

ZnO Nanosquids: Branching Nanowires from Nanotubes and Nanorods

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One-dimensional (1D) semiconductor nanostructures are promising building blocks for future nanoelectronic and nanophotonic devices. ZnO has proven to be a multifunctional and multistructural nanomaterial with promising properties. Here we report the growth of ZnO nanosquids which can be directly grown on planar oxidized Si substrates without using catalysts and templates. The formation of these nanosquids can be explained by the theory of nucleation, and the vapor-solid crystal growth mechanism. The branching nanowires of these ZnO nanosquids could have potential application in multiplexing future nanoelectronic devices. The sharp band-edge emission at ~380 nm indicates that these ZnO nanosquids are also applicable for interesting optoelectronic devices.

Keywords: ZnO Nanosquids, Nanowires, Nanorods, Nanotubes.

1. INTRODUCTION

ZnO has proven to be a multifunctional material with prospective properties. It has a wide direct band gap of 3.37 eV at room temperature making it suitable for short-wavelength opto-electronic devices such as Laser Diodes and Light Emitting Diodes. Their high exciton energy (60 meV) renders them most applicable for making these room temperature optoelectronic devices. Another important property of ZnO is its piezoelectricity which is attributed to its non-centrosymmetric structure. In addition to their multifunctional properties, ZnO nanostructures can appeared in various morphologies such as nanowires,¹ nanorods,² nanobelts,³ nanocombs,⁴ nanonails,5 nanocastles,6 nanotubes7 etc. Some of these ZnO nanostructures have been reported for their electronic,^{8,9} optics,² mechanical,¹⁰ and piezoelectric¹¹ applications. These nanostructures will enable production of increasingly complex electronic components.

Here, we report another type of ZnO nanostructures that would be useful for device multiplexing. We call these nanostructures ZnO nanosquids. These nanosquids consist of multiple ZnO nanowires with diameters range from \sim 80 to \sim 150 nm. These nanowires are branching out from one end of a ZnO nanorod or a ZnO nanotube. These branching ZnO nanowires could be used as the multiplexing conduction channels from one device to other devices. The sharp band-edge emission at \sim 380 nm indicates that these ZnO nanosquids are also applicable for interesting optoelectronic devices.

2. RESULTS AND DISCUSSION

The formation of these nanosquids is identical to the growth of single crystalline ZnO nanotubes reported earlier.⁷ In brief, the growth was performed in a doubletube horizontal furnace. This system consists of a quartz tube vacuum chamber. A smaller quartz tube (one end closed, 60 cm long and 2 cm in diameter) contained the precursor materials and the substrates, was placed within the vacuum chamber so that the closed end is at the center for the furnace. A mixture of ZnO (0.2 g) and graphite (0.1 g) powder in an alumina boat was used as the precursor materials. These are placed at the closed end of the smaller quartz tube as shown in Figure 1(a). A series of oxidized silicon substrates (1 to 4) were then placed down stream from the mixture in the small quartz tube as shown. At \sim 350 °C, oxygen gas was introduced into the furnace at a flow rate of 40 sccm. The furnace was held at 1100 °C for 30 minutes and turned off to allow cooling to 600-700 °C in \sim 30 mins. Then experiments are terminated by cooling the system to RT by opening the heating panel of the furnace. According to a calibration experiment, when the furnace is heated to 1100 °C, the temperatures of substrates 1 to 4 are about 700 °C, 600 °C, 500 °C, and 420 °C, respectively. These temperatures will be lower as the furnace temperatures decrease from 1100 °C. All samples were examined with scanning electron microscopy (SEM), Raman spectroscopy and photoluminescence (PL). We found that ZnO nanosquids are always formed on substrate 3 and 4.

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Fig. 1. (a) Experimental setup in a double-tube horizontal furnace. (b) Nucleation sites on a surface with a step. (c) Preferential condensation of growth species at the *c*-plane edges of a ZnO nanorod. (d) Appearance of a ZnO nanotubes.

In fact, the growth mechanism of these ZnO nanosquids can be explained by the theory of nucleation, and the vapor solid crystal growth mechanism, which is related with the growth of ZnO nanotubes.⁷ Theory suggests that growth species prefers to condense on locations with the maximum number of nearest neighbors.¹² Thus for a growth surface with a step as shown in Figure 1(b), growth species prefers to condense at sites 6, 5, 1, 4, 2, 3, according to sequence since $\beta_6 > \beta_5 > \beta_1 > \beta_4 > \beta_2 > \beta_3$.¹² Here, β is a numerical factor directly proportional to the binding energy of the ionic growth species *E*, where $\beta = E \frac{a}{q^2}$. In this relation, *a* is the lattice spacing and *q* is the charge of the ion.

For a flat 2D growth surface without steps, only site 1, 2, and 3 exist. In this case, higher binding energies at the edges (sites 1 and 2) will enable selective condensation of growth species at the edges. For ZnO, it is well known that the growth rate along the *c*-axis is relatively faster.¹ At decreased growth temperatures, the nucleation probability $P_{\rm N}$, and the surface migration will be suppressed. Here $P_{\rm N} = N \exp(-\pi\sigma^2/k^2T^2In\alpha)$, where 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

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Thus if the growth temperatures are low enough to suppress migration along the atomically flat 2D surface of the c-plane but high enough to sustain the growth along the c-axis, the condensation and the growth will be limited at the edges of the c-plane of a ZnO nanorod base as shown in Figure 1(c). Under these conditions, the growth of ZnO nanotubes along the c-axis of the nanorod base will occur as shown in Figure 1(d).

However, during the cooling process, if steps or vacancies are formed, nucleation will preferentially take place at these sites due to their higher β values than those at the edges [like sites 5 and 6 in Fig. 1(b)]. Since the rapid cooling process in our experiments was introduced by turning off the power supply of the furnace and lack precise controls. Thus fluctuation of the growth condition will happen during this cooling process. This has induced the formation of two types of ZnO nanosquids. The first type of nanosquids was formed when the initial nanorod base failed to nucleate into a nanotube. Due to BIDS/in the fluctuation of the growth condition, steps or vacan-IP: 193.63 cies will be formed on the growth surface of the nanorod Wed. 13 Feb 20base and 3 induced nucleation as schematically shown in Figure 2(a). As these nuclei continue to grow into stable ZnO islands, they will prefer to form nanowires along the c-axis. In this way, multiple ZnO nanowires will be formed on the nanorod base. The SEM images of this type of ZnO nanosquids are as shown in Figures 2(b) and (c) at different magnification (detector tilted at 40°). The growth of the second type nanosquids was induced after the formation of ZnO nanotubes. In this case, the fluctuation of the growth condition disrupted the continuous growth of ZnO nanotubes and initiated steps or vacancies at the tubular edges. This gives rise to the preferential attachment of new growth species at the defects as schematically shown in Figure 2(d). The growth of multiple ZnO nanowires was then initiated at these defects. The appearance of this type of ZnO nanosquids are shown in the SEM images at Figures 2(e) and (f) at low and high magnification, respectively (detector tilted at 40°). The cavities of the ZnO nanotubes can be clearly observed in these images. In addition, the branching nanowires of these nanosquids are having well faceted hexagonal shapes like the nanorod base, as also highlighted in Figures 2(g) and (h). These appearances indicate that these nanowires are growing along the *c*-axis as explained by the theory discussed earlier.

> Figure 3(a) shows the typical X-ray diffraction spectra of these nanosquid samples by using the Cu K_{α} source (wavelength ~0.154 nm). 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 mm, and c = 0.521 nm, which are corresponding to ZnO according to the JCPDS database. The predominated (002) peak indicates that the nanorod base of these ZnO nanosquids are preferentially grown



Fig. 2. (a) Schematic of nucleation at the defects formed on the *c*-surface of a nanorod. The corresponding SEM images of ZnO nanosquids at (b) low, and (c) high magnification. (d) Schematic of nucleation at the defects formed on the edges of a nanotube. The corresponding SEM images of ZnO nanosquids at (e) low, and (f) high magnification. The branching nanowires are having hexagonal facets (g), (h).

along the *c*-axis as also suggested by their hexagonal morphologies. The (101), (102) and (103) peaks are induced by the imperfect vertical alignment of these nanorod bases and the branching nanowires. These spectra are also identical to those detected from our ZnO nanotubes samples.⁷ 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

These ZnO nanosquids are then analyzed by photoluminescence (PL) as excited by a HeCd laser (wavelength \sim 325 nm). A predominant emission peak at \sim 380 nm is observed as shown in Figure 3(b) and corresponds to the band-edge emission of ZnO attributed to the recombination of the free excitons. A weak broad emission at ~770 nm is attributed to intra-band defect levels including the singly ionized oxygen vacancy in ZnO.¹⁵ These ZnO nanosquids were also characterized with Raman spectroscopy using a HeNe laser (wavelength ~633 nm) as the excitation source. As shown in Figure 3(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.^{7, 16–18} The detected XRD, PL and Raman



Fig. 3. (a) XRD, (b) PL and (c) Raman spectra of ZnO nanosquids.

signals indicate that the ZnO nanosquids maintain the band structures and crystalline structures of the bulk wurtzite ZnO crystals.

3. CONCLUSION

In summary, we demonstrate a promising route of growing single crystalline ZnO nanosquids without catalysts and templates by conventional thermal CVD technique. These ZnO 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 could have potential application in multiplexing future nanoelectronic devices. The sharp band-edge emission at ~380 nm indicates that these ZnO nanosquids are also applicable for interesting optoelectronic devices.

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References and Notes

- 1. Y. Li, G. W. Meng, L. D. Zhang, and F. Phillipp, <u>Appl. Phys. Lett.</u> 76, 2011 (2000).
- 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).
- 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).
- S. L. Mensah, V. K. Kayastha, I. N. Ivanov, D. B. Geohegan, and Y. K. Yap, *Appl. Phys. Lett.* 90, 113108 (2007).
- 8. M. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, J. Phys. Chem. B 107, 659 (2003).
- H. T. Ng, J. Han, T. Yamada, P. Nguyen, Y. P. Chen, and M. Meyyappan, *Nano Lett.* 4, 1247 (2004).
- X. D. Bai, P. X. Gao, Z. L. Wang, and E. G. Wang, <u>Appl. Phys. Lett.</u> 82, 4806 (2003).
- 11. Z. L. Wang and J. H. Song, Science 312, 242 (2006).
- **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). 15. K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voigt, and B. E. Gnade, *J. Appl. Phys.* 79, 7983 (1996).
- 16. T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 570 (1966).
- 17. R. P. Wang, G. Xu, and P. Jin, Phys. Rev. B 69, 113303 (2004).
- 18. S. L. Mensah, V. K. Kayastha, and Y. K. Yap, J. Phys. Chem. C 111 (Letters) 16092 (2007).

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