

# Fabrication and photoluminescence of zinc silicate/silica modulated ZnO nanowires

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## Abstract

Zinc silicate/silica modulated ZnO nanowires have been successfully prepared by a chemical vapour deposition route. The nanowires have a uniform diameter of  $\sim 30$  nm and length of 1  $\mu\text{m}$ . Photoluminescence spectra show four peaks at 382, 398, 478 and 520 nm. Two new additional peaks at 398 and 478 nm are assigned to modulation between ZnO and SiO<sub>2</sub>. The formation mechanism of the surface modified ZnO-based nanowires is also proposed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Zinc oxide nanostructures have been regarded as one of the most important semiconductor materials due to their potential applications in nanoscale electronic and optoelectronic devices. Enormous work has been done so far in the fabrication of ZnO-based nanostructures such as pure and doped ZnO nanowires as well as heterostructure ZnO nanorods. Highly oriented ZnO nanowire arrays can be employed to design a UV nanolaser at room temperature [1]. Mn-doped ZnO nanowires have a possible application in spintronics [2] as a spin field effect transistor (FET). Ga-doped ZnO nanowires can enhance the carrier concentration and make the observation of optical properties [3, 4]. Heterostructure ZnMgO/ZnO nanorods enable one to observe the quantum confinement effect [5]. ZnO loaded in mesoporous silica is also technologically of significance and interest since its wavelength of the fundamental transition can be tailored easily to tune the photoluminescence of ZnO. A ZnO cluster embedded in an SiO<sub>2</sub> matrix can be employed to fabricate a waveguide laser [6]. Recently, surface-modified ZnO nanoparticles or ZnO nanoparticles introduced into different matrices were found to show an enhanced photoluminescence and to have a better time stability [7–10]. ZnO nanoparticles embedded in silica enable one to realize applications in nonlinear optics [11],

plasma display panels [12, 13], filters, catalyst supports, varistor, and gas sensors. Moreover, ZnO/silicate glass has been widely used as a transparent conducting oxide buffer in the construction of semiconductor film solar cells [14].

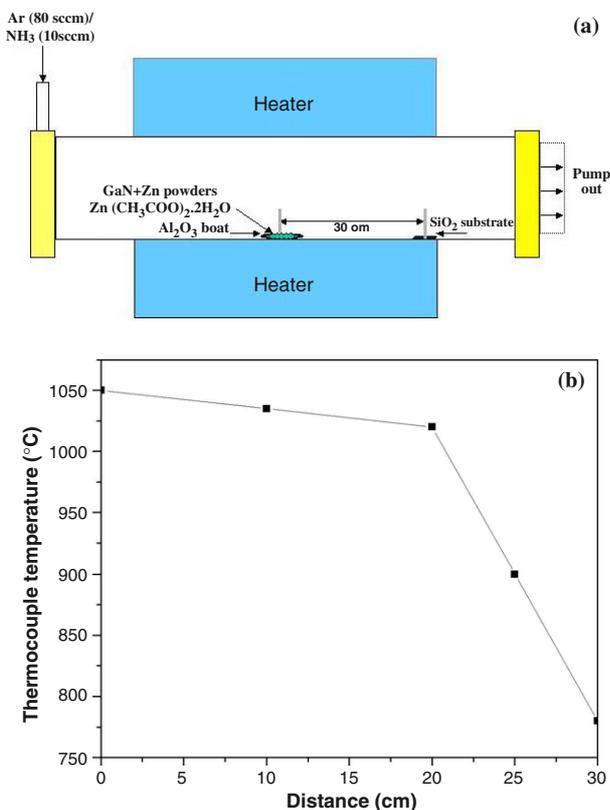
Dai *et al* prepared ZnO/SiO<sub>2</sub> nanocables [15] and Wang *et al* fabricated porous ZnO nanowires epitaxially sheathed zinc silicate [16]. However, the good luminescence efficiency, the functionality and stability of ZnO-based nanostructures are desirable for application. Moreover, photonic composite materials are also very appealing for their possible application. For example, photonic crystals with periodical dielectric variations can lead to the formation of a spectral gap that screens certain frequencies of photons. It is necessary to fabricate zinc silicate/silica modulated ZnO nanowires and subsequently observe their luminescence properties.

In this work, a route is presented for the fabrication of zinc silicate modulated ZnO nanowires via using Ar/NH<sub>3</sub> as carrier gas and GaN as a mediator. The photoluminescence of zinc silicate/silica modulated ZnO nanowires is observed and the formation mechanism is also proposed.

## 2. Experiments

An alumina boat containing a mixture of GaN powder (Aldrich, 99.99%), Zn (Aldrich, 100 mesh, 99.999%) and Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (Aldrich, 99.999%) was kept at the centre of a quartz tube placed horizontally in a tubular furnace

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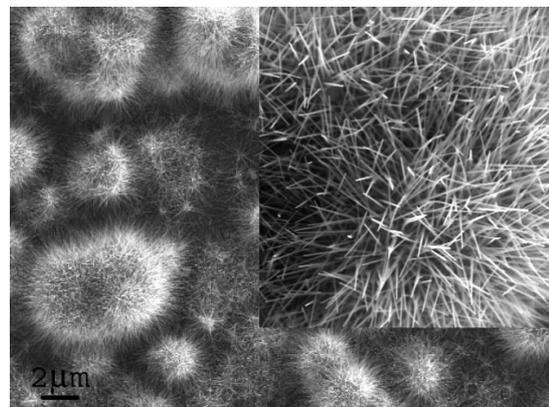
**Figure 1.** (a) Schematic diagram of the horizontal furnace used in the synthesis. (b) The temperature distribution curve in the furnace.

as shown in figure 1(a). The silica substrates were located downstream about 300 mm from the source. The base vacuum was kept at 200 mTorr. The powder was heated up to 900 °C at the rate of 15 °C min<sup>-1</sup> with a constant flow of 10 sccm NH<sub>3</sub> and 80 sccm Ar. The NH<sub>3</sub> was then turned off but the system was heated up to 1050 °C (the substrate temperature is ~800 °C) at which point air was introduced for about one minute. Subsequently the temperature was held for 160 min. The temperature distribution is shown in figure 1(b). After the system was cooled down to room temperature under an Ar flow, the wool-like products were obtained from the substrates.

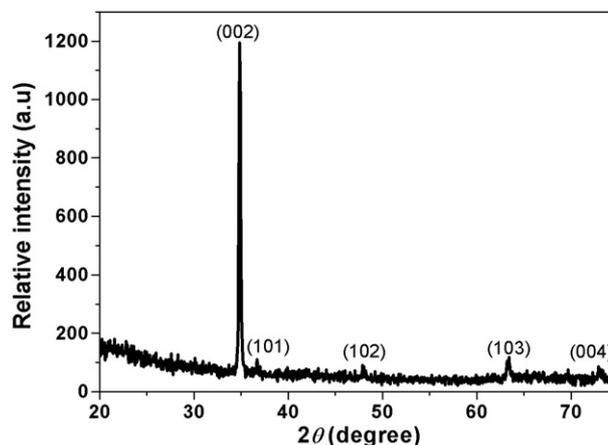
As-grown samples were characterized and analysed by x-ray diffractometer (XRD, RIGAKU D/MAX-IIA) with Cu K $\alpha$  radiation. Field emission scanning electron microscopy (FE-SEM, HITACHI S-4300), and transmission electron microscopy (TEM, JEOL-2010) equipped with energy-dispersive x-ray spectroscopy (EDX) were also used. The photoluminescence (PL) measurements were conducted at room temperature with an excitation source at 325 nm.

### 3. Results and discussion

Figure 2 shows SEM images of the samples grown on silica substrates. The nanowires are locally grown on the substrate. The cluster of nanowires looks like a sea urchin. The inset is a high-magnification SEM image of as-prepared samples, revealing that the diameter of the nanowires is about 30 nm and the length is up to about 1  $\mu$ m (the aspect ratio is 35:1).



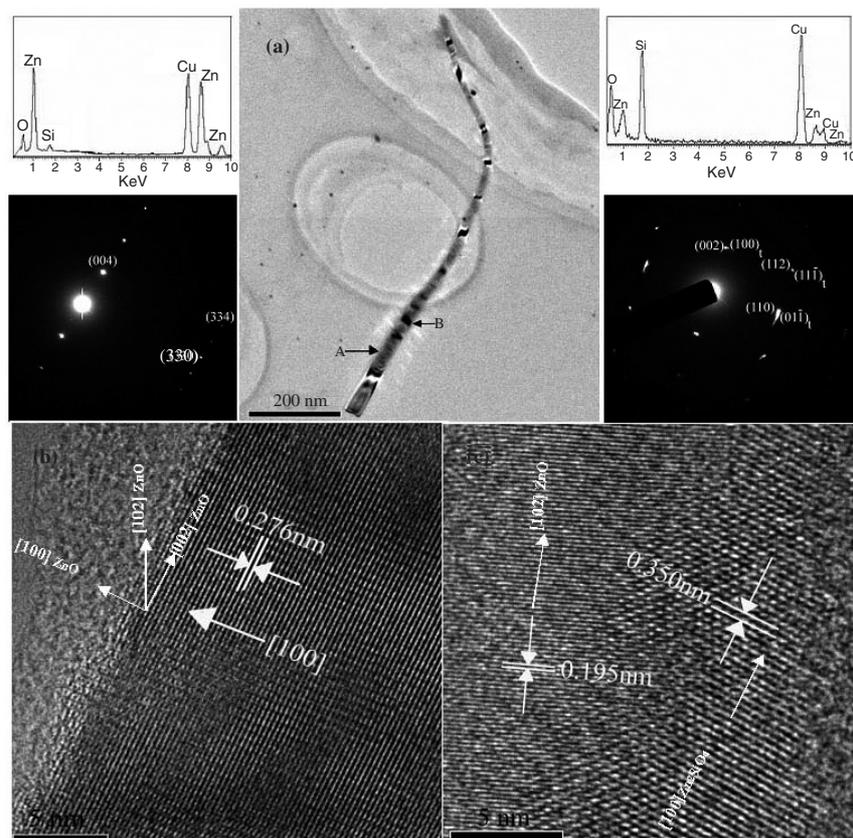
**Figure 2.** SEM images of nanowires like a sea urchin grown on silica substrates. The inset is a magnified SEM image of a sea urchin-like cluster.



**Figure 3.** XRD patterns of as-prepared samples.

Figure 3 is the XRD patterns of as-prepared samples. The diffraction pattern shows that the sample is hexagonal ZnO crystal structure with lattice constants of  $a = 3.248 \text{ \AA}$  and  $c = 5.199 \text{ \AA}$ , being in a good agreement with the standard values of ZnO bulk crystal (JCPDS 36-1451).

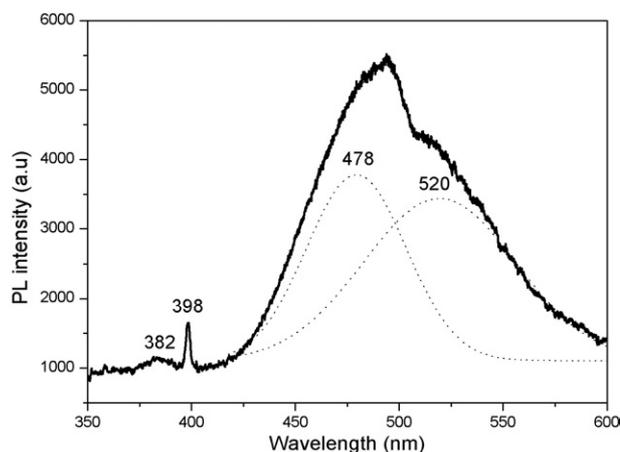
Figure 4(a) depicts the TEM image of a typical as-prepared nanowire on the silica substrate. The diameter of the nanowire is about 35 nm, and the surface is clean and smooth. However, the colour of the nanowire is not uniform: some areas are grey and other areas black. For the grey section (position A), EDX analysis (the left upper inset) indicates that it consists of Zn, O and Si. The atomic ratio between Zn, O and Si is 56:39:5. The selected area electron diffraction (SAED) pattern (the left lower inset) indicates that it is single-crystal hexagonal wurtzite ZnO ( $a = 3.18 \text{ \AA}$ ,  $c = 5.18 \text{ \AA}$ ) with a  $[\bar{1}100]$  zone axis. For the black section (position B), EDX analysis (the right upper inset) shows that it is also composed of Zn, O and Si with an atomic ratio of 14:29:57. However, the Si concentration is relatively high. The SAED pattern demonstrates that there exist two sets of diffraction spots: one is assigned to hexagonal wurtzite ZnO with a  $[\bar{1}100]$  zone axis; the other is tetragonal Zn<sub>2</sub>SiO<sub>4</sub> ( $a = 7.007 \text{ \AA}$ ,  $c = 6.464 \text{ \AA}$ ) with a  $[011]$  zone axis, which was not detected by XRD. This may be due to either blur



**Figure 4.** (a) TEM image of a nanowire grown on silica substrate. The left upper inset is EDX and the left lower inset SAED for the grey section (position A). The right upper inset and lower inset are EDX and SAED for the black section (position B), respectively. (b) An HRTEM image corresponding to section A. (c) An HRTEM image corresponding to section B.

background of the XRD or minor volume of  $\text{Zn}_2\text{SiO}_4$  in the bulk quantity of sample. It is noteworthy that the grey section and black section are repeated in turn along the axial direction of the nanowires. Figure 4(b) exhibits a high-resolution TEM (HRTEM) image corresponding to section A of the nanowires in figure 4(a). It clearly indicates that section A consists of distinct fringes and an amorphous layer; the amorphous region is a shell surrounding the crystalline region. The fringes, with an interplanar spacing of 0.276 nm, corresponding to the (10 $\bar{1}$ 0) plane of hexagonal ZnO, are perpendicular to the axis direction. The amorphous thin layer can be attributed to silica. Figure 4(c) exhibits an HRTEM image corresponding to section B of the nanowires in figure 4(a). It indicates that area B possesses a heterostructure between the inner layer and outer layer. The fringes in the inner layer have an interplanar spacing of 0.195 nm, corresponding to the (10 $\bar{1}$ 2) plane of hexagonal ZnO. The outer layer also has distinct fringes with an interplanar spacing of 0.35 nm, corresponding to the (200) plane of tetragonal  $\text{Zn}_2\text{SiO}_4$ . In addition, the  $\text{Zn}_2\text{SiO}_4$  outer layer also is surrounded by a thin layer of amorphous silica. The HRTEM image clearly reveals that tetragonal  $\text{Zn}_2\text{SiO}_4$  has a good epitaxial relation with hexagonal ZnO.

Figure 5 shows the PL spectra of zinc silicate/silica modulated ZnO nanowires with an excitation source at 325 nm at room temperature. It has been reported that ZnO nanowires show near-UV emission around 380 nm due to the recombination of free excitons and a green emission band

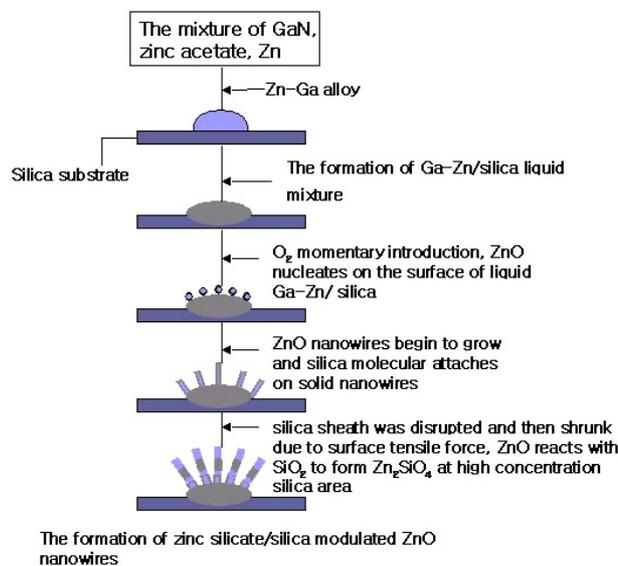


**Figure 5.** PL spectra of zinc silicate/silica modulated ZnO nanowires at room temperature with an excitation wavelength at 325 nm.

centred at 520 nm [17] due to singly ionized oxygen vacancy.  $\text{Zn}_2\text{SiO}_4$  bulk crystal has a luminescence peak at  $\sim 520$  nm. ZnO/SiO $_2$  composites with highly dispersed ZnO particles within silica pores show four PL peaks at 395, 420, 475 and 525 nm [18]. The difference between pure ZnO nanowires and ZnO/SiO $_2$  composites is assigned to the coupling effect of

the interface pore walls and ZnO. In our case, several peaks at 382, 398 nm and a broad peak were observed. The broad peak can be well fitted into two peaks at 478 and 520 nm with Gaussian symmetry. According to the above analyses, the green band at 520 nm is the overlap of the ZnO green band and  $\text{Zn}_2\text{SiO}_4$  green band. The broadening of the peak at 382 nm can be assigned to the modulation because this peak is sharper in the PL of pure ZnO nanowires [8]. Referring to the PL of ZnO/SiO<sub>2</sub> composites with highly dispersed ZnO within silica pores [19], the emission around 398 nm could be the annihilation of bound excitons, i.e., electron-hole pairs from the excited state  $[\text{Zn}^+-\text{O}^-]$  to the initial state  $[\text{Zn}^{2+}-\text{O}^{2-}]$  [20]. The emission at 478 nm may arise from the surface state of ZnO as observed by Yao *et al* [18] and Mahamuni *et al* [19] in the ZnO/SiO<sub>2</sub> system. They proposed that oxygen vacancies and interstitial oxygen are responsible for the feature. As can be seen, the green luminescence intensities of composition modulated ZnO nanowires are much higher than that of UV, which is similar to the photoluminescence from assemblies of nano-ZnO particles/silica aerogels [7]. Apparently, the interaction between the interface of zinc oxide and silica has an effect on the optical properties of ZnO/SiO<sub>2</sub> nanowires, especially, the surface of ZnO nanowires.

The experiments indicated that zinc silicate/silica modulated ZnO nanowires formed on silica substrate rather than on the sapphire substrate under the same condition. Accordingly, we suggest that silica substrates play an important role in the formation of as-grown nanostructures instead of the quartz tube. In accordance with the structural information obtained by various analytical techniques, a possible spontaneous growth model is proposed in figure 6. First, when heating the mixture in the alumina boat, Zn and Ga vapour were generated and carried away to deposit the downstream silica substrate by gas carrier and form Zn-Ga; second, the surface of the silica substrate can be melted because of the low melting point (29.8 °C) of gallium. Our separate experiments verified that the substrate surface could be etched to form silica nanowires with the presence of either NH<sub>3</sub> or H<sub>2</sub> at the rate of 15 sccm; the surface was seriously corroded to yield more silica nanowires with the presence of both NH<sub>3</sub>/H<sub>2</sub> and Ga. The sea urchin clusters also gave an indirect indication that the substrate was etched locally. When O<sub>2</sub> is introduced momentarily, the alloy ball embedded in the fused silica can absorb oxygen to nucleate. The nanowires began to grow. Since Ga can act as a mediator/activator, it is easy to form the amorphous SiO<sub>x</sub> nanowires and/or nanotubes on both silica and silicon substrates [15]. Meanwhile, the amorphous silicon oxide with isotropic growth was most probably attached onto the solid ZnO surface and formed the so-called amorphous outer sheath [16]. It is noteworthy that our substrate temperature (~800 °C) is between those of ZnO/SiO<sub>2</sub> nanocables and ZnO nanowires epitaxially sheathed Zn<sub>2</sub>SiO<sub>4</sub>. Furthermore, the ZnO-SiO<sub>2</sub> system around 800 °C is easily transformed into a mixed phase including a hexagonal ZnO, a tetragonal Zn<sub>2</sub>SiO<sub>4</sub> and an amorphous SiO<sub>2</sub> [21]. When the nanowires grew to a certain length, the amorphous silicon oxide sheath was disrupted and then shrunk into a small area with high silica concentration because of surface tensile force. From the chemical reaction dynamics point of view, the following reaction may occur at the interface of ZnO/SiO<sub>2</sub>



**Figure 6.** A schematic diagram for the formation mechanism of zinc silicate/silica modulated ZnO nanowires.

under the circumstance of a higher silica concentration:  $2\text{ZnO} + \text{SiO}_2 \rightarrow \text{Zn}_2\text{SiO}_4$ . The zinc silicate/silica modulated ZnO nanowires are finally formed. If the growth parameters such as temperature and pressure are optimized, we may adjust the A and B volume ratio of figure 4(a) to form the desired periodic superlattice. These nanowire composites may have a potential future application. However, well-controlled periodic superlattices are still required.

#### 4. Conclusions

In summary, zinc silicate/silica modulated ZnO nanowires have been successfully prepared by a chemical vapour deposition route. The as-prepared nanowires have a uniform diameter of approximately 30 nm and length of 1  $\mu\text{m}$ . PL spectra show four peaks at 382, 398, 478 and 520 nm. Two new additional peaks at 398 and 478 nm are assigned to modulation between ZnO and SiO<sub>2</sub>. The formation mechanism of these composition modulated ZnO based nanowires is also proposed. The results may be interesting for further application.

#### Acknowledgments

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#### References

- [1] Huang M H, Mao S, Feik H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897
- [2] Ronning C, Gao P X, Ding Y, Wang Z L and Schwen D 2004 *Appl. Phys. Lett.* **84** 783
- [3] Xu C, Kim M, Chun J and Kim D 2005 *Appl. Phys. Lett.* **86** 133107
- [4] Zhong J, Muthukumar S, Chen Y, Lu Y, Ng H M, Jiang W and Garfunkel E L 2003 *Appl. Phys. Lett.* **83** 3401

- [5] Park W, Yi G, Kim M and Pennycook S J 2003 *Adv. Mater.* **15** 526
- [6] Leong E S P, Chong M K, Yu S F and Pita K 2004 *IEEE Photon. Technol. Lett.* **16** 2418
- [7] Mo C M, Li Y H, Lin Y S, Zhang Y and Zhang L D 1998 *J. Appl. Phys.* **83** 4389
- [8] Mikrajuddin, Iskandar F, Okuyama K and Shi F G 2001 *J. Appl. Phys.* **89** 6431
- [9] Guo L, Yang S H, Yang C L, Yu P, Wang J N, Ge W K and Wong G K L 2000 *Appl. Phys. Lett.* **76** 2901
- [10] Li J F, Yao L Z, Ye C H, Mo C M, Cai W L, Zhang Y and Zhang L D 2001 *J. Cryst. Growth* **223** 53511
- [11] Armelao L, Fabrizio M, Gialanella S and Zordan F 2001 *Thin Solid Films* **394** 89
- [12] Zhang Q Y, Pita K and Kam C H 2003 *J. Phys. Chem. Solids* **64** 333
- [13] Justel T and Nikol H 2004 *Adv. Mater.* **12** 527
- [14] Detchprohm T, Hiramatsu K, Amano H and Akasaki I 1992 *Appl. Phys. Lett.* **61** 688
- [15] Dai L, Chen X L, Zhang X, Zhou T and Hu B 2004 *Appl. Phys. A* **78** 557
- [16] Wang X, Summers C J and Wang Z L 2004 *Adv. Mater.* **16** 1215
- [17] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater.* **13** 113
- [18] Yao B, Shi H, Bi H and Zhang L 2000 *J. Phys.: Condens. Matter* **12** 6265
- [19] Anpo M and Kubokawa Y 1984 *J. Phys. Chem.* **88** 5556
- [20] Mahamuni S, Borgohain K, Bendre B S, Leppert V J and Risbud S H 1999 *J. Appl. Phys.* **85** 2861
- [21] Xu X, Wang P Qi Z, Ming H, Xu J, Liu H, Shi C, Lu G and Ge W 2003 *J. Phys.: Condens. Matter* **15** L607