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# Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires

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**Abstract**

Well-aligned single-crystalline zinc oxide (ZnO) nanowires with high density were successfully synthesized on nickel monoxide (NiO) catalyzed alumina substrate through a simple metal–vapor deposition method at an extremely low temperature (450 °C). The single-crystalline ZnO nanowires had a hexagonal wurzite structure and diameters of about 55 nm, and lengths up to 2.6 μm. The photoluminescence spectra under excitation 325 nm showed a ultra-violet (UV) emission at 3.26 eV and a green emission at 2.44 eV. The UV emission and green emission bands were attributed to near band-edge transition and radial combination of a singly ionized oxygen vacancy with a photo-induced hole, respectively. 

## 1. Introduction

One-dimensional nanomaterials such as GaN nanowire, GaP nanowire, and ZnO nanowire have attracted much interests because of various remarkable physical and chemical properties distinctive from conventional bulk materials [1–4]. Recently many research groups have actively reported the synthesis and characteristics of various wide band gap semiconductor nanowires [5–10]. Among the wide band gap nanowires, zinc oxide, which has a direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, can ensure an efficient exciton UV emission at a room temperature under a low excitation energy [11]. Due to the radial quantum confinement effect, ZnO nanowires possess high density of states at the band-edge. So the ZnO nanowire based nanodevice, which can realize UV lasing action at room temperature with low lasing threshold, is quite potentially feasible [12]. A few works have been reported for synthesizing one-dimensional ZnO material by various methods such as arc discharge, laser vaporization, pyrolysis, electrodeposition, and chemical vapor deposition (CVD). ZnO whiskers with large diameters were

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previously synthesized through electrodeposition method [13]. ZnO polycrystalline nanowires were successfully fabricated within nanochannels of porous alumina template [14]. Well-aligned ZnO nanowire arrays were fabricated on sapphire or silicon substrates using carbon thermal-reduction vapor transport method (880 °C) [15]. In addition, zinc oxide nanobelts were obtained by directly evaporating zinc oxide powder at a high temperature (1400 °C) [16]. The nanometer sized ZnO wires were also prepared by a physical vapor deposition method (1100 °C) using a mixture of Zn/Se powder as source [17]. Recently ZnO nanorods were grown directly on bare silica or silicon substrate at a temperature of 500 °C in a two-heating-zone furnace using evaporated zinc acetylacetonate hydrate ($Zn(C_5H_7O_2)_2 \cdot xH_2O$) as precursor [18].

In this Letter, we report that well-aligned high-crystalline ZnO nanowire arrays can be synthesized onto alumina substrate using a very simple metal–vapor deposition method at a quite low growth temperature (450 °C). The optical property of the ZnO nanowire array was also investigated by photoluminescence (PL) measurement at a room temperature.

## 2. Experimental

The ZnO nanowire array was fabricated by a following procedure. A nickel nitrate/ethanol solution with concentration of 0.01 M was dropped onto an alumina substrate (10 mm × 5 mm in size). After drying in air ambient, the substrate was loaded on a quartz boat filled with metal zinc powder (100 mesh, 99.998%, Sigma–Aldrich). And then the quartz boat was inserted into a quartz tube under a constant flow of argon (flow rate: 500 sccm). The vertical distance between the zinc source and the catalyzed alumina substrate was about 3–5 mm. The quartz tube was heated up to 450 °C under a constant flow of argon (flow rate: 500 sccm). After reaction at the temperature range of 450–950 °C for 60 min under the argon flow of 500 sccm, the substrate surface appeared white wax-like materials. The deposited products were characterized by scanning electron microscopy (SEM) [Hitachi S-4700], transmission electron microscopy (TEM) [Hitachi H-9000 NAR], and X-ray diffraction (XRD) [Rigaku DMAX PSPC MDG 2000]. The PL measurement was performed at a room temperature using He–Cd laser line of 325 nm as an excitation source.

## 3. Results and discussion

XRD analysis shows that the deposited products on an alumina substrate are ZnO nanowires with hexagonal wurtzite structure in Fig. 1. The strong intensity of ZnO diffraction peaks indicates that resulting products have high-purity of ZnO wurtzite phase.

SEM images indicate that ZnO nanowires are vertically well-aligned to the substrate with very high density as shown in Fig. 2. The ZnO nanowires grown at 450 °C have uniform diameter about 55 nm and lengths up to 2.6 μm, resulting in average aspect ratio estimated about 50 (Figs. 2a,b). Increasing growth temperature to 500 °C leads to the formation of nanowires with morphology of perfect hexagonal symmetry (Fig. 2d). All ends of ZnO nanowires are well faceted, and hexagonal end faces of ZnO nanowires may serve as mirror planes for the laser cavities.

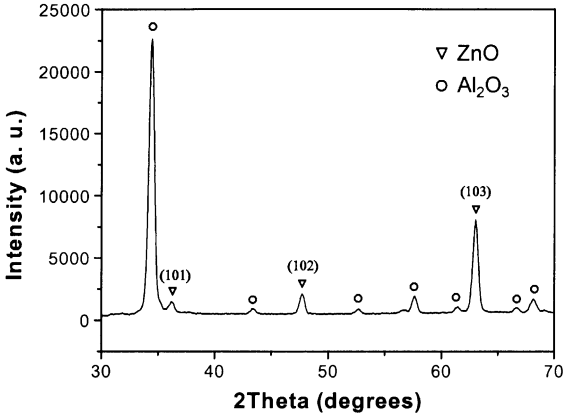


Fig. 1. XRD diffraction of ZnO nanowires on alumina substrate. Only (1 0 $l$) peaks ($l = 1, 2, 3$) corresponding to wurtzite phase are observed, implying well-aligned growth direction of nanowires.

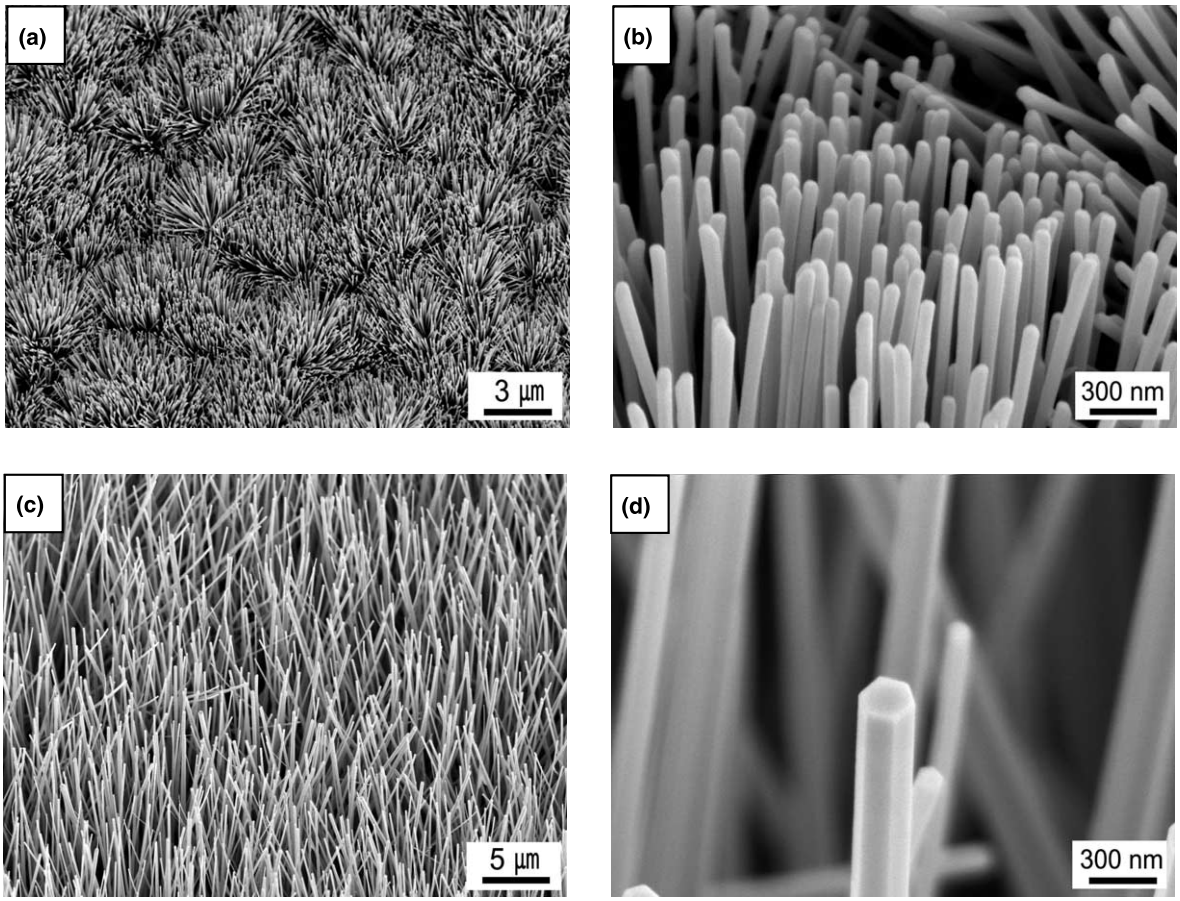


Fig. 2. SEM micrographs of ZnO nanowires vertically aligned on alumina substrates. (a)–(b): ZnO nanowires grown at 450 °C have a diameter of 55 nm and a length of 2.6 μm. (c)–(d): ZnO nanowires grown at 500 °C have a diameter of 190 nm and a length of 15 μm.

In Fig. 3a, low-resolution TEM image of ZnO nanowires shows that high-purity nanowires have a straight shape and an uniform diameter. High-resolution TEM shows that a ZnO nanowire has single-crystalline structure and its *c* axial growth direction in Fig. 3b. Inset indicates that selected area electron diffraction also reveals a single-crystalline structure of ZnO nanowire. We could successfully synthesized high-crystalline structured ZnO nanowires at higher growth temperature (550–950 °C).

It is well known that transition metal oxides, such as nickel and iron monoxides (NiO and FeO), also have a good catalyst effect on the growth of semiconductor nanowire, which is similar to the metal catalyst [19]. Our experimental results show that no nanowires were grown on pure alumina substrate without NiO catalyst. Here, we consider that the NiO nanoparticles play a key role for the synthesis of ZnO nanowire arrays on alumina substrate. Our results demonstrate that ZnO nanowires can be effectively synthesized at 450 °C by keeping the vertical distance between Zn source and NiO catalyzed substrate within a range of 3–5 mm. Such a low temperature growth technique may open up many opportunities for fabricating ZnO nanowire based devices onto various low temperature endurance substrates.

The PL of ZnO array at a room temperature is shown in Fig. 4. The narrow UV band at 3.26 eV (about 381 nm in wavelength) and a broad green band at 2.44 eV (about 506 nm in wavelength) are

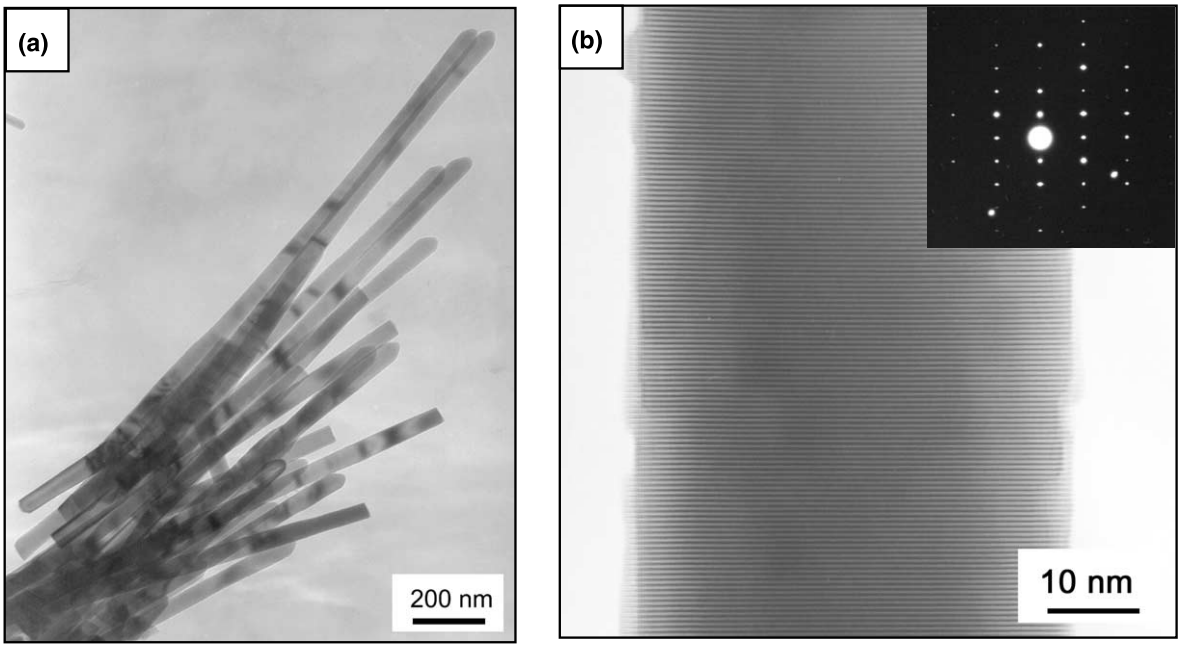


Fig. 3. TEM micrograph of ZnO nanowires: (a) a low-resolution TEM image of ZnO nanowires; (b) a high-resolution TEM image of a typical ZnO nanowire with its *c* axial growth direction. Inset shows that selected area electron diffraction of a single ZnO nanowire, indicating single-crystalline structure of ZnO nanowire.

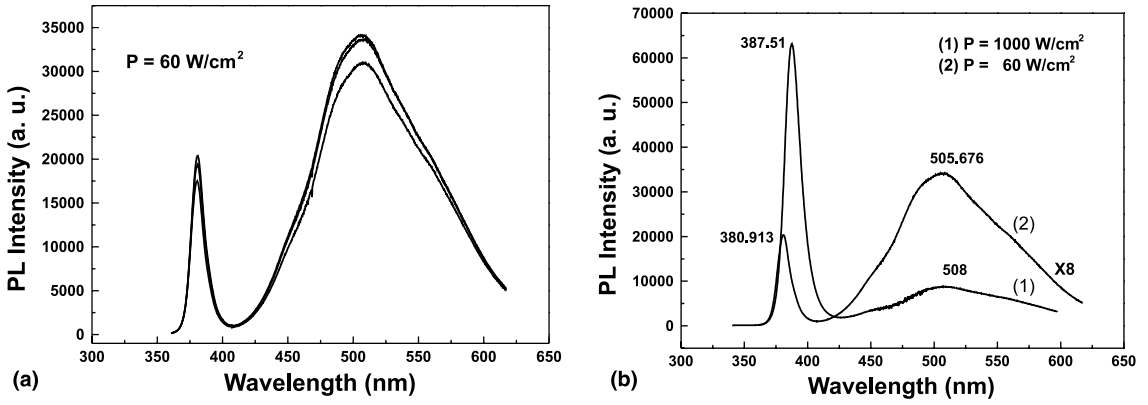


Fig. 4. Photoluminescence of the ZnO nanowires measured at room temperature: (a) PL spectra measured at different three positions of ZnO nanowire array; (b) PL spectra measured with different excitation energy intensity.

observed in the PL spectra at low excitation intensity (60 W/cm$^2$) as shown in Fig. 4a. The UV emission band must be explained by a near band-edge transition of wide band gap ZnO nanowires, namely the recombination of free excitons through an exciton–exciton collision process [17]. The appearance of UV band emission with low excitation intensity at a room temperature can be attributed to the radial quantum confinement effect of ZnO nanowire. The green band emission results from the radial recombination of a photo-generated hole with an electron that belongs to a singly

ionized oxygen vacancy [20]. The PL from different positions of the ZnO array on alumina substrate were detected by selecting various incident positions of excitation laser beams. In our experiment, the PL indicates similar emission intensities regardless of measured positions. Fig. 4b shows PL spectra measured with different excitation energy intensity. The UV emission is strengthened as excitation intensity increases from 60 to 1000 W/cm$^2$ but the green band emission is almost same. It indicates that the green band emission reaches saturation with low excitation intensity because the energy density of green emission centers is lower than that of free excitons.

In summary, well-aligned ZnO nanowire arrays, which have single-crystalline structure, were successfully grown on NiO catalyzed alumina substrate at 450 °C. Such a low temperature growth of ZnO nanowires may provide a possibility to fabricate nanodevices onto various low temperature endurance substrates. The PL spectra at a room temperature showed the UV emission at 3.26 eV and the green emission at 2.44 eV. The UV emission and green emission bands are attributed to near band-edge transition and radial combination of a singly ionized oxygen vacancy with a photo-induced hole, respectively.

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