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Synthesis of ZnO nanowires on Si substrate by thermal evaporation method without catalyst: Structural and optical properties

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Abstract−Synthesis of ZnO nanowires was achieved on Si(100) substrate by the thermal evaporation of high purity metallic zinc powder without the use of any metal catalyst or additives. The diameter and length of the as-grown nanowires were in the range of 20-35 nm and few micrometers, respectively. The shapes and sizes of ZnO nanowires were dependent on the growth time. The high resolution transmission electron microscopy and selected area electron diffraction patterns indicated that the as-grown products are single crystalline with wurtzite hexagonal phase. Room temperature photoluminescence studies exhibited a strong UV emission and a suppressed green emission, confirming the good optical properties for the deposited nanowires.

Key words: ZnO Nanowires, Thermal Evaporation, Structural and Optical Properties

INTRODUCTION

The hexagonal wurtzite crystal structured ZnO have a great importance because of its versatility in academic as well as applications view point. Due to its wide band gap (3.37 eV), high exciton binding energy (60 meV), and high mechanical and thermal stabilities, it is highly applicable in UV light emitters [Lee et al., 2005], varistors, transparent light power electronics [Keis et al., 1999], sensors [Arnold et al., 2003], surface acoustic wave devices [Golra et al., 1999], dye sensitized oxide solar cells [Gordillo, 2002], windows materials for displays, photocatalysts [Pal et al., 2002], etc. Interestingly, because of its non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric properties which is highly useful for the fabrication of devices such as electromagnetic coupled sensors, actuators, etc [Minne et al., 1995].

Recently, one dimensional nanostructures have pulled a great attention towards itself due to their exotic, tremendous and marvelous qualities in the electrical, optical, and mechanical properties as compared to their bulk materials. So far various types of ZnO nano and microstructures have been reported in the literature such as nanorods [Umar et al., 2005; Kim et al., 2005], nanowires [Sekar et al., 2005], nanoneedles [Kim et al., 2004], nanosprings and nanorings [Kong et al., 2003], nanostars [Umar et al., 2005], nanobelts [Pam et al., 2001], microtubes [Jeong et al., 2005], flower-shaped ZnO nanostructures [Umar et al., 2005] and so on. In addition of these morphologies various other morphologies have also been synthesized through different fabrication techniques by various research groups. Recently Chu et al. [2005] used the ZnO nanotetrapods for gas sensing applications. Among all the morphologies, the ZnO nanowires have a great importance not only because of their versatile applications for the fabrication of different types of nanodevices [Kind et al., 2002; Peng et al., 2001; Cui et al., 2001] but also to understand the basic quantum mechanism of the nanostructures [Ma et al., 2003].

In this paper, we present the synthesis of ZnO nanowires prepared simply by the oxidation of high purity metallic zinc powder without the use of catalysts or additives at 650 °C. The effects of processing time for the formation of these nanowires are also studied in detail. Additionally, the grown ZnO nanowires at different processing time have been examined in terms of their structural and optical properties.

EXPERIMENTAL

The ZnO nanowires were prepared by the thermal evaporation of high purity metallic zinc powder without the use of any catalysts or additives. The experimental setup consists of a 50 cm long horizontal quartz tube furnace with the halogen lamp heating system having the heating rate of 10 °C/s, a rotary pump system, and a gas controlling system. In all the experiments, Si(100) substrates were used for the deposition of the nanowires. Before using the substrates they were treated for 10 minutes with a buffer solution to remove the native oxide layer and keenly washed with de-ionized water, then ultrasonically cleaned with isopropyl alcohol and acetone, finally dried with inert gas (N_2) flow. Commercially available high purity metallic Zn powder (99.99%) and oxygen gas (99.999%) have been used as precursors of Zn and oxygen, respectively. About 3 gram of the source material, metallic zinc powder, was put into a quartz boat and positioned at the centre of the quartz tube furnace. High purity nitrogen gas (99.999%) was also used as a carrier gas and to create the inert atmosphere inside the furnace during the whole reaction process. The chamber pressure was down up to 1-2 Torr using a rotary vacuum pump prior to start the reaction, which was slightly increased after the introduction of the reactant gases. The evaporation process for the growth of ZnO nanowires was conducted at 650 °C for a period of 30-90 min. The source material, metallic zinc powder, was rapidly heated up to the temperature 650 °C under a constant flow of high-purity nitrogen carrier gas with the flow rate of 15-20 sccm (standard cubic centimeters per minute).

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When the furnace reached the temperature at 650 °C, the oxygen gas was flowed with the flow rate of 20-40 sccm into the reaction chamber during the whole period of growth. After the growth process, the whitish gray colored products were deposited onto the whole surface of the substrate. These deposited products on Si(100) substrate were examined in terms of their structural and optical properties.

General morphology of the deposited ZnO nanowires was observed using the scanning electron microscopy (SEM) equipped with the energy dispersive x-ray spectroscopy (EDX). The detailed structural characterization was done by the transmission electron microscope (TEM, JEOL 2010, Curf.) contains the selected area electron diffraction (SAED) patterns. The crystal phase and crystallinity of the deposited structures were investigated by x-ray diffraction (XRD) pattern measured with Cu-Kα radiation. The room temperature photoluminescence (PL) spectroscopy with He-Cd (325 nm) laser line as the exciton sources was used to examine the optical properties of the as-grown time dependent different ZnO nanowires.

RESULTS AND DISCUSSION

Typical SEM images for ZnO nanowires grown for different processing time are shown in Figs. 1 to 3. These images show that there is an extensive nucleation and growth of ZnO nanowires in all the cases. Fig. 1(a) and (b) show the low and high magnified SEM images of the ZnO nanowires grown for 30 min and indicate that the

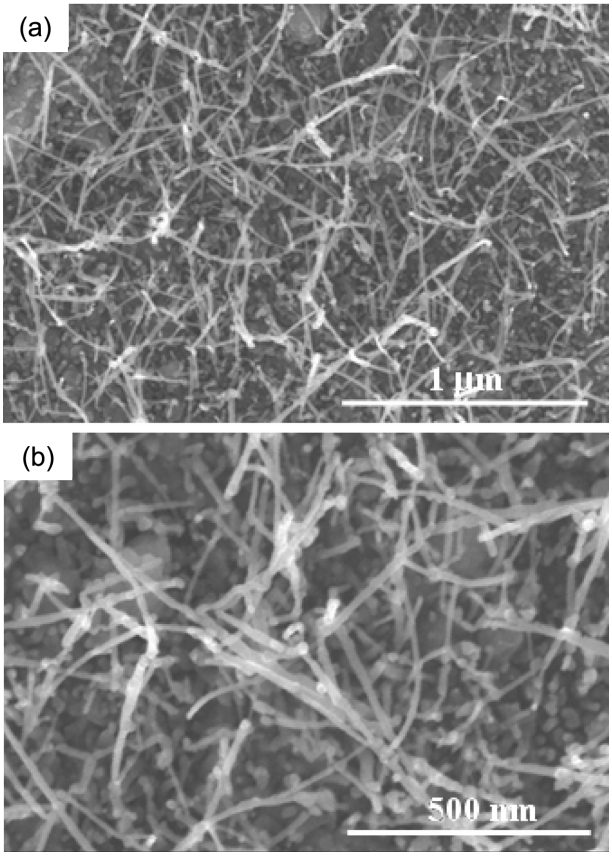

Fig. 1. (a) Low and (b) high magnification SEM images of ZnO nanowires grown for 30 min.

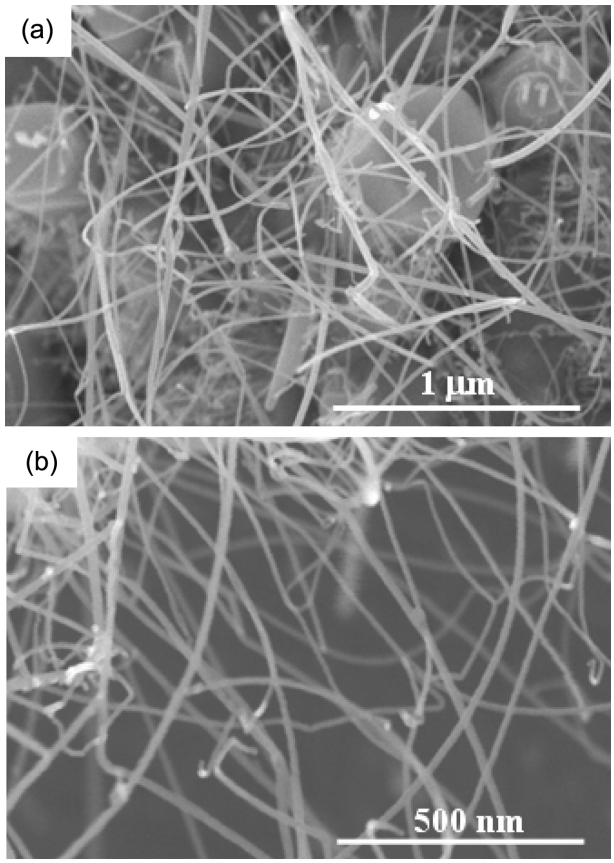

Fig. 2. (a) Low and (b) high magnification SEM images of ZnO nanowires grown for 60 min.

average diameter of the grown nanowires is 25-30 nm with the length of 2-3 μm. Most of the nanowires are joined one to another and form interconnects to each other. It is interesting to note that some very small ZnO nanoparticles with the diameter of 10-15 nm are also seen in the SEM images. The appearances of these ZnO nanoparticles may be originated due to the short duration of reaction. With increasing the processing time these ZnO nanoparticles become bigger and form the mircoparticles on the surface of the substrate. The SEM images of ZnO nanowires grown for 60 min are at different magnifications shown in Fig. 2. The diameters of most of the as-grown ZnO nanowires are in the range of 25-35 nm. The observed nanowires show smooth curvature with smooth surface. The lengths of these nanowires are up to several tens of micrometers. Moreover, hexagonal shaped some ZnO mircoparticles have also been observed onto the substrate. Fig. 3(a) and (b) shows the low and high magnified images of ZnO nanowires grown on Si(100) substrate for 90 min. The average diametes of the nanowires range from 20 to 30 nm and their lengths are, however, observed similar to the earlier case. It is observed that the diameter of the nanowire is uniform throughout its length. It is also interesting to see that the nanowires bend (kink) at specific angles and parts in between kinks are straight. These nanowires are kinked randomly, i.e. some nanowires are curved and kinked at ~85°, ~37°, ~100° etc. The formation of such type of nanowires is also reported earlier [Wu et al., 2003]. It is argued that during the random growth of nanowires, when two wires come in contact, they induce strain on each other leading to the formation of

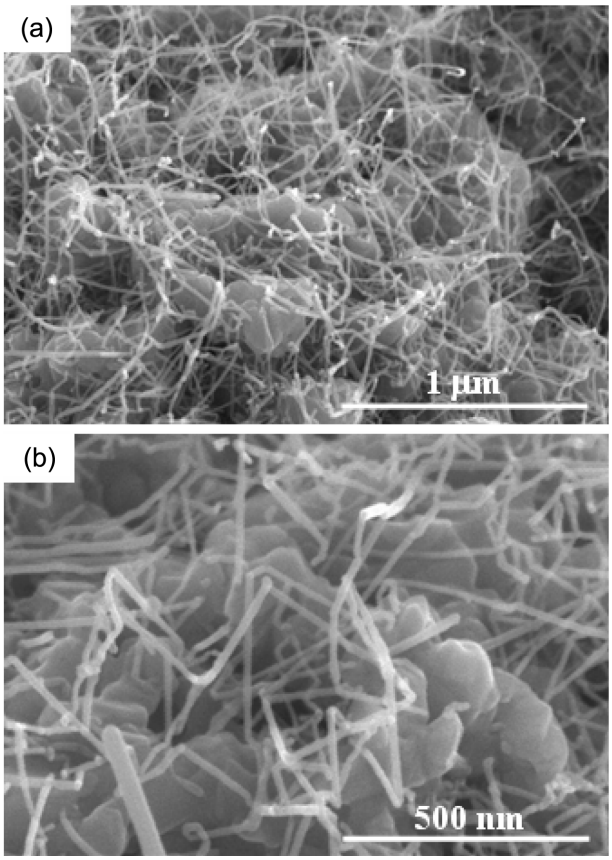

Fig. 3. (a) Low and (b) high magnification SEM images of ZnO nanowires grown for 90 min.

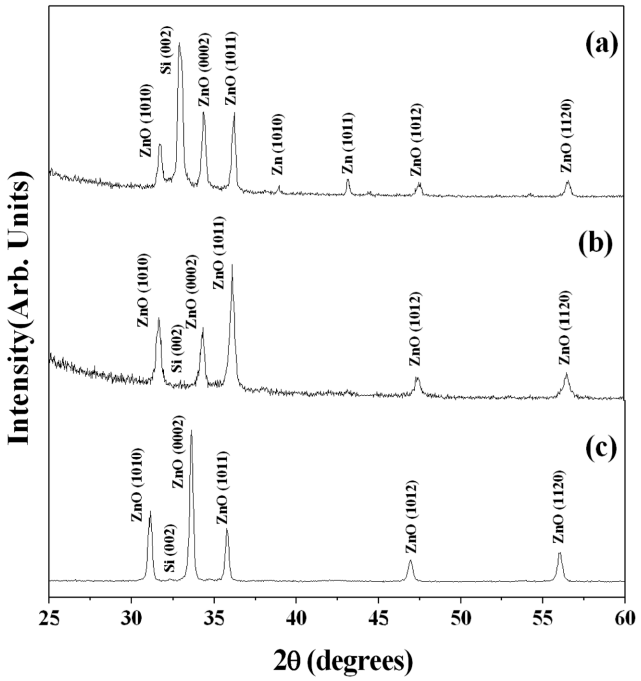

Fig. 4. XRD patterns of the ZnO nanowires grown for (a) 30, (b) 60 and (c) 90 min: the indexed peaks are corresponding to the typical wurtzite hexagonal structure for the grown products.

kinks [Wu et al., 2003]. Some randomly grown ZnO crystals are also obtained beneath the grown ZnO nanowires. It is interestingly noted that the size of the ZnO particles increases with increasing the time because of an increase of deposition rate with increasing the time. From these SEM images, it is clearly indicated that the optimum time is very important factor to get the good quality, smooth and long-sized nanowires.

The crystallinity and phase identification of the ZnO nanowires grown at different processing time have been ascertained by X-ray diffraction (XRD) analysis and the results are shown in Fig. 4. As can be seen, in all the cases, sharp diffraction peaks corresponding to the wurtzite (hexagonal) structure of ZnO have been observed. There exists a little contribution due to unreacted Zn in sample processing for 30 min (a). This may be attributed to premature growth of ZnO nanowires. At a longer processing time, however, precipitation of stoichiometric ZnO phase results with no indication of formation of other non-stoichiometric phase of ZnO. Finally, the obtained diffraction peaks in all the spectra correspond to the single crystallinity with the wurtzite hexagonal phase for the deposited ZnO nanowires.

The transmission electron microscopy (TEM) provides further information regarding the structural aspects of as-grown ZnO nanowires. The typical result corresponding to 60 min. processing time is shown in Fig. 5. Low magnified image shows that the average diameter of nanowires found to be 30-40 nm and having smooth surface topology throughout their length (a). This result is consistent with the SEM observations. The dark and light colors are observed on the most part of the nanowires which are most probably due to the strains. The selected area electron diffraction pattern reveals a well defined, ordered diffraction pattern indicating very high crystallinity (single crystal) of the observed ZnO nanowires. The lattice spacing calculated from the results reveals lattice spacing of 0.52 nm, which is an excellent agreement with the lattice constant of single crystalline ZnO and indicates that the deposited materials have wurtzite structure. It further reveals that the nanowires grow preferentially along the [0001] c-axis direction.

The growth process for the ZnO nanowires grown on silicon substrate at different processing time follows the phase transformation of metallic zinc powder into the ZnO through the thermal oxidation process without the use of any metal catalyst or additives. It is known that the melting point of Zn or Zn suboxides is approximately 419 °C. So in the initial stage of evaporation, as the temperature of the furnace increases above the melting point of Zn, the zinc vapor from the quartz boat is transferred to the substrate surface and forms Zn or Zn suboxide liquid phase droplets. These liquid phases of Zn or Zn suboxides play an important role in the nucleation of ZnO nanowires rather than alloy droplets as happens in the vapor-liquid-solid (VLS) growth mechanism [Wagner et al., 1964; Duan et al., 2000]. Crystalline ZnO is formed when the Zn or Zn suboxides becomes saturated and forms nucleation sites. The liquid phase droplets boosted the Zn to react with the oxygen at its nucleated site and leads to the formation of one dimensional single crystalline ZnO. As the deposition time increases, the precipitation on these liquid droplets increases, results the formation of longer length nanowires. It was noted in our experimental results that the optimum deposition time is one of the most important parameter to obtain the

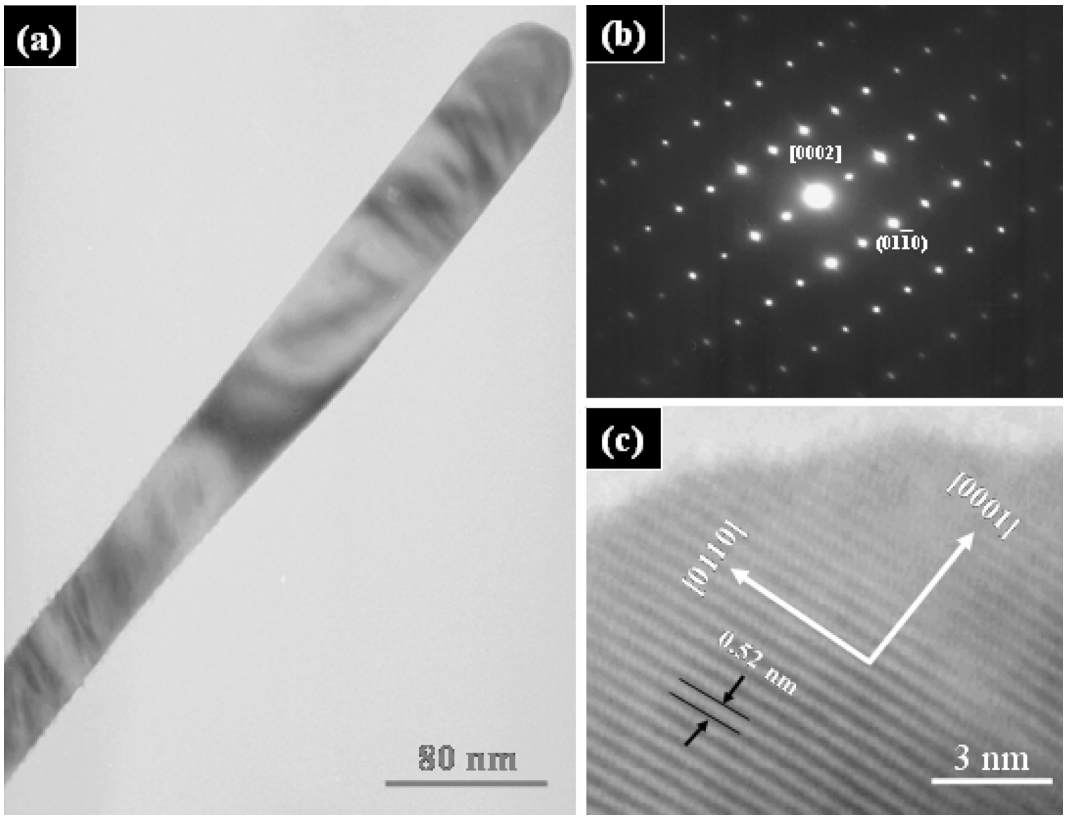

Fig. 5. (a) Low magnification TEM image and (b) selected area electron diffraction (SAED) pattern, and (c) high-resolution TEM image of the ZnO nanowire grown for 60 min.

good quality and long length ZnO nanowires. At the deposition time of 30 min, very small length and collapsed ZnO nanowires were obtained onto the substrate while nanowires observed on the substrate deposited for 90 min exhibited the kinked and curved morphologies. Smooth surface with smooth curvature nanowires were obtained for 60 min growth. In addition of these, the ZnO has a faster growth rate in the [0001] direction and the HRTEM and SAED pattern of as-grown nanowires confirm that the nanowires are grown in the [0001] and preferentially oriented in the c-axis direction.

To determine the optical properties of the as-grown ZnO nanowires at different process time, the PL measurements were done at room temperature. Fig. 6 shows the room temperature photoluminescence spectrum of the synthesized ZnO nanowires using a He-Cd laser with an excitation wavelength of 325 nm. Generally two bands have been observed in the PL spectrum for ZnO nanostructures: a UV peak attributed as near band edge emission of the wide band gap of ZnO and a green band peak in the visible region. The UV emission is originated because of the free-exciton recombination and the green emission is attributed to a deep level emission caused by the impurities and the structural defects such as zinc interstitials and oxygen vacancies. In all the cases, a strong, sharp and dominated UV emission at 380 nm was observed while broad and suppressed green band at 510-515 nm was observed from the nanowires grown for 30 min. No and very suppressed green band was exhibited in the PL spectra of ZnO nanowires grown for 60 and 90 min, respectively. The appearance of green band in the visible region is due to the recombination of a photogenerated hole with

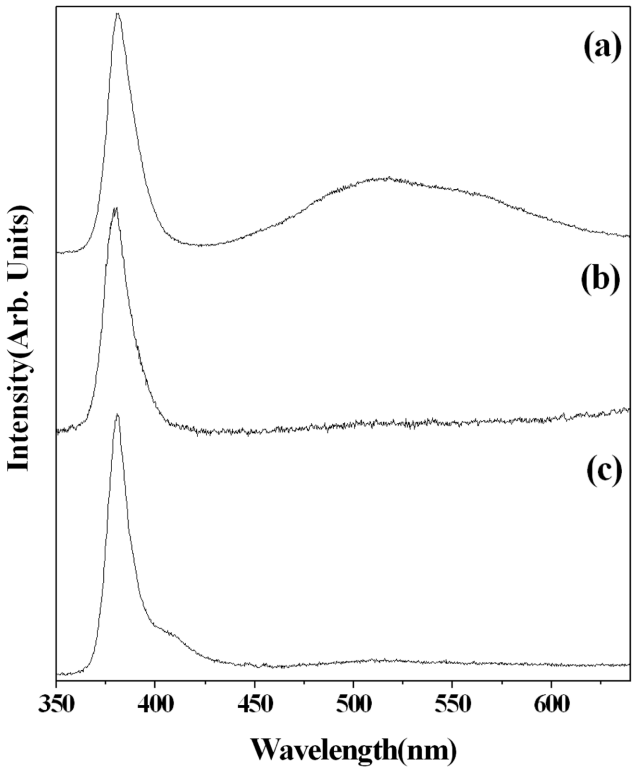

Fig. 6. Room temperature photoluminescence spectra of the synthesized ZnO nanowires at (a) 30, (b) 60 and (c) 90 min using a He-Cd laser with an excitation wavelength of 325 nm.

the single ionized charged state of the defects in the ZnO [Vanheusden et al., 1996; Xing et al., 2003]. So the appearance of sharp and strong UV emission in all the cases indicates that the as-grown ZnO nanowires are good in crystal quality. However, the existence of broad green emission from the nanowires grown for 30 min exhibits that they have few structural defects, which are originated most probably because of the early growth of nanowires and the presence of unreacted zinc with the ZnO nanostructures as observed from the XRD which confirms the presence of zinc peak in the spectrum. For 90 min growth, defects are found in the kink parts of the nanowires growing along the [0001] direction, resulting in very suppressed but broad green emission. It was reported that the kink parts in the ZnO nanowires may be able to cause stacking faults and dislocation which are responsible for the appearance of green emission in the visible region [Wang et al., 2004]. Overall the obtained ZnO nanowires on different processing times show the good optical properties with good crystal perfection and may be applicable for the fabrication of optoelectronic, and nanodevices in the near future.

CONCLUSIONS

In summary, the time dependent synthesis of ZnO nanowires synthesized by the thermal evaporation of high purity metallic zinc powder on Si(100) substrate at 650 °C without the use of any metal catalyst or additives. The examination of the grown nanowires using scanning electron microscopy (SEM) exhibited that by extending the growth time, the length of ZnO nanowires increases. The high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction patterns indicated that the as-grown products are high crystalline with wurtzite hexagonal phase and preferentially oriented in the [0001] direction. Room temperature photoluminescence studies exhibited a strong UV emission and a suppressed green emission indicated good optical properties for the grown ZnO nanowires.

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