First ZnO Rectangular Nanorod Arrays grown with Al Doping Concentration Fluctuation
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Composition fluctuation induced growth of Al:ZnO rectangular nanorod arrays, Nanotechnology 19 035605 (2008).

Low dimensional nanomaterials have attracted great interests because of their unique and fascinating optical, electrical, mechanical, and piezoelectric properties together with their wide uses in fundamental scientific researches and potential technical applications. In addition to the conventional nanowires, many interesting morphologies have been synthesized recently, such as nanocombs [1], nanorings [2], nanowalls [3], nanopencils [4], and conic nanotubes [5]. Those fantastic structures not only provide valuable models for understanding crystal growth mechanisms at nanometer scale, but also exhibit great potential for fabricating excellent optoelectronic nanodevices, such as comb gratings [6], field emission [4,5], and photocatalysts [7], etc. However, while the possible growth mechanisms of many fantastic nanostructures have been proposed, the influence of impurities and defects on formation of the nanostructures has rarely been studied.

In the article, we provide another interesting route of fabricating Al: ZnO rectangular nanorods by doping induced composition fluctuations. The rectangular nanorods are nucleated from a sheet-like nanostructure with periodic thickness fluctuations resulting from doping concentration modulation. Transmission electron microscopy (TEM) characterization shows the difference in Al concentration and lattice constant between the rectangular nanorods and neighboring nanosheets.
The Al doped ZnO rectangular nanorods were synthesized via alloy evaporation deposition (AED) method on Si(100) substrate [8]. Zn and Al mixed powder (weigh ratio=93:7) was placed in an aluminum boat located inside a 1 in. diameter horizontal quartz tube reactor. The sources were heated at a rate of 20 °C/min from room temperature to an alloying treatment temperature. Argon was introduced as the carrier gas at the beginning with a flow rate of 8 sccm and the working pressure was kept at 50 Torr. The alloying treatment for the Al:ZnO nanostructures was carried out at 500 °C for 30 min. After the alloying treatment, the pressure was decreased to 1 Torr and the system was heated again at a rate of 20 °C/min to 650 °C. Once the temperature was raised to 650 oC, oxygen was introduced into the chamber with a flow rate of 1 sccm. After heating at 650 oC for one hour, the substrate was slowly cooled down to room temperature in the furnace.

A typical scanning electron microscopy (SEM) image of Al: ZnO rectangular nanorod array is shown in Figure 1(a). This structure exhibits rare four-fold or two-fold symmetry instead of the common six-fold symmetry of ZnO. An entire view of the rectangular nanorod arrays is shown in the inset of Figure 1(a).

Figure 2(a) shows a low-magnification TEM image of the Al: ZnO rectangular nanorod arrays. The uniform contrast indicates uniform thickness over individual nanorods. A corresponding diffraction pattern in Figure 2(b) reveals that the rectangular nanorods are single-crystalline wurtzite structure growing along the c-axis, while the top and side facets were (2 1 0) and (1 0 0) planes, respectively. A HRTEM image of the interface region of a rectangular nanorod and contiguous nanosheet is shown in Figure 2(c). The lattice constants of the rectangular nanorod and nanosheet are 5.10 Å and 5.12 Å, respectively, from fast Fourier transform patterns of the corresponding areas in Fig. 2(c). Besides, there are obvious lattice distortions and dislocations near the interface region as shown in the dashed circles. The atomic ratios of Al to (Al+Zn) in the rectangular nanorod and nanosheet calculated from the EELS spectrum are around 6.13 at.% and 4.07 at.%, respectively. Apparently, the lattice distortions, dislocations, and differences in lattice constant are caused by the difference in Al concentration of rectangular rods and intermediate nanosheets.
Figure 2. (a) A low-magnification bright-field TEM image of an array of Al: ZnO rectangular nanorods with (b) the corresponding electron diffraction pattern; (c) high-resolution TEM image, after Fourier filter, showing the dislocations at the interface of the sheet and rectangular nanorod.

The rectangular nanorods were not grown via a conventional catalyst-assisted vapor-liquid-solid mechanism as reported previously because no catalysts were employed and found [9]. Instead, they were nucleated from single-crystalline ZnO nanobelts with periodic thickness fluctuation resulting from Al concentration modulation. In order to verify the thickness modulation, a bright-field image and the corresponding thickness map of a ZnO rectangular nanorod array derived by EELS are shown in figure 3 (a) and 3(b), respectively. Fig. 3(b) demonstrates that different contrast level is associated with different region for different thickness. Figure 3(c) shows an embryo of the rectangular nanorod array, which exhibits a nanosheet with partly developed periodic surface undulation along the length direction. Therefore, the growth mechanism of the rectangular nanorod arrays were proposed as follows. The first stage involved the growth of nanobelts along the [01\(\bar{1}\)0] direction [10]. In the second stage, Al dopants may tend to redistribute due to the high diffusion rate at high temperature to reduce the overall lattice strain induced by Al doping, resulting in doping concentration modulation along the length direction of the sheet-like structure. The strain induced composition modulation may explain the growth mechanism here since the doped belts should endure some degree of strain due to doping. Furthermore, the regions with higher Al concentration are energetically favorable for higher deposition rate of ZnO and larger local thickness. Thus, an Al:ZnO nanosheet with periodic thickness variations was consequently formed. Finally, the thicker parts of the nanostructure grew continuously along the c-axis out of the sheet since the (0001) platform on the sides of nanosheets with periodic thickness could act as an ideal site for deposition to promote the growth of thicker rod-like part, and the array of the rectangular nanorods was developed. The schematic diagrams and the corresponding SEM images showing the different growth stages of the Al:ZnO rectangular nanorod arrays are shown in Figures 3(d) and 3(e), respectively.
In summary, arrays of single-crystalline Al: ZnO rectangular nanorods were synthesized by the AED method. The nanostructures started with the growth of single-crystalline ZnO nanobelts with periodic thickness and Al concentration modulation. The composition modulation induced by doping may serve as a driving force for creating more interesting nanostructures with tunable properties.