Published in final edited form as:

J Alloys Compd. 2017 April 25; 702: 700–709. doi:10.1016/j.jallcom.2017.01.273.

Low-temperature hydrothermally grown 100 μm vertically well-aligned ultralong and ultradense ZnO nanorod arrays with improved PL property

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Abstract

The hydrothermal synthesis of ZnO nanorods (NRs) has been investigated using ammonium hydroxide and polyethyleneimine as additives to the conventional nitrate based synthesis route, to obtain thin-films of well-aligned, ultradense and ultralong nanostructures. ZnO NRs longer than 60 μm were obtained in a one-cycle growth run and rod lengths $\sim 100 \mu\text{m}$ by a two-cycle growth. The lengths of the rods were distributed uniformly across the substrate in all samples and highly dense NR arrays were observed. These conditions were obtained by a careful review of the nucleation and growth kinetics for this material system, such that the supersaturation of the solution was only relieved by precipitation on and in the presence of crystalline ZnO, and by the exploitation of a second growth phase due to the chelating behavior of PEI and the products of HMTA. Also, the growth behavior was correlated to the solution pH values. The structural and optical data were found to be supportive of the growth conditions. The photoluminescence (PL) spectra from as-grown ultralong ZnO NRs exhibited a strong broad (580–625 nm) visible emission peak. However, annealing in a forming gas atmosphere at 623K (350°C) revealed a PL spectrum with a significantly decreased visible emission and an increased near band gap UV emission at 379 nm. Thus, the mechanisms associated with ammonium hydroxide and PEI addition provide a simple route for synthesizing ultralong and dense arrays of ZnO NRs at low temperature i.e. 368K (95°C).

Keywords

ZnO; Nanorod Synthesis; Photoluminescence; Annealing

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1. Introduction

Nanostructures such as nanorods (NRs) or nanowires (NWs) are of great interest due to their potential device applications e.g., ultraviolet lasers [1], photodetectors [2], gas sensors [3], nanogenerators [4], solar cells [5], and more recently for radiation and X-ray detection [6]. For these applications precise control is needed over both the structure (rod length, diameter and crystallinity) in addition to highly efficient luminescence. ZnO is a promising nanomaterial with a direct bandgap of 3.37 eV at room temperature whose large exciton binding energy (60 meV) results in lower self-absorption making this material a very efficient emitter. Additionally, the non-centrosymmetric structure and large electrochemical coupling in ZnO lead to strong piezoelectric and pyroelectric effects. These properties make ZnO nanorod arrays of potential use in the above mentioned applications and consequently have promoted many studies on their growth optimization.

Many methods have been investigated for the growth of ZnO nanostructures: including metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition, chemical vapor transport, electrodeposition, radio-frequency magnetron sputtering, molecular beam epitaxy and hydrothermal synthesis [7–18]. Most of these methods only yield high quality ZnO nanostructures when single-crystal or conductive substrates and high growth/synthesis temperatures are used. Ultralong ZnO NRs, 85–100 μm in length have been synthesized by VLS, PVD and CVD, however, the extremely high synthesis temperatures (1190–1223K (917–950°C)), indispensable requirement for catalysts, and the resulting high defect densities, not only severely limit their application to particular substrates but also contribute to their high cost [19–21]. In contrast, hydrothermal synthesis has some superior properties over the above mentioned methods such as a low growth temperature (<623K (350°C)), use of simple equipment and less hazardous chemicals and the potential for scale up at low cost. Thus several studies have been reported on ultralong ZnO NRs synthesized by the hydrothermal method. For example: Ko *et al.* [22] reported using multiple growth steps to grow 40–50 μm long ZnO NR arrays from a single hydrothermal reaction process that only produced 2–8 μm long, vertically aligned ZnO NRs. Qiu *et al.* [23] prepared vertically aligned ZnO NR arrays ~40 μm long using several growth cycles of a PEI-assisted preheating hydrothermal method. While investigating seedless hydrothermal synthesis using an adequate content of ammonia in the nutrient solution, Tian *et al.* [24] obtained dense and ultralong ZnO NR arrays up to 22 μm long without refreshing the solution. Liu *et al.* [25] studied ultralong ZnO NRs using PEI as an additive combined with a step heating procedure to grow ultralong ZnO NRs ~30 μm long by refreshing the solution three times. Pradel *et al.* [26] successfully applied the hydrothermal method to grow antimony doped p-type ultralong well-aligned ZnO NR arrays up to 60 μm long. However, most of the studies regarding aligned and vertical ultralong ZnO nanowire growth are restricted to all or some of the limitations as a) use of expensive or high temperature required methods b) as long as 20–80 micron but not vertically aligned c) not vertically well-aligned d) not longer than a few micron e) not longer than 60 micron f) less dense. It should be noted that solution grown 100 μm ultralong vertically well-aligned NR arrays grown under low temperature hydrothermal method has not been reported yet. Thus, although vapour deposition and transport techniques produce high-quality well-aligned ZnO nanostructures, they generally require

high temperature, strict elaboration conditions and expensive equipment. The solution grown methods such as low temperature hydrothermal growth appear to be not only economical, user-friendly and ecological, but also good candidates for low-cost and large-scale industry production of ZnO nanowires&nanorods. However, several important parameters such as growth time, preheating time, zinc salt concentrations, and particularly the possible additive content (polyethylenimine (PEI) and/or ammonium hydroxide), and their effect on solution pH, etc, need further study. PEI has been identified as an important additive playing a role in reducing rod diameter and increasing rod length [5,25,27–29]. However, one study showed that PEI is of no benefit to the nucleation of ZnO [24]. The variability of these studies clearly confirms that in order to obtain optimum growth conditions, additional studies on the effect of additives on ZnO nanorod growth need to be performed; and in the context of a deeper understanding of the relevant nucleation and growth mechanisms,. Therefore in the present work, we first review the current understanding of NR nucleation and apply this understanding to develop, using PEI and ammonium hydroxide additions; simple and efficient hydrothermal synthesis protocols to obtain ultralong (up to 100 μm) and ultradense well-aligned ZnO NRs. The growth conditions have been studied as a function of growth time and pH values. The structural properties were characterized by SEM and the optical properties analyzed using photoluminescence (PL) spectra of the as-grown ZnO NRs. Moreover, annealing effects on the PL properties were also investigated.

2. Experimental section

ZnO NRs were grown on glass substrates for periods from 3 to 27 hours at an oven temperature of 368K (95°C). The glass substrates were prepared with a 100 nm thick sputtered ZnO seed layer. The primary precursors were zinc nitrate ($(\text{Zn}(\text{NO}_3)_2)$) and hexamethylenetetramine (HMTA: $\text{C}_6\text{H}_{12}\text{N}_4$) with polyethylenimine ($(\text{C}_2\text{H}_5\text{N})_n$ linear form) (800 M_w PEI) and ammonium hydroxide (NH_4OH) as additive chemicals in the solution. All the chemicals were analytical grade (Sigma-Aldrich). For time growth studies, a series of solutions were prepared in a 50 ml deionized water solution such that the molarities of the zinc nitrate, HMTA, PEI and ammonium hydroxide were 25 mM, 12.5 mM, 5 mM and 0.8 M, respectively. The first set of same solutions were prepared and kept in different jars in the same oven at a temperature of 368K (95°C). Then, the jars were taken out separately at time intervals of 3,6,9,12,18,21,24,27 hrs. For the second set of prepared solutions, the jars were taken out after 21, 22.5 and 24 hrs to confirm reproducibility and to obtain longer nanorods. The as-grown samples were thoroughly washed with DI water to remove any residual salt or amino complexes and were dried and kept at room temperature in air. The structure of the samples was characterized by SEM (LEO 1550 Thermally-Assisted Field Emission (TFE) Scanning Electron Microscope (SEM)) and the photoluminescence properties of the samples were excited by a He-Cd 325 nm UV laser and characterized using a PL spectrometer. The annealing studies were performed using a forming gas atmosphere (90% N_2 , 10% H_2) in an annealing furnace (Thermolyne 21100 Tube Furnace). pH values of the solutions just before and after growth were measured using a pH meter (Milwaukee, pH56).

3. Results and discussion

3.1. Kinetic of growth

Growth is driven by the minimization of the Gibbs free energy for the whole system. The dynamics of the growth process is similar to that for nanocrystal growth as depicted elsewhere [30]. It schematically illustrates the processes of nucleation and subsequent growth [30]. When the solute concentration increases as a function of time, nucleation does not occur (even above the equilibrium solubility) until the supersaturation reaches a critical value above the solubility. This value corresponds to the energy barrier that a nucleation process must overcome for the formation of nuclei. After the initial nucleation, the concentration (or supersaturation) of the growth species decreases and the Gibbs free energy is reduced. When the concentration drops below a critical concentration there is no further nucleation, but growth continues until the concentration of the growth species reaches the equilibrium concentration or solubility. A state of rapid nucleation promotes the formation of many small mono-sized particles (NRs), but ultimately the size distribution depends on the growth processes after nucleation.

3.2. Growth mechanism

The growth of ZnO NR by hydrothermal synthesis is represented in Fig. 1. In the most common and successful hydrothermal methods developed for ZnO nanostructure growth, zinc nitrate and HMTA were used as the primary sources of zinc (Zn^{+2}) and hydroxyl ions (OH^-), respectively. The basic chemical reactions that take place during growth are then:

Zinc ions are supplied through the dissolution of zinc nitrate in the solution (Eq. (1)). HMTA dissolves into formaldehyde (HCHO) and ammonia (NH_3) (Eq. (2)), and then the ammonia hydrolyzes into ammonium hydroxide to supply OH^- ions (Eq. (3)). The HMTA also acts as a buffer and maintains the continuous growth of ZnO since it slows down the release of OH^-

ions. In the final stages of growth Zn^{+2} complexes with OH^- to form several monomeric hydroxyl species, including $ZnOH^+(aq)$, $Zn(OH)_2(aq)$, $Zn(OH)_2(s)$, $Zn(OH)_3^-(aq)$ and $Zn(OH)_4^{2-}(aq)$ (Eqns. 4, 5) [24]. After dehydration of these hydroxyl groups, ZnO nucleation occurs (Eqns. 4, 5) and growth continues by the condensation of surface hydroxyl groups with the zinc hydroxyl complexes [31,32]. The reaction parameters such as concentration, growth temperature, growth time, surface pressure all affect the growth mechanism. Also, additives such as ammonium hydroxide and polyethyleneimine (PEI) can be used to control growth by coordinating to Zn^{+2} and maintaining a low concentration of free Zn^{+2} . Additionally, they coordinate to the ZnO crystal in different configurations, thereby hindering the growth of certain surfaces [30].

It is well known that ZnO has a polar hexagonal wurtzite structure consisting of the negative basal O^{2-} plane (000 $\bar{1}$), the positive top Zn^{+2} plane (0001) and the non-polar (10 $\bar{1}0$), (01 $\bar{1}0$) and (1 $\bar{1}00$) “side” planes (Fig. 2(a)). The positive (0001) plane has the highest surface energy and thus the intrinsic properties of ZnO result in the fastest growth rate along the c-axis [33]. This mechanism can be enhanced by tuning the solution properties. When the pH of the solution is made higher due to the OH^- ions released through the dissolution of ammonium hydroxide, the nonpolar side planes are forced to become negatively charged and this strongly attracts the negatively charged Zn-hydroxyl species to adsorb onto the top positive Zn^{+2} plane. Additionally, the positively charged PEI molecule, which is formed after protonation, adsorbs on the non-polar (10 $\bar{1}0$), (01 $\bar{1}0$) and (1 $\bar{1}00$) side planes, which as mentioned become negatively charged due to the high pH engineered in the solution [34]. Hence, growth is fastest along the c-axis and longer NRs will be obtained.

According to the kinetics of growth, it can be briefly mentioned that in uniaxial structures to minimize the surface energy over the whole volume of the structure, ions are most favorably absorbed on the highly energetic polar surfaces along the c-axis, and not on the side facets. The polar surfaces of the wurtzite structure alternate between Zn^{+2} and O^{2-} planes; thus polarity is always maintained during growth and the absorption on this face is continuous and promotes a one-dimensional structure with the maximum area of non-polar surfaces exposed (energy minimization) to the solution.

3.3. Effect of ammonium hydroxide, PEI and pH

In the present work, by adding ammonium hydroxide and PEI into the solution, vertically well-aligned, long and dense NR arrays were obtained. Also it was observed that there was negligible precipitation at the bottom of the reaction chamber in the presence of ammonium hydroxide and PEI. This is evidence of the higher coordination of ammonium hydroxide and PEI molecules to Zn^{+2} , which reduces the free Zn^{+2} ion concentration and controls the rate of Zn^{+2} ion generation. Also some of the Zn^{+2} ions formed by the dissolution of zinc nitrate can coordinate to PEI molecules by the chelating mechanism, thus further minimizing any precipitation and deposition at the bottom of the autoclave. This mechanism is described by equation (Eq. 6):

Other Zn^{+2} ions form hydroxyl complexes with OH^- ions, which are supplied by the high concentration of ammonium hydroxide in solution. (Note: $NH_4OH \rightarrow NH_3 + H_2O$) The ZnO NRs grow by the dehydration of these complexes along the c -axis in the presence of the positive surface (0001) of ZnO. Since the pH of the solution (11.30) is higher than the PZC of ZnO (the pH at which the ZnO surface has a net neutral charge in the growth solution; and its value has been reported to be between 8.7 and 9.7. [35,36]), a positively charged polar surface (0001) of ZnO and the presence of negatively charged growth species such as $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ lead to a fast growth rate along the (0001) direction [34]. Thus the Zn^{+2} ions, which are required for a hexagonal ZnO structure, were supplied slowly and consequently both defect formation and spontaneous precipitation in solution were reduced. Also, Francisco et al. has explained that growth is favored due to the preference space of the reacting species ($Zn(OH)_4^{2-}$), as illustrated in Fig. 2(b, c) [37]. This shows the structure for the face (0001), where the dots above the polyhedral structure correspond to OH surface groups. It has been noted that the growth process is facilitated by the tetrahedral structure of the species $Zn(OH)_4^{2-}$ which fits well with the planar structure of the (0001) polyhedral surface, this spatial resonance further increases the growth rate along this direction more than on any other face.

The hydroxyl ions in the initial solution are supplied by the high content of ammonium hydroxide, thus the pH value is high enough not only to promote growth, but also to initially inhibit the dissolution of HMTA. However, after a while HMTA slowly dissolves to form HCHO and NH_3 . Also, the NH_3 so formed decreases the dissolution rate of HMTA. Therefore, HCHO molecules are formed slowly. Kuanfei Liu et al. [25] concluded that the NH_2 groups of PEI react with the produced HCHO, thus freeing Zn^{+2} ions and they observed a color change in the solution due to this reaction. However, in our study no color change was observed which was attributed to the fact that the dissolution rate of HMTA was forced to be very low due to the excessive amount of ammonium hydroxide present in the solution. As a consequence, due to the low concentration of HMTA, the HCHO-PEI- NH_2 reaction was not fast enough to lead to a color change. Also, since the pH of the solution decreases with time compared to its initial value, the pH range (3–11) becomes available for protonization of PEI. Due to the protonization of PEI, which consists of a large amount of side amino groups, and is a non-polar polymer, the PEI molecule becomes positively charged (Eq. 7).

Because the solution pH is higher than the PZC of ZnO, the positively charged PEI molecules now prevent growth in the “radial” direction by adsorbing (due to electrostatic affinity) to the six negatively charged lateral planes of ZnO. This hindering mechanism additionally promotes a faster growth rate along the c -axis, and therefore longer NRs should be obtained, as observed in the present study.

However, if the concentration of ammonium hydroxide, and the corresponding solution pH value, becomes so high such that the dissolution of ZnO into hydroxyl groups is faster than the growth rate, then the length of the nanorods is expected to be shorter (not shown here). Or it could be due to the fact that a slow growth rate is observed due to the low degree of saturation (thus low free Zn^{+2}). Also, a high concentration of PEI will lead to the strong chelating of Zn^{+2} to PEI, this will lead to less free Zn^{+2} and suppress the formation of $\text{Zn}(\text{OH})_4^{-2}$ growth units [25]. Hence, shorter nanorods should be obtained. Therefore, optimization of the PEI as well as ammonium hydroxide contents is of vital importance to obtain ZnO nanorods with maximum length and aspect ratio. (We note that in a previous unpublished study we showed that the addition of excess NH_4OH greatly accelerated growth (Eqn. 3) but that uneven structural characteristics were obtained; which the presence of PEI is found to significantly improve)

3.3. Growth time dependence

The ZnO NR arrays were synthesized in a nutrient solution containing 25 mM $\text{Zn}(\text{NO}_3)_2$, 12.5 mM HMTA, 5 mM PEI and 0.8 M NH_4OH (total volume: 50 ml) for different periods and characterized by SEM for their morphology, length and diameter. The results of these studies are shown in Fig. 3. For 3, 6 and 9 h growth times the length of the NRs are around $15 \pm 0.4 \mu\text{m}$, $18 \pm 0.6 \mu\text{m}$ and $24 \pm 0.3 \mu\text{m}$ and the “diameters” lie in the ranges 100–120 nm, 140–180 nm and 150–200 nm, respectively. Thus, for these incubation times, an increase was observed not only in length, but also in the diameter of the NRs. We also found that for these times the tips of most of the NRs were tower-like structures. After 12 h and 18 h growths, the length of the NRs was constant ($\sim 30 \pm 0.4 \mu\text{m}$ for 12 h and $\sim 30 \pm 0.3 \mu\text{m}$ for 18 h) but the diameters increased to 300–500 nm and 400–800 nm, respectively; and the morphology of the NRs changed from tower-like to flat-top structures. After a 21 h growth, the length of the NRs increased to around $42 \pm 0.6 \mu\text{m}$ and their diameter to 500–900 nm. That is the length and the diameter of the NRs still increased during this time. However, for 24 h and 27 h growth periods the length of the NRs decreased to around $36 \pm 0.3 \mu\text{m}$ and $34 \pm 0.5 \mu\text{m}$, but the diameters continued to increase to 600–1200 nm and 500–1000 nm, respectively. The length of the NRs started to decrease for longer growth times from 24–27 h. According to the relationship established between length and growth time, additional synthesis were initiated at 21, 22.5 and 24 h to investigate if longer NRs could be obtained. The results showed that NRs $62 \pm 1.5 \mu\text{m}$ in length and 300–600 nm in diameter were obtained for a 22.5 h growth time. Also, a two-cycle growth was performed and for a total growth time of 45 h, resulting in NRs up to $100 \pm 1.5 \mu\text{m}$ long. The SEM images for these ultralong (and ultradense) NR arrays are shown in Fig. 4. We note that the increase in length for the second growth is smaller than for the first growth, although the diameter of the NRs is larger and in the range 800–1500 nm. This can be because during the second growth cycle the lateral growth was faster than the axial growth; or for the second growth, the NRs grow on top of the one cycle grown ZnO NRs, which are wider than the first ZnO seed layer. From the SEM images, it was clearly seen that the thin-film NR array is very uniformly distributed over the substrate for all the samples investigated.

To find an explanation for these results in terms of the models for nucleation and growth, we studied the length variation of ZnO NRs as a function of growth time over the whole

incubation period (Fig. 5) and made a comparison of the different growth regimes to more clearly identify the different growth mechanisms. In the first region (3–12 h), ZnO nuclei were formed on the ZnO seeded substrate through heterogeneous crystallization to initiate NR growth. The growth rate was $\sim 1.7 \mu\text{m/h}$. While the length, as well as the diameter, of the NR increased during this time, this was accompanied by a decrease in the pH of the solution from 11.30 to 10.56. This was attributed to the decomposition of HMTA which initially is slow due to the high concentration of ammonium hydroxide added into the solution. For the second region (12–18 h), the length of the NRs was observed to be constant (around $30 \mu\text{m}$) while their diameters continued to increase, during this phase the pH values decreased from 10.56 to 10.20. Thus, the lateral growth is faster than the axial growth in this region. For the third region (18–21 h), the axial growth of ZnO NRs became faster with a growth rate of $\sim 4 \mu\text{m/h}$ and also the diameter of the rods increased while the pH of the solution decreased from 10.20 to 10.08. For the fourth region between 21 and 27 h, the length of the rods decreased while the diameters first increased from 21 h to 24 h and then decreased in the time interval 24 to 27 h. The pH of the solutions decreased from 10.08 to 9.88. The decrease in diameter from 24 to 27 h is attributed to the depletion of the Zn precursor after 24 h due to the long incubation time while the decrease in length in this region is consistent with the erosion of formed ZnO NRs by excess OH^- ions in solution [38]. As seen in Fig. 6, the pH decreases at a faster rate over the range 0–18 h than in the range 18–27 h. The faster decreasing rate in the first range is attributed to the rapid decomposition of ammonium hydroxide and the lower rate at longer times to the slower decomposition of HMTA. This is a direct consequence of the suppression of HMTA decomposition by the high ammonium hydroxide content.

3.4. Optical properties and annealing effect

The ZnO samples usually exhibit two emission bands. One band, the band edge (UV) emission, is attributed to free exciton recombination and the second band to visible light emission, which is produced by transitions excited from optical centers or deep levels to the valance level [39]. The reason for the visible emission in ZnO is still unclear and has been attributed to different types of defect centers leading to green, yellow and red emissions. For example, the green emission centered at 560 nm has been attributed to an oxygen deficiency, while a broadband orange-red emission centered at 650 nm was attributed to excess (interstitial) oxygen [40–42]. In another study, a red emission at 652 nm and 640 nm was attributed to the presence of interstitial zinc [43,44]. Hsu et al. showed that as-grown NRs displayed a strong yellow-orange sub-bandgap emission (at $\sim 625 \text{ nm}$) that is different from the more widely observed green emission in oxygen-deficient ZnO [45]. The yellow emission was clearly shown to be due to interstitial oxygen defects [44,46,47]. Further, it was reported that the yellow emission was unaffected by surface modifications in contrast to the green emission [46] and the assignment of this emission to interstitial oxygen has been confirmed by the reduction of this emission after annealing in a reducing environment [46,48]. Green and yellow emissions in ZnO were also attributed to the presence of hydroxyl groups on the surface [49–52]. Enhancement of the UV emission due to water desorption has also been demonstrated [53].

As shown in Figure 8 in this study for growth times of 21, 22.5, 24 and 45 h, a very broad yellow-orange emission band extending from 580 nm to ~750 nm and centered at ~625 nm was observed in all as-grown samples that was replaced by a red emission band centered at ~650 nm after annealing (Fig. 8). The intensity of this yellow-orange emission was dramatically reduced in all cases by factors between 10 and 5 after annealing at a temperature of 623K (350°C) in forming gas and accompanied by the emergence of a strong and very narrow (~16.6 nm) near band gap intrinsic emission at 379–381 nm. A similar trend was reported in a previous study [54]. Also Sui et al, have shown that the desorption rate of hydroxyl groups peaks at 423K (150°C) [51], and this is expected to lead to a reduction in the yellow defect emission intensity after annealing at temperatures >423K (150°C). Additionally, the association between the yellow defect emission and desorption of hydroxyl groups has been confirmed by Zhou et al. [49], Norberg and Gamelin [50] and Tam et al. [54].

The large decrease in intensity, red shift and remaining presence of the long wavelength part of the defect emission band at 650 nm is therefore consistent with the presence of interstitial oxygen that is expected from the fact that these samples were synthesized from solutions with very high pH values that lead to the presence of surface hydroxyl groups and/or interstitial oxygen (O_i). The spectral signatures associated with these two defects produce the broadband emission centered at 625 nm (the orange-yellow emission band). The implied reduction in the interstitial oxygen concentration results in greater crystal perfection which is consistent with the increase observed in the intrinsic emission intensity of ZnO at ~379 nm. Thus, the interpretation of the annealing data is well explained by the fact that annealing above 423K (150°C) in forming gas causes the rapid desorption of surface hydroxyl groups whose primary emission is centered at 625 nm and the reduced concentration of interstitial oxygen whose signature emission is centered at ~650 nm. This behavior and identification of the yellow-orange emission with adsorbed surface hydroxyl is also consistent with the fact that since the solution pH is $\gg$ PZC, the negative hydroxyl species ($Zn(OH)_4^{2-}$) will adsorb on the positively charged (0001) polar surface of ZnO. Also, since the reaction described by Eq. (4) is more likely than that described by Eq. (5), there will be more hydroxyl ions at the surface (Fig. 2(b, c)). Additionally, the defect peaks observed for 24 and 27 hours growth are more intense than at growth times of 21 and 22.5 hours. As shown in Eq. (4), at 21 and 22.5 hours, ZnO growth occurs by dehydration of hydroxyl species and hydroxyl ions are formed subsequently. However, at 24 hours growth the reaction takes place reversely in Eq. (4) as the OH^- ions in the solution dissolve the as-grown ZnO structures and more hydroxyl ions are released. Therefore, the defect emission bands observed after 21, 22.5 and 24 hours growth can be attributed to the hydroxyl groups. As shown by Fig. 8, after the annealing treatment, there is a significant increase in the UV emission and a corresponding decrease in the visible emission intensity in addition to a red shift. The decrease in visible emission originates from desorption of surface hydroxyl groups after the 623K (350°C) anneal, and the increase in UV emission to the fact that annealing was performed in a reducing atmosphere. (Anecdotally, we note that a H_2 anneal can also introduce shallow donor states, resulting in an increased electron density and shift in the Fermi level position, which in turn can change the occupation of deep levels and affect the branching ratio between exciton and defect recombination [55])

The annealing study confirms that there are still defects present in the structure after the current treatment and suggests that further optimization can be beneficial. The longest ZnO NRs, 62 μm long, grown in a 22.5 h long single cycle growth were found to exhibit one of the highest UV peak emission intensities and the narrowest FWHM (FWHMs: 21h-17.09 nm, 22.5h-16.46 nm, 24h-16.51 nm, 45h-16.87 nm). The PL data for two-cycle growths also showed similar behavior; a significantly decreased and red shifted impurity band but a weaker UV emission peak than the other samples, suggesting that maybe a modified annealing treatment could be beneficial.

4. Summary and Conclusions

Thin-film arrays of vertically well-aligned ultradense and ultralong ZnO NRs up to 62 μm and 100 μm long have been obtained in the present study using one- and two-cycle growths, respectively at low temperature i.e. 368K (95°C). In the present study a simple route based on hydrothermal method has been presented from an understanding of the growth mechanisms associated with ammonium hydroxide and PEI additions for synthesizing ultradense and ultralong ZnO NRs. The behavior of the growth rate with synthesis time has been explained by consideration of the kinetic and chemical reactions occurring in solution. This behavior is divided into four regimes. In region I nucleation and growth occurs by Zn^{+2} ions freed by the dissolution of zinc nitrate and the decomposition of the excess ammonia hydroxide to form OH^- . In parallel the decomposition of HMTA (the reactions described by Eqns. 2 and 3) is slowed by the excess ammonia added to the solution, but the chelating of Zn^{+2} ions continues due to the presence of HCHO, and the added PEI, resulting in a large concentration of associated Zn^{+2} ions that are temporary removed from the growth process. In region II, growth is slowed almost to zero because of the depletion of Zn^{2+} ions in solution, both due to NR growth and by the continued chelating of Zn by the products of HMTA and PEI that occurs throughout Region 1. In region III these processes are abruptly reversed when the OH^- ion concentration increases to a level such that a non-equilibrium condition drives a large release of Zn^{2+} ions into solution thereby promoting a very rapid growth rate. The very high deposition rate on both the c-plane and the side planes of ZnO (note: both the length and diameter are observed to increase) returns the solution conditions to very low nutrient concentrations and therefore a near zero growth rate (Region IV) as indicated by the data at 27 h. Under these conditions the growth reaction (Eqn. 5) can be reversed leading to tapered, or cone-like tips to the nanorods. This can also occur at the end of region II. The increase in diameter also strongly suggests that PEI molecules attach to side planes (and which in region I have limited the lateral growth rate) are stripped off before Region II in order to maintain solution equilibrium. Thus, under these conditions there is a two-stage growth mechanism.

The photoluminescence (PL) spectra of as-grown ultralong ZnO NRs showed a strong broad orange-yellow emission band (580–725 nm) and also support the growth properties as the fast growth region exhibits a smaller PL signal; that is attributed to a higher defect density resulting from the faster growth rate. However, annealing these ZnO NR structures in a forming gas atmosphere at 623K (350°C) revealed a PL spectrum with a significantly decreased visible emission band (>80%) and an increased UV emission. The strong visible emission features resulting from the high pH of the growth solution are attributed to the

presence of both absorbed surface hydroxyl groups and interstitial oxygen, where we attribute the shorter wavelength region centered at 625 nm to absorbed hydroxyl groups and the longer wavelength band centered at 650 nm to the interstitial oxygen concentration remaining after the anneal.

Further studies on optimization of the seed layer, additives and temperature, are expected to result in longer NRs in a one-cycle growth and for shorter synthesis times. Also, further optimization of the annealing process should result in higher quality crystal structures so as to further reduce visible (defect associated) emissions.

Acknowledgments

We sincerely thank Prof. Z. L. Wang, Georgia Institute of Technology for his advice and encouragement during the course of this project. Sinem V. Kurudirek would like to thank TUBITAK for financial support through grant number 1059B141300554. This work was supported in part by NIH through contract number 9 R44 EB 017606 – 01.

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- Preliminary results on solution grown 100 μm vertically well-aligned ultralong and ultradense ZnO nanorod arrays
- A simple route associated with ammonium hydroxide and PEI additions for synthesizing ultradense and ultralong ZnO NRs
- Annealing in a forming gas atmosphere revealed a PL spectrum with a significantly increased near band gap UV emission at 379 nm

Fig. 1.
Schematic representation of ZnO NR synthesis

Fig. 2.

(a) Schematic view of the planes of ZnO hexagonal structure. The active polar planes for fast growth are (0001) and $(000\bar{1})$. The non-polar planes $(10\bar{1}0)$, $(01\bar{1}0)$ and $(1\bar{1}00)$ become negatively charged due to the high pH of the solution. (b),(c) Growth process of ZnO nanorods in the direction $[0001]$. The growth process is facilitated by the tetrahedral structure of the species Zn(OH)_4^{2-} which fits well with the (0001) surface polyhedra, this phenomenon (spatial resonance) increases the growth in this direction more than on other faces [36].

Fig. 3. SEM characterization of growth time dependence of ZnO NRs (3, 6, 9, 12, 18, 21, 24, and 27 h). Note that although the formation, or nucleation, of nanorods is shown to be reasonably high for periods up to 12 h, there is a significant increase in the areal density of NRs for longer growth times. The side-view SEMs show well formed, well spaced, vertically aligned NWs with excellent length uniformity and very good morphology.

Fig. 4. SEM characterization of growth time dependence of ZnO NRs (21, 22.5, 24 and 45 h). Note that the top-view SEMs show well formed hexagonal cross-sections and are well spaced and vertically aligned.

Fig. 5.

Variation of NR length with growth time. The plot is divided into four regimes. In region I nucleation and growth occurs by Zn ions from the dissolution of zinc nitrate and the decomposition of the excess ammonia hydroxide to form OH^- ions. In parallel the decomposition of HMTA (the reactions described by Eqns. 2 and 3) are slowed by the excess ammonia added to the solution but chelating of Zn^{+2} ions continues due to the HCHO and the added PEI resulting in a large concentration of associated Zn^{+2} ions that are temporary removed from the growth process. In region II, growth is slowed almost to zero because of the depletion of Zn^{+2} by the continued chelating of Zn by the products of HMTA and PEI that occurs throughout region 1: essentially all active Zn^{+2} ions are removed from solution. In region III these processes are reversed when the continued production of OH^- ions builds to a concentration that triggers an abrupt release of a large amount of Zn^{+2} into solution, thus promoting a very rapid growth rate. The very high deposition rate on both the c-plane and the side planes of ZnO (note both the length and diameter increase) returns the solution conditions to very low nutrient concentrations and therefore a near zero growth rate (Region IV) as indicated by the data at 27 h. Under these conditions the growth reaction (Eqn. 5) can be reversed leading to tapered, or cone-like tips to the nanorods. This can also occur at the end of region II.

Fig. 6.

Variation of the solution pH with growth time. The curve is fitted to demonstrate the change in the decreasing rate of pH as its value approaches the ZPC value of ZnO.

Fig. 7.

Dependence of normalized (Gaussian fitted) PL spectra on growth time for periods between 3 and 27 hours. PL spectra excited by a 325 nm laser. The broad emission peak is centered at 590 nm and progressively increases in intensity for low growth times to reach a peak intensity between 21–25 h, before decreasing at longer growth times.

Fig. 8.
The PL spectra of as-grown and annealed samples for 21, 22.5, 24 and 45 h growth times