

Growth of Single Crystalline ZnO Nanotubes and Nanosquids

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ABSTRACT

The growth of ZnO nanotubes and nanosquids is obtained by conventional thermal chemical vapor deposition (CVD) without the use of catalysts or templates. Characterization of these ZnO nanostructures was conducted by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), Raman spectroscopy, and photoluminescence (PL). Results indicate that these ZnO nanostructures maintain the crystalline structures of the bulk wurtzite ZnO crystals. Our results show that rapid cooling can be used to induce the formation of ZnO nanotubes and ZnO nanosquids. The self-assembly of these novel ZnO nanostructures are guided by the theory of nucleation and the vapor-solid crystal growth mechanism.

INTRODUCTION

ZnO is a useful direct band gap (3.37 eV) semiconductor for short-wavelength optoelectronic devices such as laser diodes and light emitting diodes. ZnO has a high exciton binding energy (60 meV) which makes it useful for room temperature optoelectronic devices. ZnO is also a piezoelectric material due to its non-centrosymmetric structure. ZnO nanostructures have been synthesized in various morphologies such as nanowires [1], nanorods [2], nanobelts [3], nanocombs [4], nanonails [5], nanocastles [6], etc. Various kinds of ZnO nanostructures have been used in different electronic [7, 8], optics [2], mechanical [9], and piezoelectric [10] devices.

In this proceeding, we will discuss about the growth of ZnO Nanotubes (ZnO NTs) [11] and Nanosquids (ZnO NSqs) by using thermal chemical vapor deposition (CVD). ZnO Nanosquids are a new type of ZnO nanostructures. These novel nanostructures contain multiple ZnO nanowires branching out from a ZnO nanotube or a ZnO Nanorod. From the structure of these ZnO Nanosquids, we speculate that they can be useful for future multiplexing devices.

EXPERIMENT

The synthesis of ZnO nanotubes and Nanosquids was conducted in a double quartz tube horizontal furnace. This furnace has one large quartz tube which acts as the vacuum chamber. Another smaller quartz tube is closed at one end, 60 cm long and 2 cm in diameter. The precursor materials for the growth of ZnO nanotubes and ZnO nanosquids were placed in a boron nitride boat and inserted to the closed-end of the small quartz tube. These precursors are a mixture of ZnO (0.2 g) and graphite (0.1 g) powders. A series of oxidized silicon substrates (1 to 4) were then placed downstream from the mixture in the small quartz tube as shown in Figure 1. The smaller quartz tube is inserted into the vacuum chamber such that the closed end is at the center of the vacuum chamber. When furnace temperature is around 350 °C, oxygen gas was introduced into the chamber at a flow rate of 40 sccm. The temperature of the vacuum chamber was held constant at 1100 °C for 30 minutes for the formation of ZnO nanorods. The power of the furnace was then switched off and cooled to 600 to 700 °C in about 30 mins. The

experiments were usually terminated by cooling the furnace to room temperature by opening the heating panel of the furnace. The as grown samples were then analyzed by using scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Raman spectroscopy and photoluminescence (PL) spectroscopy.

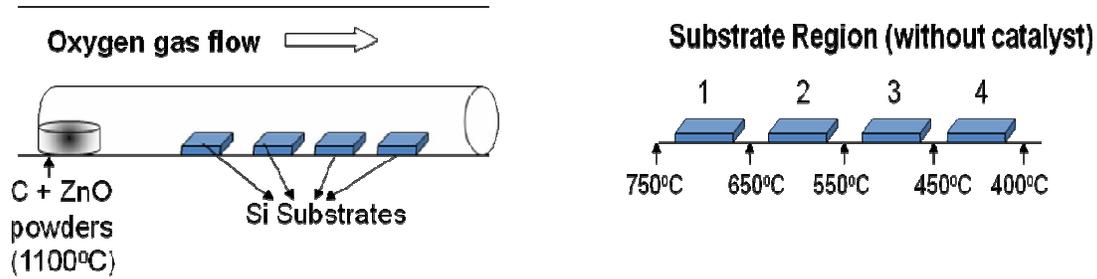


Figure 1. Schematic experimental setup for the growth of ZnO nanotubes and nanosquids.

DISCUSSION

The growth mechanism of these ZnO nanotubes and nanosquids are related and can be explained by the theory of nucleation and the vapor-solid crystal growth mechanism [11]. The heating of ZnO and graphite powders to a high temperature produces volatile Zn vapors in a reduction process. These vapors react with oxygen in the growth chamber and condense as ZnO growth species at lower temperature regions, i.e., on the silicon substrates placed downstream. Under the catalyst-free growth condition, results indicate that these growth vapors will preferentially condense as ZnO nanorods.

According to theory of nucleation, growth species prefer to condense on locations with maximum binding energy $E = \beta (q^2/a)$ [12]. Therefore for a growth surface with a step as shown in Figure 2, growth species prefers to condense at sites in the following descending order: 6, 5, 1, 4, 2, 3. This preference is because $\beta_6 > \beta_5 > \beta_1 > \beta_4 > \beta_2 > \beta_3$, where β is a numerical factor which is related to the binding energy. Here, a is the lattice spacing and q is the charge of the ionic species. For an atomically flat surface, only sites 1, 2 and 3 sites are available for the nucleation of new growth species.

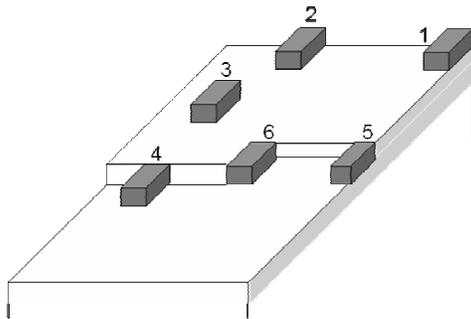


Figure 2. Nucleation sites on a flat surface with a step

On the other hand, the theory of nucleation also suggests that the probability of nucleation P_N will increase with the growth temperatures (T) since $P_N = A \exp [-\pi\sigma^2 / (k^2T^2 \ln \alpha)]$, where A is a constant, σ is the surface energy, $\alpha - 1$ is the supersaturation, $\alpha = p/p_o$, p is the pressure of vapor, p_o is the equilibrium vapor pressure of the condensed phase at that

temperature, k is the Boltzmann constant, and T is the temperature in Kelvin [13]. Thus nucleation and formation of a 2D surface will be suppressed when the growth temperature is reduced. In addition, it is well known that ZnO nanowires and nanorods are formed due to the relatively high growth rate along the c -axis [1]. Thus cooling process in our experiments will confine the nucleation of ZnO growth species at the edges of the already grown c -plane of ZnO nanorods as shown in Figure 3(a). Since 2D nucleation is suppressed and the growth rate along the c -axis is relatively faster, our cooling process will lead to the confined growth at the edges of the ZnO nanorods and initiate the growth of ZnO nanotubes as shown in Figure 3(b). Detailed characterization (XRD, PL etc.) of these single crystalline ZnO nanotubes has been reported elsewhere [11].

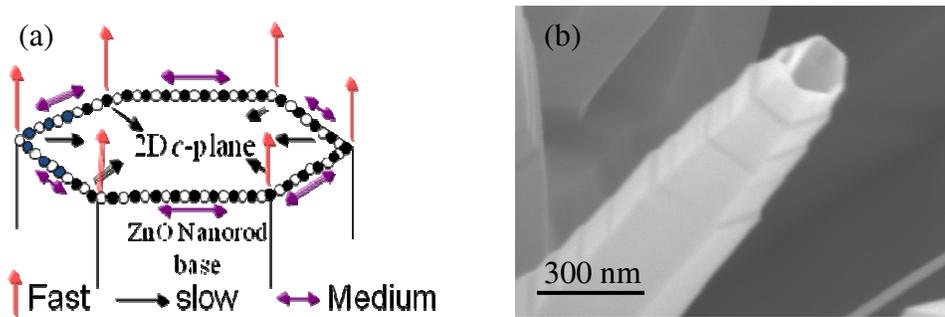


Figure 3. (a) Preferential condensation of growth species at the edges of the c -plane of a ZnO nanorod. (b) SEM image of a ZnO nanotube.

The growth of ZnO nanosquids was sometime detected from samples grown by the same procedure. In our approach, system cooling was done by switching off the power supply to the furnace. This process lacks precise control and therefore is probable to create fluctuations in the cooling rates and growth condition. These fluctuations can cause formation of steps or vacancies. Because of the formation of these defects, nucleation and subsequent growth will preferentially take place at these sites due to their higher β factor as discussed in Figure 2.

The first type of ZnO nanosquids was formed when steps were formed on the c -surfaces of the ZnO nanorods as shown in Figure 4(a). These nuclei will continue to grow into nanowires and results in the formation of ZnO nanosquids as shown in Figure 4(b).

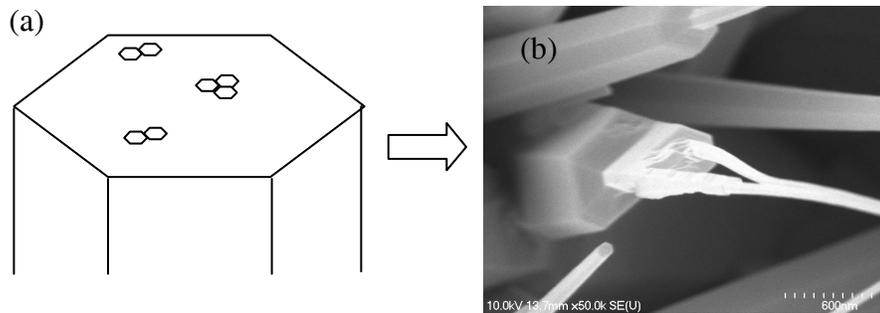


Figure 4. (a) Schematic of nucleation at the defects on the c -surface of a nanorod base. (b) SEM image of a type-one ZnO nanosquid.

The second type of ZnO nanosquids were nucleated after the formation of ZnO nanotubes. In this case, temperature fluctuation disrupts the growth of ZnO nanotubes and initiated steps or vacancies at the edges of the ZnO nanotube. Hence preferential nucleation will take place at these defects as schematically shown in Figure 5(a). This will initiate the growth of multiple ZnO nanowires at these defects. SEM image of this type of ZnO nanosquids is shown in Figure 5(b). The tubular cavity of the ZnO nanotube can be clearly seen in the SEM image.

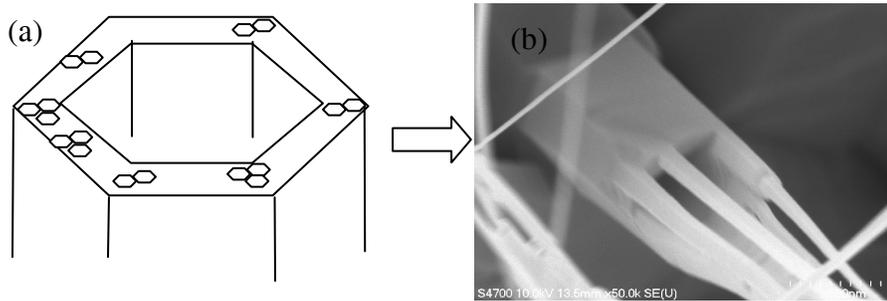


Figure 5. (a) Schematic of nucleation at the defects on the edges of a nanotube. (b) SEM image of a type-two ZnO nanosquid.

Figure 6(a) shows the typical XRD spectra of ZnO nanosquid samples. The major X-ray peaks in these spectra can be indexed for diffractions from the (002), (101), (102), and (103) planes of wurtzite crystals with lattice constants $a = 0.325$ nm, and $c = 0.521$ nm, which are corresponding to ZnO according to the JCPDS database. An X-ray peak at 32.97° is also detected, which could be related to the zinc silicate (Zn_2SiO_4) (112) diffraction peak (33.06°) [14]. ZnO nanotubes are then analyzed by photoluminescence (PL) as shown in Figure 6(b). A predominant emission peak at ~ 380 nm is observed and corresponds to the near-band-edge emission of ZnO attributed to the recombination of the free excitons. A weak broad emission at ~ 770 nm is attributed to intraband defect levels including the singly ionized oxygen vacancy in ZnO [11]. ZnO nanosquids were also characterized with Raman spectroscopy using a HeNe laser. As shown in Figure 6(c), multiple Raman shifts were detected at 333, 378, 438, and 583 cm^{-1} , which are corresponding to the $E_{2H} - E_{2L}$, A_{1T} , E_{2H} , and E_{1L} phonon modes of ZnO [11]. The detected XRD, PL and Raman signals indicate that the ZnO nanotubes and nanosquids maintain the band structures and crystalline structures of the bulk wurtzite ZnO crystals.

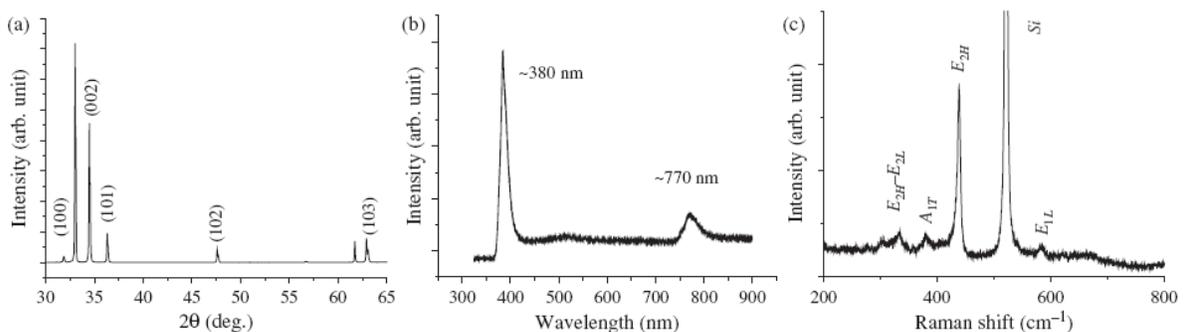


Figure 6. (a) XRD spectra, (b) PL spectra, and (c) Raman spectra of the ZnO Nanosquids

CONCLUSIONS

We have demonstrated a promising route of growing ZnO nanotubes and nanosquids without catalysts and templates. These ZnO nanotubes and nanosquids were grown on the *c*-surfaces of ZnO nanorods and nanotubes and can be explained by the theory of nucleation, and the vapor-solid crystals growth mechanism. The branching nanowires of these ZnO nanosquids have potential application in multiplexing devices. Sharp band-edge emission at 380 nm indicates that these ZnO nanotubes and nanosquids are also useful in optoelectronic devices.

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REFERENCES

1. Y. Li, G. W. Meng, L. D. Zhang, and F. Phillipp, *Appl. Phys. Lett.* **76**, 2011 (2000).
2. M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science* **292**, 1897 (2001).
3. Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science* **291**, 1947 (2001).
4. H. Q. Yan, R. R. He, J. Johnson, M. Law, R. J. Saykally, and P. D. Yang, *J. Am. Chem. Soc.* **125**, 4728 (2003).
5. J. Y. Lao, J. Y. Huang, D. Z. Wang, and Z. F. Ren, *Nano Lett.* **3**, 235 (2003).
6. X. Wang, J. Song, and Z. L. Wang, *Chem. Phys. Lett.* **424**, 86 (2006).
7. M. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, *J. Phys. Chem. B* **107**, 659 (2003).
8. H. T. Ng, J. Han, T. Yamada, P. Nguyen, Y. P. Chen, and M. Meyyappan, *Nano Lett.* **4**, 1247 (2004).
9. X. D. Bai, P. X. Gao, Z. L. Wang, and E. G. Wang, *Appl. Phys. Lett.* **82**, 4806 (2003).
10. Z. L. Wang and J. H. Song, *Science* **312**, 242 (2006).
11. S. L. Mensah, V. K. Kayastha, I. N. Ivanov, D. B. Geohegan, and Y. K. Yap, *Appl. Phys. Lett.* **90**, 113108 (2007).
12. I. Tarjan and M. Matrai (eds.), *Laboratory Manual on Crystal Growth*, Akadémiai Kiadó, Budapest (1972), pp.29–30.
13. J. M. Blakely and K. A. Jackson, *J. Chem. Phys.* **37**, 428 (1962).
14. Y. Syono, S. Akimoto, and Y. Matsui, *J. Solid State Chem.* **3**, 369 (1971).