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Synthesis and characterization of well-aligned catalyst-free phosphorus-doped ZnO nanowires

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ABSTRACT

Highly crystalline P-doped ZnO nanowires were grown by physical vapour transport technique without presence of any catalysts. Grown nanowires were well aligned and had good crystallinity with evolution of preferred orientation (0 0 2). Both EDX and Rutherford backscattering spectrometry (RBS) results revealed that phosphorus atoms were incorporated in the ZnO nanowires with the content of less than 1%. The XRD results confirmed an increase in lattice spacing which is attributed to substitution of P on oxygen sites. The photoluminescence spectra of grown nanowires showed a strong emission peak at 3.248 eV with a shoulder at 3.184 eV, corresponding with FA (free electron to acceptor) and DAP (donor–acceptor pair) levels of P-doped ZnO. The lattice spacing from HRTEM agrees with the achieved results from XRD measurement.

1. Introduction

Recent investigations on zinc oxide (ZnO) nanostructures, a II–VI compound semiconductor with high band gap energy (3.37 eV) and large exciton binding energy (60 meV), have made important progress in its utilization in lasing applications and light emitting diodes (LEDs) [1–6]. Its high band gap energy can be tuned up in a wide range by doping with other materials [7]. These unique properties, along with the demands for production of one dimensional nano devices, make ZnO nanowires a more promising material for fabricating LEDs, field effect transistors, sensors, optoelectronic devices, logic circuits, and lasers with a wide range of lasing wavelengths [6,8].

To realize most of these applications, it is essential to have both n-type and p-type ZnO nanowires. However, wurtzite crystalline ZnO is naturally n-type and because of asymmetry in doping, synthesizing p-type ZnO with high dopant concentration and stability is still difficult. Up to now, only a few results have been reported in fabrication of p-type ZnO nanostructures (nanowires and nanobelts) [9–13]. In these reports usually group I and V elements were used as acceptors to make p-type ZnO, especially, elements of group V were widely investigated [14]. Among the elements of group V, nitrogen can be substituted at oxygen sites without significant change in the ZnO lattice constant and phase due to its close radius to oxygen. However, its substitution inside the ZnO forms both p- and n-type doping, with a domination of n-type in most cases. Moreover, some researchers have reported the low stability of N-doped ZnO materials [11,16]. Recently, some groups have considered phosphorus as a p-type dopant for ZnO nanostructures, particularly on ZnO thin films [7,12,15,17–20]. There are only a few reports on characterization of phosphorus-doped ZnO nanowires. Among them, Kim et al. [18] reported successful synthesizing phosphorus-doped ZnO nanowires (ZnO:P) via a vapour transport process based on a single source precursor, Zn_3P_2, and Au as a metal catalyst. However, the nanowires were not well aligned, and the metal catalyst resulted in impurity of the nanowires.

In this paper, an easy method is used to fabricate well-aligned high density phosphorus-doped ZnO nanowires on (1 0 0) silicon substrates in the absence of any catalysts. For the first time we used a phosphorus-doped ZnO powder as the source material in a conventional physical vapour transport (PVD) system. We also investigated characteristics of these ZnO:P nanowires which confirmed the incorporation of phosphorus in individual ZnO nanowires.

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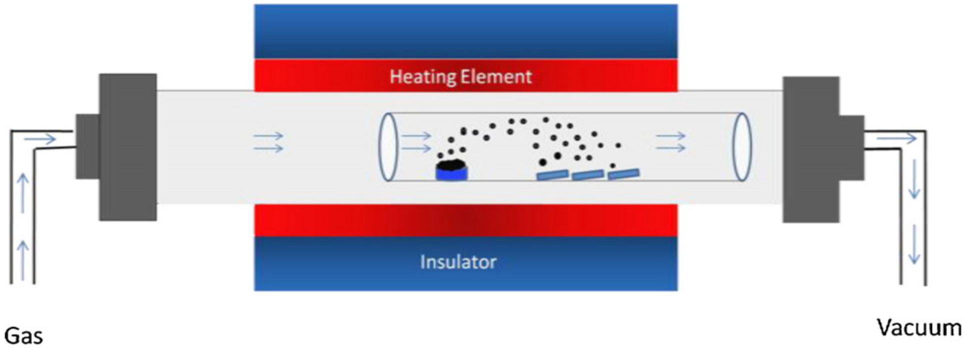

Fig. 1. Schematic diagram of vacuum PVD system including inner and outer tubes in vacuum pressure.

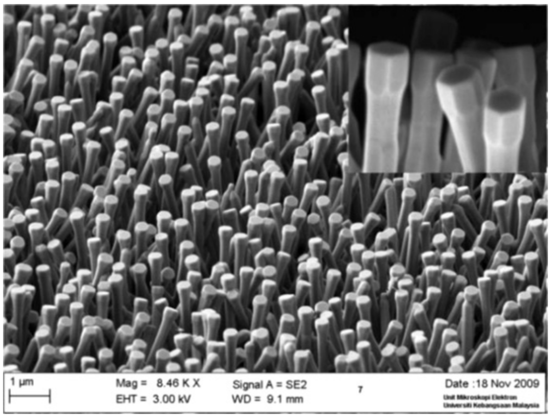

Fig. 2. Low magnification FESEM image of ZnO:P nanowires, the inset is high resolution image of nanowires.

2. Experimental

Well aligned ZnO:P nanowires are grown by thermal evaporation of a mixed source of a chemical compound of phosphorus and ZnO powder (Plasmaterials – 99.99%) and graphite powder (99.99%) with a weight ratio of 1:1, in a setup shown schematically in Fig. 1. The growth chamber consists of an open/open quartz tube which is placed inside the bigger quartz tube furnace. The (1 0 0) Si wafers were cleaned by normal cleaning procedures. Subsequently, the boats containing powder materials and cleaned substrates are loaded into the centre of inner tube (hot zone) and 14 cm downstream of the centre point, respectively. The substrates are slightly inclined in order to get more uniformity in growth. This inner tube was then placed inside a horizontal quartz tube furnace. After loading the powder materials and samples, the chamber is evacuated to a pressure around 1 Torr by using a rotary pump (Edwards 500). Then, the heater is warmed up to 1050 °C at a constant rate of 30 °C/min from the room temperature and the mass flow controller is set to 50 sccm. By introducing the carrier gas, the pressure increases towards 10 Torr. The growth process lasted for 90 min. After cooling down the tubes, light yellowish white colour product was visible on the surface of the substrates. The same process with pure ZnO and C powder was used for growing pure ZnO nanowires for comparison. The structural and morphological properties of grown nanowires were characterized by field emission scanning electron microscopy (FESEM) [Zeiss model SUPRA 55VP], energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM). X-ray diffraction (XRD) technique [PANalytical Xpert Pro XRD diffractometer] and photoluminescence (PL) spectroscopy [Jobin Yvon HR 800 UV spectrometer system] were used for understanding the crystallinity and purity of grown nanowires. Moreover, Rutherford backscattering Spectrometer (RBS) measurements were performed to examine and reconfirm the elemental composition of the phosphorus-doped ZnO nanowires by utilizing a collimated 2.0 MeV He$^+$ beam produced by 5UDH-2 Pelletron accelerator. The sample was mounted on a high precision (0.01°) three-axis goniometer in a vacuum chamber, so the orientation of this sample relative to the He$^+$ beam could be precisely controlled. The backscattered particles were collected by an Au–Si surface barrier detector. The detection angle was 165° and its energy resolution was about 15 keV.

3. Results and discussion

Surface morphology of as-grown ZnO:P nanowires were studied by FESEM. Fig. 2 shows the low magnification image of the sample, which indicates that entangled and uniform ZnO:P nanowires were grown on the Si substrate. High resolution image of nanowires,

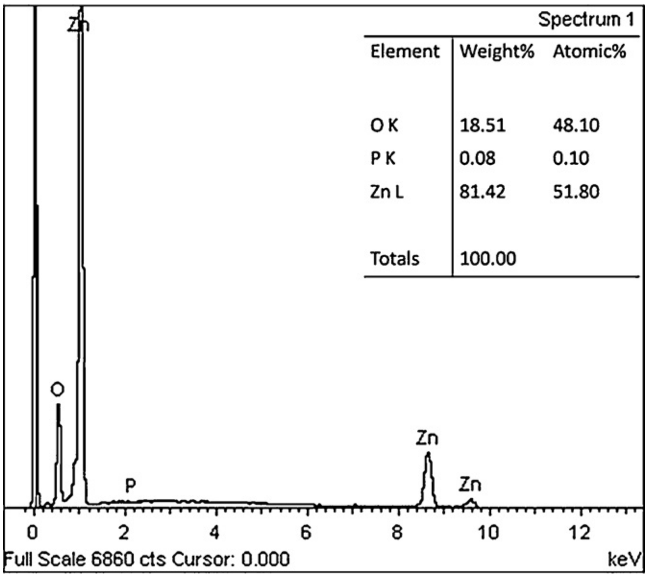

Fig. 3. The EDX spectrum reveals that as grown nanowires do not have other dopants or catalysts except P along with Zn and O.

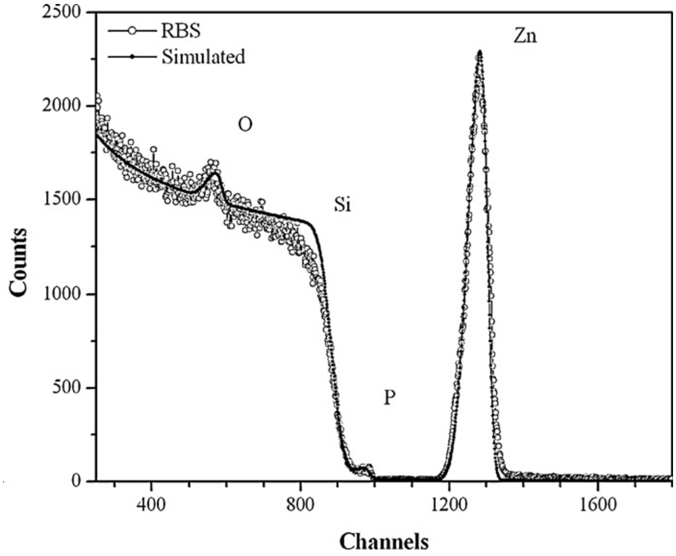

Fig. 4. Rutherford back scattering (RBS) spectra of ZnO:P nanowires exhibits the incorporation of phosphorus inside the nanowires.

which is shown in the inset of Fig. 2, revealed that the ZnO:P nanowires were straight and had smooth surface and hexagonal shape. The average diameter and length of nanowires were 80–120 nm and 2–3 μm, respectively.

Elemental analysis of grown ZnO:P nanowires, which was examined by an EDX spectrometer attached to SEM [Oxford INCA PentaFETx3] is shown in Fig. 3. According to these results, Zn, O and P peaks were observed at 1.012 keV, 0.523 keV and 2.013 keV, respectively. No other peaks belonging to other metals, which could act as catalysts, were found. The percentage of elements which are shown in the inset of Fig. 3 reveals that there is no considerable O vacancy, the ratio of O to Zn is near to one, and P atoms are incorporated in the ZnO structure with the content of around 0.1%. Further EDX measurements on the tip and stem of individual nanowires resulted in roughly the same results.

Since, the peak of phosphorus in the EDX spectra is not so strong, to confirm the successful doping of ZnO nanowires; Rutherford backscattering Spectrometer (RBS) measurements were utilized too. A simulation of random spectrum was performed by RUMP program. The P peak obviously can be recognized in the RBS spectrum, which is shown in Fig. 4.

X-ray diffraction spectra of undoped and phosphorus-doped ZnO nanowires, grown under the same conditions, are shown in Fig. 5. These patterns confirmed that both samples have wurtzite crystalline structures, and no secondary phases are formed in them.

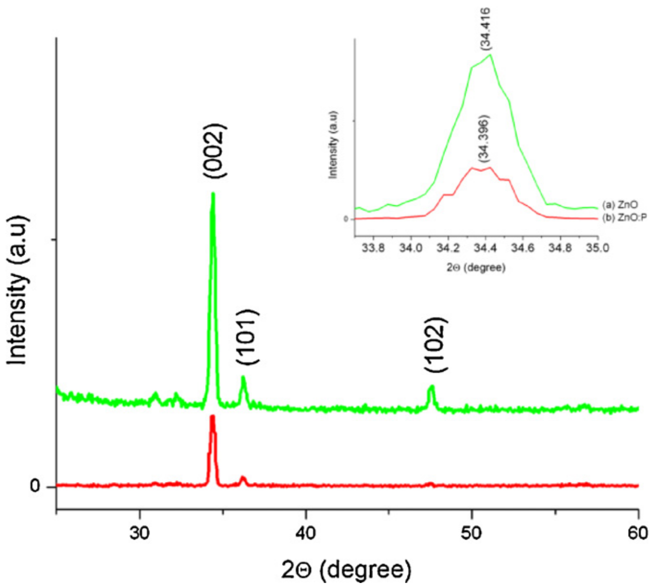

Fig. 5. XRD spectra of pure ZnO and ZnO:P nanowires that were grown in same conditions.

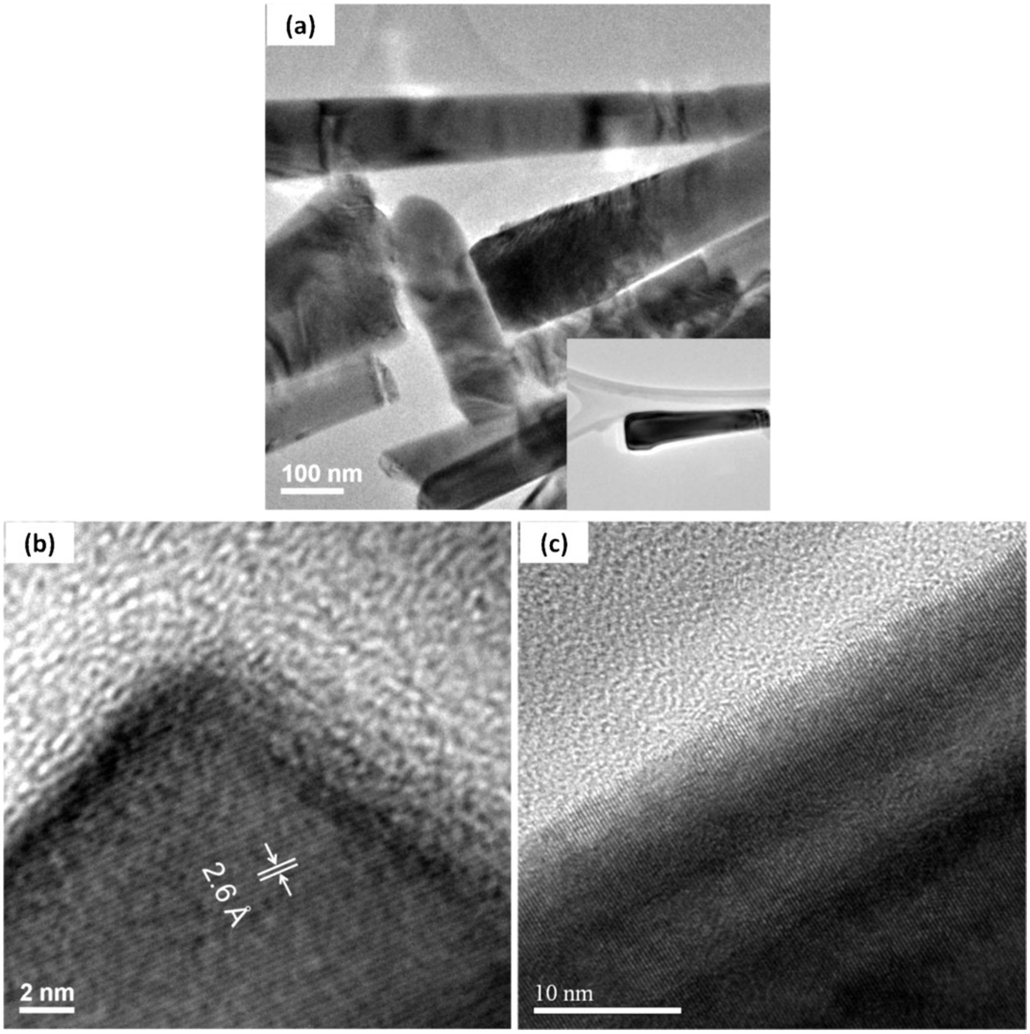

Fig. 6. TEM images of P doped and pure ZnO nanowires, (a) the TEM images of nanowires, the insets shows the high magnification image of a single nanowire; (b) HRTEM image of ZnO:P nanowire; and (c) the HRTEM image of pure ZnO nanowire grown at same condition.

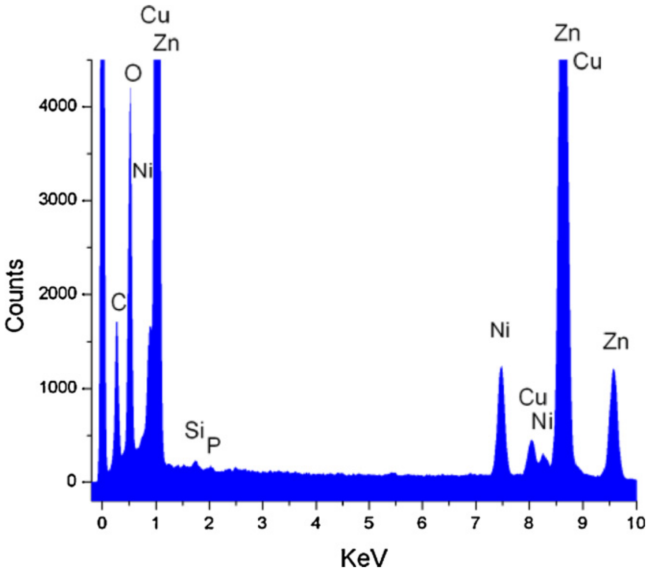

Fig. 7. The EDX result of HRTEM from a single nanowire shows the P peak at 2.013 keV.

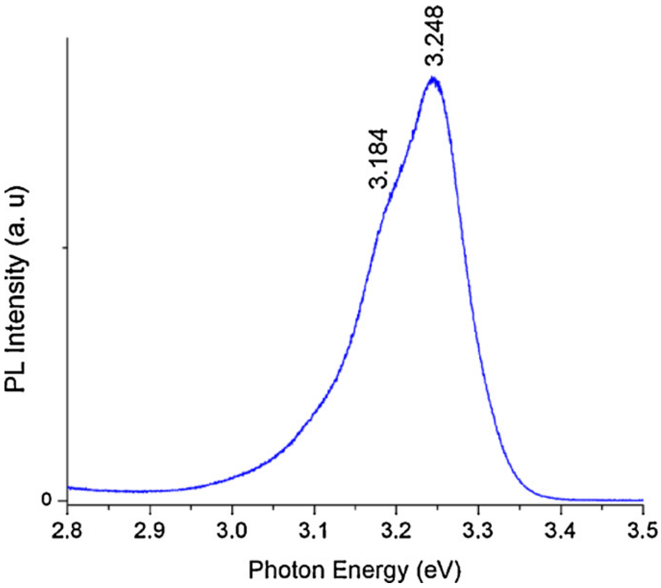

Fig. 8. The room temperature PL spectra of ZnO:P nanowires grown on (1 0 0) Si substrate, It can be seen that the position of UV peak is slightly blue-shifted compared to corresponding peak position of pure ZnO.

The structures have diffraction peaks around 34.4° and 36.5° corresponding with the indexes of (0 0 2) and (1 0 1) (ICCD-PDF no. 03-065-3411). The predomination of the (0 0 2) peak and absence of other peaks in the spectra confirms that the ZnO:P nanowires have wurtzite crystalline structures with a preferential orientation along the c-axis and almost perpendicular to the Si substrate. A decrease in diffraction intensity of the ZnO:P peak was observed compared to pure ZnO peak. This degradation in crystalline quality can be attributed to incorporation of phosphorus in the ZnO lattice. The high resolution XRD image, which is shown in the inset of Fig. 5, reveals that the position of (0 0 2) peak is slightly shifted towards a lower angle compared to the corresponding peak position of an undoped sample, also the full width at half maximum (FWHM) values of 0.344° and 0.394° were obtained for pure and doped ZnO nanowires, respectively. Based on comparison of ionic radii of P, Zn and O, an increase in lattice spacing is expectable with substitution of P on oxygen sites.

Fig. 6 shows the morphology and atomic arrangement of pure and P-doped ZnO nanowires, which are investigated by HRTEM. Fig. 6a illustrates the TEM image of nanowires; the inset of Fig. 6a shows the high magnification image of a single ZnO:P nanowire. Shown in Fig. 6b, is the HRTEM image of doped ZnO nanowire. It reveals that the lattice fringes are in the ordered atomic arrangement on the surface of nanowires with a lattices spacing about 2.6 Å, corresponding to the (0 0 2) fringes of the wurtzite hexagonal ZnO. The lattice spacing of pure ZnO nanowire, grown at same conditions, was measured 2.57 Å (shown in Fig. 6c). The increment of lattice spacing in P-doped nanowire compared to pure nanowire, agrees with the achieved results from XRD measurement.

For confirmation of elemental composition in an individual nanowire, EDX measurements were carried out by the EDX spectrometer attached to TEM. The EDX spectrum, which is shown in Fig. 7, confirms the existence of trace amounts of phosphorus, as well as Zn and O. It should be noted that the corresponding peaks of Zn were intentionally limited to reveal the low intensity spectra. The other peaks such as Cu, Ni, C and Si come from copper grid and substrate contamination.

PL measurement was performed at room temperature by using a helium cadmium laser (325 nm) as an excitation source, with diameter of the laser spot on the sample around 1 μm. Fig. 8 shows the room temperature PL spectrum of ZnO:P nanowires grown on Si substrate in the range of 2.8–3.5 eV. The PL spectra show a main peak at 3.248 eV with a shoulder on the lower energy side around 3.184 eV. For phosphorus-doped ZnO, the peaks corresponded with FA (free electron to acceptor level) and DAP (donor–acceptor pair) levels, respectively, which were reported elsewhere [18,20,21]. Beside of this UV emission peak, a strong and broad luminescence band was observed around 2 eV which is not shown here. It has been suggested that this green band peak is related to the deep level emission (DLE), which is resulted by the impurities and structural defects in the crystal [22].

4. Conclusions

In summary, well aligned phosphorus-doped ZnO nanowires were grown on (1 0 0) Si wafer by thermally vaporizing a mixed source of phosphorus and ZnO compound powder (99.99%) and graphite powder (99.9%) in a PVD reactor consisting of inner and outer tubes. No metal catalyst was used in the growth process. The results from EDX of TEM and RBS measurement revealed an incorporation of phosphorus atoms in grown nanowires. The atomic percentage of dopants was measured at about 0.1%. The XRD pattern confirmed wurtzite crystalline growth of ZnO:P nanowires with preferential (0 0 2) peak which is slightly shifted towards a lower angle compared to the corresponding peak of pure ZnO. Moreover, the results from HRTEM, confirmed the ordered atomic arrangement of nanowires with a lattice spacing of 2.6 Å and 2.57 Å for doped and pure ZnO nanowires, respectively, which agrees with the achieved XRD results. The PL spectra showed a strong emission at 3.248 eV with a shoulder at 3.184 eV which have been reported for FA (free electron to acceptor) and DAP (donor–acceptor pair) levels of phosphorus-doped ZnO, respectively. This peak is slightly blue shifted compared to the UV peak of pure ZnO.

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