# Vertically well aligned P-doped ZnO nanowires synthesized on ZnO–Ga/glass templates

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**Vertically well aligned P-doped ZnO nanowires were prepared on ZnO–Ga/glass templates at 550 °C by reactive evaporation without metal catalysts and the nanowires were found to be single crystalline with the würtzite structure, oriented in the *c*-axis direction; the P-doping shortened the physical lengths of the ZnO nanowires without changing their diameter, and furthermore, the introduction of P atoms resulted in a much weaker and broader ZnO band edge emission.**

ZnO is an n-type semiconductor with a large exciton binding energy (60 meV) and a large bandgap energy (3.37 eV at room temperature). These properties make it one of the most promising materials for optoelectronic devices that operate in the blue and ultraviolet (UV) regions. In recent years, one-dimensional (1D) ZnO nanostructures, including nanotubes,[1,2] nanowires,[3] nanobelts,[4] nanorods,[5] nanocables[6] and nanoribbons[7] have attracted substantial interest because of their potential applications in nanoelectronics and nano-optoelectronics. For practical device applications, proper dopants must be introduced into the nanowires. The morphology, conductivity and optical properties of 1D ZnO nanowires depend strongly on the concentration of impurities.[8–16] Group III metals such as Al,[10] Ga[9,11] and In,[12] and transition metals such as Cu,[13] Cd,[14] Mn[15] and Co[16] can all be doped into 1D ZnO nanowires. Group V elements must be introduced into the 1D ZnO nanowires to achieve p-type behavior. Although N[17] and As[18,19] can also be doped into 1D ZnO nanowires, no P-doping in 1D ZnO nanowires has been reported to the authors' knowledge.

The other important issue is the choice of substrate materials. Glass substrates are transparent and inexpensive. They are also commercially available in large sizes. Therefore, glass is an ideal substrate material for large optoelectronic devices, such as 1D-based light emitters, photodetectors and field emission displays (FEDs). However, glass substrates are amorphous and weak at high temperatures. Very recently, the authors reported the fabrication of pure ZnO nanowires grown on ZnO–Ga/glass templates at 600 °C.[20] This investigation reports the reactive evaporation growth of P-doped ZnO single crystal nanowires on ZnO–Ga/glass templates. The physical and optical properties of the P-doped ZnO nanowires will also be discussed.

Before P-doped ZnO nanowires were grown, a 50 nm-thick (002) oriented ZnO–Ga film was deposited onto glass substrates by magnetron sputtering. P-doped ZnO nanowires were then grown on the ZnO–Ga/glass templates. 99.9% pure Zn (0.3 g) and 99% pure $Zn_3P_2$ (0.05 g) metal powders were mixed by grinding. The ZnO–Ga/glass template and the Zn–$Zn_3P_2$ mixture powder were then placed on an alumina boat, and inserted into the quartz tube of a horizontal tube furnace. Constant streams of argon (54.4 sccm) and oxygen (0.8 sccm) gases were then introduced into the furnace. During growth, the pressure inside the quartz tube, the heating ramp rate, the growth time and the growth temperature were maintained at 9 Torr, 20 °C $min^{-1}$, 60 min and 550 °C, respectively. For comparison, pure ZnO nanowires without P-doping were also prepared under exactly the same conditions.

A Philips PW3710 X-ray diffractometer (XRD) and a JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM), operated at 200 kV, were used to characterize the crystallography and structure of the as-grown samples. The surface morphologies of the samples and the size distribution of the nanowires were characterized using a JEOL JSM-6500F field emission scanning electron microscope (FESEM), operated at 5 keV. Photoluminescence (PL) properties of the nanowires were also characterized using a Jobin Yvon-Spex fluorolog-3 spectrophotometer. A Xe lamp, emitting at 254 nm, was used as the excitation source during PL measurements.

Fig. 1(a) presents a cross-sectional FESEM image with a 15° tilt angle of the P-doped ZnO nanowires. The insert in the upper left-hand corner of Fig. 1(a) displays an enlarged image of the same sample. These images demonstrate that high-density nanowires were grown uniformly in the sample. Fig. 1(b) shows the XRD $2\theta$-scan pattern of the P-doped ZnO nanowires. That the extremely sharp ZnO (002) and (004) diffraction peaks are present in the diffraction pattern demonstrates that the P-doped ZnO nanowires had a preferred orientation along the *c*-axis direction. Fig. 1(c) presents an HRTEM image taken from the sidewall portion of one P-doped ZnO nanowire. The crystal lattices of the nanowires were clearly well oriented with no observable defects suggesting that the P-doped ZnO nanowires prepared in this investigation were structurally uniform and defect-free. The lower left-hand corner of Fig. 1(c) presents a selected area electron diffraction (SAED) image of the P-doped ZnO nanowires. Such a diffraction pattern reveals that the P-doped ZnO nanowires reported herein are single crystalline with the würtzite structure. The 0.52 nm lattice spacing observed from Fig. 1(c) is equivalent to the spacing between two

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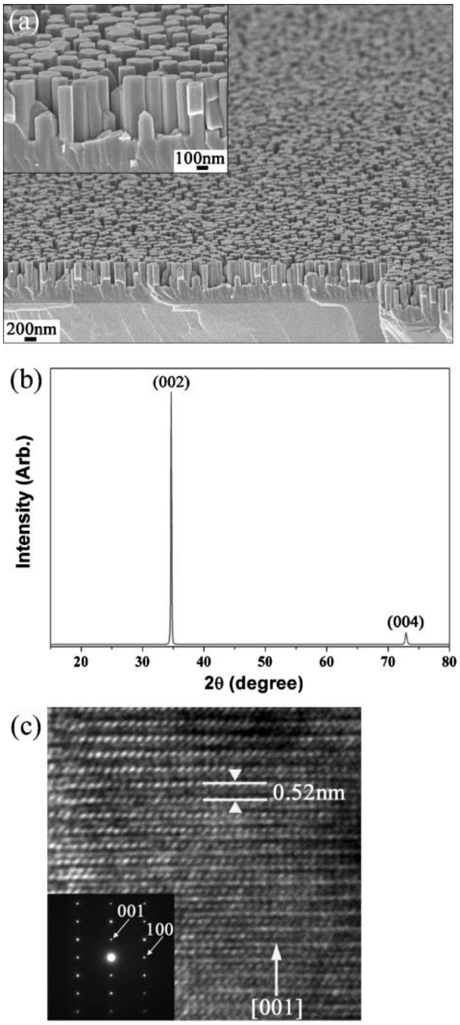
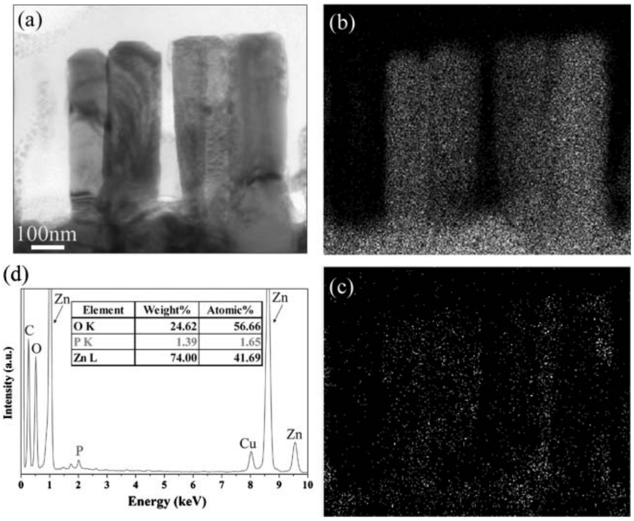


**Fig. 1** (a) Cross-sectional FESEM image, (b) XRD spectrum and (c) HRTEM image of the P-doped ZnO nanowires grown on the ZnO–Ga/galss templates. The insert in (a) is an enlarged image and the inset in (c) is the SAED image of the same sample.



| Element | Weight% | Atomic% |
|---|---|---|
| O K | 24.62 | 56.66 |
| P K | 1.39 | 1.65 |
| Zn L | 74.00 | 41.69 |

**Fig. 2** (a) Cross-sectional HRTEM image, (b) Zn EDX mapping image, (c) P DEX mapping image and (d) EDX spectrum of the P-doped ZnO nanowires grown on the ZnO–Ga/galss templates.

ZnO (002) crystal planes. This value is exactly the same as that of bulk würtzite ZnO crystal.

Fig. 2(a) displays the cross-sectional HRTEM image of P-doped ZnO nanowires. The brightness contrast observed in this image could be attributed to the various crystallographic planes. The authors thus believe that the sputtered ZnO–Ga layer has a grainy and columnar structure and that the P-doped ZnO nanowires formed were grown along the columnar grains of the sputtered ZnO–Ga layer. However, the average length of the P-doped ZnO nanowires was approximately 500 nm and the diameters were 80–160 nm. In contrast, the lengths and diameters of the pure ZnO nanowires were around 2.0–2.5 μm and 120–180 nm, respectively. Restated, P-doping markedly shortens the physical lengths and reduces the diameters of the ZnO nanowires. Figs. 2(b) and 2(c) show corresponding Zn and P energy dispersive X-ray (EDX) spectroscopic mapping images, respectively. The observation of the P-related image also demonstrates that P atoms were indeed doped into the ZnO nanowires. These two EDX mapping images reveal that Zn and P atoms were distributed uniformly in the P-doped ZnO nanowires. Fig. 2(d) depicts an EDX spectrum of the P-doped ZnO nanowires. The weak copper and carbon signals originated from the TEM copper grids and the carbon adhesion film, as shown by the inset of Fig. 2(d). The intensity ratios among the Zn, O and P peaks suggests that the P content in the nanowires was approximately 1.65 atom%.

Fig. 3 plots the room temperature PL spectra of pure and P-doped ZnO nanowires grown on ZnO–Ga/glass templates. Introducing P atoms substantially weakened and broadened the ZnO band edge emission.[21] The P atoms also caused a slight red shift in the ZnO band edge emission from 378 to 380 nm. The authors believe that such a red shift is related to the lattice strain caused by the P atoms. Moreover, P-doped ZnO nanowires exhibited much stronger deep level emission at 545 nm. This deep level emission had been shown to be related to the singly ionized oxygen vacancies in ZnO.[22] The stronger deep level emission seems to indicate that P-doping increased the number of oxygen vacancies in the ZnO nanowires and so degraded the optical properties.

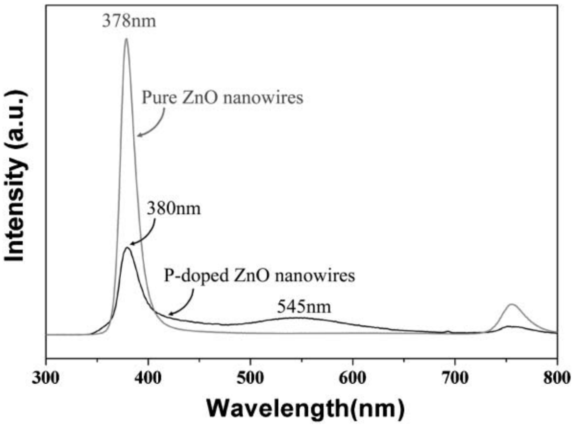


**Fig. 3** Room temperature PL spectra of the pure and P-doped ZnO nanowires grown on ZnO–Ga/glass templates.

In summary, vertically well aligned P-doped ZnO nanowires were prepared on ZnO–Ga/glass templates at 550 °C. P-doped ZnO nanowires were single crystalline with the würtzite structure oriented in the *c*-axis direction. P-doping markedly shortened the physical lengths and slightly reduced the diameters of the ZnO nanowires. Introducing P atoms substantially weakened and broadened ZnO band edge emission.

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