we then obtain:

$$\frac{\pi d^2}{4} \rho_n = \frac{\pi \alpha^2 l}{4 L_0} \cdot \frac{M_{\text{ZnO}}}{\rho_{\text{ZnO}}} C. \quad (5)$$

The quantity on the left side of the equation can be interpreted as the ratio of the substrate area that is covered by the ZnO nanowires. Equation (5) indicates that the coverage ratio is proportional to the precursor concentration. This was indeed observed in our experimental results as shown in Fig. 8 supporting our simple model for the nucleation process.

Fig. 8. Coverage ratio versus concentration for unseeded substrates. Open circles are data, and the solid line is a best fit to the data using a linear function. The concentration ranges are the same as Fig. 5.

From the slope of the straight line, we can then obtain the value for length of the ZnO nuclei right after the nucleation process to be:

$$L_0 = 0.018\alpha^2 l. \quad (6)$$

If we estimate the value of α to be around 30 by taking a ratio of the final diameter of the ZnO nanowires (~300 nm for 20 mM concentration) to the initial diameter of the ZnO nuclei (~10 nm), and approximate the small length l to be the sum of the van der Waals radii of O and Au (around 0.5 nm), we arrive at a value of 8.1 nm for the length of ZnO nuclei, which is comparable to the diameter of the nuclei.

For pre-seeded samples, nucleation is not required, for this reason density almost only depends on the density of nanowire seeds on the substrate [33], as demonstrated by a constant density in the concentration range between 10 mM and 20 mM. However, as the diameter of nanowires increases with concentration, the distance

between neighboring wires decreases and the wires tend to fuse together to form a smaller number of larger nanowires. In addition, as the density further increases with precursor concentration, some nanowires can attain more ions than their neighbors, which would effectively suppress the growth of subsidiary nanowires, resulting in a seemingly lower density of nanowires.

3.5. Length of nanowire

The dependence of nanowire length on precursor concentration for both unseeded and pre-seeded substrates is shown in Fig. 9. It can be clearly seen that nanowires synthesized on unseeded substrates are usually 3-5 times longer than nanowires on pre-seeded substrates. For both pre-seeded and unseeded substrates, nanowire length displays a rapid increase in the low concentration range of less than 10 mM. As the concentration increases, the nanowire length starts to increase steadily at a slope of about 8.5 nm per 1 mM increase in concentration for both pre-seeded and unseeded substrates. This trend holds up until the highest concentration of 100 mM for unseeded substrates, while the length starts to increase rapidly again once the concentration surpasses 75 mM for pre-seeded samples.

Fig. 9. Nanowire length versus concentration for unseeded (open circles) and pre-seeded substrates (open squares). The solid lines are for guiding the eyes. The concentration ranges are the same as Fig. 5.

The drastic increase in nanowire length in the low concentration range can be attributed to two factors: the efficient use of precursor ions throughout the entire growth time of three hours due to a slow growth rate, and the

small nanowire diameters which require fewer ions for nanowires to grow longer. However as the nanowire size increases at concentrations above 20 mM, more ions will be needed for expanding the non-polar surfaces, and therefore fewer ions can be used for the axial growth. In addition, at higher concentrations, the reactions within the solution have sped up so much that both HMTA and Zn^{2+} are exhausted during late stages of the growth process resulting in a shortage of fresh ions both in the bulk solution and in the vicinity of nanowires. Finally, the quickening of the axial growth at concentrations above 75 mM for pre-seeded samples is observed. This is possibly because some nanowires grow so rapidly that the growth of neighboring wires gets suppressed due to their low accessibility to ions in the bulk solution. This is consistent with the observed decrease in nanowire density at higher concentrations for pre-seeded substrates as discussed above, and points to an inverse relationship between density and length for seeded substrates [34,35].

4. Conclusions

We have demonstrated the effect of substrate annealing and seeding on the morphology, dimension and distribution of ZnO nanowires synthesized in a hydrothermal environment at various precursor concentrations. Our results indicate that an annealing temperature of above 350°C is required to obtain vertically aligned nanowires on gold substrates with uniform morphology and dimension. We have found that ZnO nanowires are far denser and smaller on pre-seeded substrates than on unseeded substrates. Comparison of the nanowire diameters reveals that while the diameters of pre-seeded and unseeded substrates are drastically different as a result of nuclei formation at different stages, the diameter versus concentration follows a simple power-law function in both cases. However, the behavior of nanowire density versus concentration is very different for the two substrates. For unseeded substrates, it is described by a simple power-law function, while for pre-seeded substrates it is marked by an initial increase of density at low concentrations and a subsequent decrease for concentrations exceeding 20 mM. For unseeded samples, it was found that the fraction of substrate area covered by nanowires is proportional to the precursor concentration and a simple nucleation model was proposed to explain this behavior. Given the variety of applications ZnO nanowires have, the results we have obtained here may be useful in guiding the synthesis process to obtain nanowires of specific dimensions and densities.

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