Synthesis, microstructure and photoluminescence of well-aligned ZnO nanorods on Si substrate

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Abstract

Well-aligned zinc oxide (ZnO) nanorods were densely grown on Si substrate using ZnO thin-film seed layer without any catalysts and/or additives by a simple solid–vapour phase thermal sublimation technique. The growth mechanism can be interpreted as self-catalyst of zinc particles based on vapour–solid (VS) mechanism. High-resolution transmission electron microscopy (HRTEM) image and selected area electron diffraction (SAED) pattern confirmed that the single-crystalline growth of the nanorods were preferentially along c-axis of hexagonal crystal system. High-crystal quality ZnO nanorods with strong near band edge emission centred at 380 nm can be achieved on Si substrate by the introduction of sufficient oxygen during the nanorod growth processing.

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1. Introduction

Zinc oxide (ZnO) is a unique material that exhibits semiconducting and piezoelectric dual properties. Currently, ZnO is attracting attention for its application to ultraviolet (UV) light emitters, varistors, transparent electrode, surface acoustic wave devices, piezoelectric transducers, gas sensing and as a window materials for display and solar cells [1]. Although the research on ZnO thin film, including growth control, doping, fabrication process for devices, has became an active field from the 1960s, ZnO nanowire-like structures also received extensive attention as the ideal system for studying the transport process in one dimensionally confined objects in recent years [2]. A wide variety of nanodevices including UV photodetector [3], schottky diodes [4], and light-emitting devices arrays [5] have been fabricated utilizing ZnO nanorods (nanowires). The control of the orientation of ZnO nanowires and the ability to assemble them into three-dimensional arrays onto various substrates are essential for creating functional materials. The applications on device might be reinforced if the position, orientation, and shape of the nanostructures can be controlled to a high degree of precision.

Since Huang et al. [6] reported vapour-phase synthesis of ZnO nanowires arrays via a vapour–liquid–solid (VLS) process, several methods [7–11] were reported to synthesize aligned one-dimensional (1D) ZnO nanostructure, among which the solid–vapour phase thermal sublimation technique is most commonly used due to its low cost and mass production. Using this simple method, 1D ZnO nanostructures (especially aligned nanowire or nanorod) were grown on Si or ZnO thin film with or without catalyst [7,12–15]. For the 1D ZnO nanowires grown through VLS process, the commonly used catalyst was Au [16]. To achieve the ideal optoelectric performance, the metal impurities in the nanostructures have to be minimized.

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Therefore, instead of the widely employed VLS mechanism, a metal-free (catalyst-free) synthesis of ZnO nanorods on Si substrate will benefit on the investigation of lasing and carrier/exciton behaviour. In this regard, although there are several papers which reported the growth of well-aligned nanorods using GaN or ZnO buffer layer on Si substrate [17–19], few studies on the growth mechanism have ever been reported. In this work, well-aligned ZnO nanorods were grown on Si substrate using ZnO thin film as seed layer by solid–vapour phase thermal sublimation technique, and the morphology, microstructure and photoluminescence (PL) of the deposited nanorods were investigated to identify optimal process for the setting of strong near band edge PL spectra at 380 nm for blue optoelectronic applications such as random lasing.

2. Experiment

Raw materials of ZnO powders (99.9% in purity) and graphite powders (99.9% in purity) were mixed together and then being slided in the middle of the horizontal quartz tube, while the substrate was placed at the bottom of the tube to adjust the vapour transport direction. Then the tube was inserted into the horizontal furnace. As a seed layer, for growing ZnO nanostructures on Si substrate, ZnO thin film with 300-nm-thickness was coated on Si substrate by filtered cathodic vacuum arc (FCVA) method with a 420 nm thermal-oxidized SiO$_2$ layer [20]. Two typical samples were selected for discussion in this paper as listed in Table 1.

The morphology and micro crystal structure of the synthesized samples were observed by a scanning electron microscope (SEM, JEOL JSM-5600, 30 kV) and a transmission electron microscope (TEM, JEM-4000 EX, 400 kV, point to point resolution: 0.18 nm), respectively. The chemical states and quantitative analysis were performed by X-ray photoemission spectroscopy (XPS, ESCA-5700ci,
Physical Electronics Inc.) using non-monochromatic Mg Kα line at 1253.6 eV (14 kV, 400 W). Room temperature PL (SPEX 1702/04 Spectrometer) spectra were obtained by a He–Cd laser with a 325 nm line over the wavelength range of 300–800 nm at room temperature.

3. Results and discussion

Fig. 1 shows a SEM image of well-aligned ZnO nanorods grown on ZnO/SiO₂/Si substrate (sample 1). The shape of the nanorods is mostly candle shape. Single-thin wire with 30–40 nm in diameter is grown on the tip of the thick nanorod with diameter varied from 100 to 300 nm.

One single-nanorod TEM image is given in Fig. 2(a). The d-spacing of {001} plane for ZnO hexagonal crystal structure is clearly observed in the high-resolution TEM (HRTEM) image taken at the tip of rod as shown in Fig. 2(b). Furthermore, the selected area electron diffraction (SAED) pattern confirms the nanorod is single crystal and grows along the [001] direction as indicated in Fig. 2(b).

For further investigation of the detailed microstructure of sample 1, both bright- and dark-field TEM images taken at both the neck part and the middle part of the nanorod with candle shape are given in Fig. 3(a)–(d), respectively. The diameter of the neck part of the nanorod is about
100 nm. Number of black spots are observed in Fig. 3(a). HRTEM image of these spots are shown in Fig. 3(b) implies the existence of crystal imperfection such as stacking fault, because we can clearly identify the reverse of black and white contrast of the lattice image from the surrounding area. These spots due to stacking faults are also discerned in dark-field images at the neck and the middle part of the candle-shaped nanorod as given in Fig. 3(c) and (d), respectively.

The good crystal quality of the ZnO nanorods was obtained after the introduction of oxygen for sample 2 as identified in HRTEM image of Fig. 4. The growth direction is confirmed as c-axis which is the same as that of sample 1. In comparison with sample 1, no stacking fault has been found in sample 2 under TEM observation.

Vapour–solid (VS) and VLS mechanisms have been proposed to explain the self-catalysis of Zn or its sub-oxide $\text{ZnO}_x$. We mixed graphite powders into the raw materials for the reduction of $\text{ZnO}$ into Zn or its sub-oxide ($\text{ZnO}_x, x < 1$). In comparison with $\text{ZnO}$, Zn has low-melting point in vapour phase, which benefit the formation of the nuclei of $\text{ZnO}$ nanorods [21]. After an initial period of nucleation and growth, ZnO tends to form 1D structure along $[001]$ because they can grow by maximizing the areas of the $\{010\}$ and $\{210\}$ facets, which have lower surface energy.

XPS spectra of Zn 2p, O 1s for sample 1 before introduction of oxygen are given in Fig. 5(a) and (b), respectively. The ratio of O/Zn is 0.7 as identified by XPS quantitative analysis for sample 1 in Table 2. The atom ratio of O/Zn less than 1 suggests the formation of Zn and its sub-oxide during the deposition process. Due to the reduction effect of graphite, non-stoichiometric $\text{ZnO}_x$ was formed without the addition of oxygen in the reaction process. From the experimental results, we consider the self-catalysis of Zn or $\text{ZnO}_x$ ($x < 1$) based on

| Sample 1 | C 1s | O 1s (Oxide) | O 1s (H$_2$O, OH, CO) | Zn 3p | Oxide/Zn | H$_2$O, OH, CO /Zn |
|----------|------|-------------|----------------------|-------|----------|-------------------|
|          | 23.9 | 26.5        | 11.8                 | 37.8  | 0.70     | 0.30              |

Fig. 5. XPS spectra of Zn 2p, O 1s for sample 1 before introduction of oxygen.

Fig. 6. PL spectrum of the deposited ZnO nanorods grown on ZnO thin film of Si substrate after introduction of oxygen in the deposition process.
VS mechanism is reasonable for the present formation of 1D ZnO nanowires.

The PL spectra of sample 1 showed very weak-broad green band emission at the wavelength from 400 to 600 nm. The PL result is coincidence with the existence of stacking fault as observed in TEM images. The oxygen vacancies can be reduced by insertion of oxygen during the synthesis process which has been confirmed by the series of the successive experiments.

Fig. 6 shows the PL spectrum of sample 2 after introduction of oxygen. Very strong near band edge emission centred at 380 nm in wavelength is observed. The narrow full-width at half-maximum (FWHM) and strong intensity of the UV peak at 380 nm suggests the high purity of the fabricated ZnO nanorods. The high quality of the sample also was identified by other experiment related with the optical properties [22]. Furthermore, the disappearance of the weak green band emission confirms the oxygen deficiencies of the nanorods are greatly decreased by introduction of oxygen in the deposition process.

4. Conclusions

Well-aligned ZnO nanorods were densely grown on Si substrate without any catalysts and/or additives by a simple solid–vapour phase thermal sublimation technique. The growth mechanism can be enucleated as self-catalyst of zinc particles based on VS mechanism. The nanorods exhibited candle shape with 100–300 nm in diameter for the thick part and 30–40 nm in diameter for the thin part. Bright- and dark-field TEM images and HRTEM image confirmed the existence of stacking fault at the neck and the middle part of the candle shape nanorod.

The PL result suggested the existence of oxygen vacancies and defects in the nanorods without the introduction of oxygen during deposition processing. The reduction of oxygen vacancies were confirmed for the nanorods after the sufficient introduction of oxygen.

Consequently, high crystal quality ZnO nanorods along c-axis, that showed strong near band edge emission centred at 380 nm, can be grown on Si substrate by using ZnO thin film as a seed layer without any catalyst.

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