

## A simple method to control the alignment of ZnO rods on Si substrate

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### 1. Introduction

As an important II–VI group semiconductor compound with wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature, ZnO has been widely used in the fields of electrical, optoelectronic, and photochemical devices. Up to now, many methods have been used to fabricate ZnO micro/nanostructures. Notably, the synthesis of well aligned one-dimensional (1D) micro/nanostructure arrays is of great interest since it is an important step toward fabricating micro optoelectronic devices, including light emitting diodes and laser diodes.

ZnO 1D nanostructures on Si without catalysts, which include metal organic chemical vapor deposition (MOCVD), thermal evaporation, thermal CVD, and reactive electron beam evaporation. However, the discussion of the growth mechanisms for the alignment of nanostructures is still very limited. Apparently, it remains a challenge to reproducibly control the alignment of ZnO on Si substrates.

In this study, both the seed layer and the well-aligned ZnO micro/nanorod arrays were synthesized on bare Si without any assistance of catalysts or precoated seed layers by a one-step solution method at temperatures below 95°C. The key parameters to control the formation of seed layers and alignment of as-synthesized ZnO rods were systematically investigated and the mechanisms to control the alignment of ZnO were proposed by a bound layer model.

### 2. General Instructions

The 1D ZnO nanostructures were synthesized on Si(100) substrates with dimensions of 5 cm × 2 cm in the equimolar aqueous solution of zinc nitrate hexahydrate (Zn[NO<sub>3</sub>]<sub>2</sub> · 6H<sub>2</sub>O, Sigma Aldrich, 98%) and hexamethylenetetramine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, Sigma Aldrich, 99.5%) in sealed vitreous serum bottles. To study the influence of the substrate's angle of incline, the processes were performed at 95°C for 13 h with the precursor concentration of 0.1 M and the angles of incline of 0, 45, and 90°. To investigate the effects of reaction temperature, the experiments were carried out for 13 h with an angle of incline of 45° and a precursor concentration of 0.1 M at the temperatures of 95, 85, and 75°C. In addition, the influence of precursor concentration was examined by performing the reaction at 95°C for 13 h with an angle of incline of 45° and the con-

centrations of 0.01, 0.05, and 0.1 M. After reaction, the system was cooled to room temperature. The substrates were then removed from the aqueous solution, rinsed with distilled water, and dried overnight at room temperature.

The morphologies of the as-synthesized materials were examined using field-emission scanning electron microscopy (FE-SEM). The crystal structures and crystallographic orientations of materials were investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Room-temperature cathode-luminescence (CL) measurements were performed using a Gatan mono CL equipped on a FE-SEM.

The substrate's angle of incline plays a key role for assisting the alignment of ZnO rods. Figures 1a–c are the SEM images of the as-synthesized ZnO hexagonal rods on Si(100) with the angles of incline of 0, 45, and 90°, respectively. The diameters of the hexagonal rods are in the range of 450–700 nm.

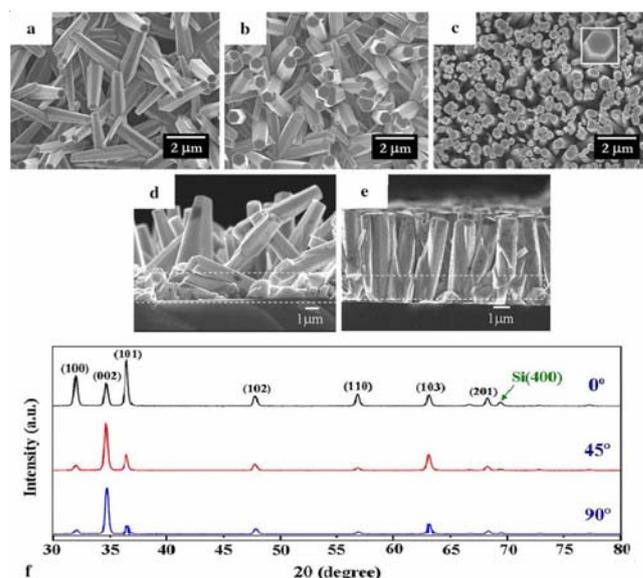


Fig. 1 SEM low-magnification images of the as-synthesized ZnO rods on a Si substrate with the incline angles of (a) 0, (b) 45, (c) 90° at 95°C; (d), (e) cross-sectional images of the sample in (a) and (c), respectively; (f) XRD patterns of the corresponding samples in (a–c)

Figures 2a–c show the SEM images of the as-synthesized ZnO rods on Si(100) with the incline angle of 90° obtained at different reaction temperatures of 95, 85, and 75°C, respectively. The rods in Figs. 2a–c exhibit aligned morphologies. According to the observation of plan-view and crosssectional images, the diameter, length, and the growth density of the rods varied gradually from 500 to 900 nm.

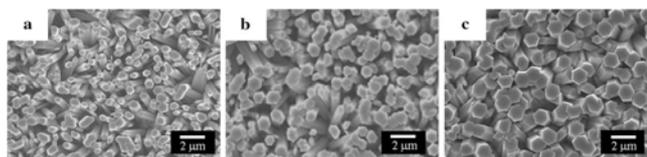


Fig. 2 SEM images of as-synthesized ZnO rods on a Si substrate with incline angle of 45° obtained at reaction temperatures of (a) 95, (b) 85, (c) 75°C;

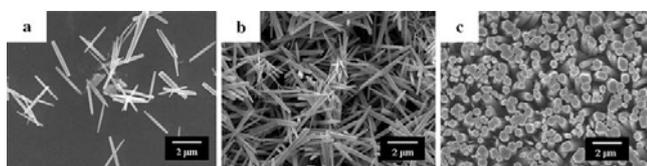


Fig. 3 SEM images of ZnO rods synthesized on a Si substrate with incline angle of 45° at 95°C with precursor Zn<sup>2+</sup> concentrations of (a) 0.01, (b) 0.05, (c) 0.1 M

The precursor concentrations of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> are usually viewed as a critical factor to control the diameter of ZnO nanorods. Figures 3a–c demonstrate the ZnO rods synthesized at different precursor concentrations of 0.01, 0.05, and 0.1 M, respectively. It can be seen that the diameters of as-synthesized ZnO nanorods reduce gradually from around 550 to 300 nm as the precursor concentration decreases from 0.1 to 0.01 M, hence the morphology is transformed from rod-like to wire-like.

Figures 4a and 4b are a high-resolution image and a corresponding electron diffraction pattern of a single ZnO rod, which reveals that the rod is a single-crystalline wurtzite structure growing along the c-axis. The d spacing of (0002) planes is 0.52 nm. The room-temperature CL spectrum of the ZnO rods is shown in Fig. 4c, which demonstrates a relatively strong and sharp ultraviolet emission centered at around 377 nm. The ultraviolet emission is attributed to the near-band-edge excitonic emission of ZnO. It indicates that the as-synthesized ZnO nanorods possess high crystal quality.

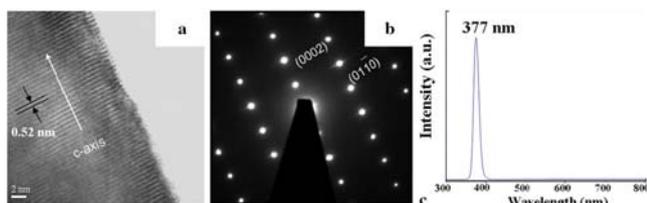


Fig. 4 (a), (b) High-resolution image and corresponding electron diffraction pattern of a single ZnO rod; (c) room-temperature CL spectrum of the ZnO rods

### 3. Conclusions

The key factors to control the formation of seed layers and vertically well-aligned ZnO rods on Si(100) by a one-step solution approach were studied systematically. SEM images and X-ray diffraction patterns demonstrate that the well-aligned ZnO rods could be synthesized on a Si substrate without the assistance of catalysts by increasing the incline angle of the substrate, lowering the synthesis temperature, and increasing the precursor concentration.

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### References

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### Appendix

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