Vertically-aligned smooth ZnO nanorod films for planar device applications

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The growth of smooth and continuous zinc oxide (ZnO) films, consisting of densely-packed vertical ZnO nanorods with (002) crystal orientation on silicon substrates, has been achieved in this work by a chemical solution method. These ZnO thin films have much stronger photoluminescence emission than those from discrete ZnO nanorods under identical conditions. Large area surface acoustic wave devices were fabricated on these films using conventional photolithography, and exhibited two well-defined resonant modes of the Sezawa wave and its harmonic mode.

One-dimensional (1D) nanostructures such as nano-wires (NWs), -rods (NRs) and -tubes (NTs) have been studied intensively in recent years owing to their unique properties such as high carrier mobility, high quantum confinement and efficiency, and excellent piezoelectric effect. These nanomaterials have been applied to electronic, optoelectronic, and microelectromechanical devices. Vertically-grown NRs and NTs are particularly useful in the fabrication of p/n junction-based devices such as laser and light emitting diodes, nanosensors and nanoactuators. However, the large-scale development for commercialization of these nanostructured devices and microsystems is limited due to the difficulty of achieving controlled growth of the materials (particle size, morphology, structure, or growth location etc.), especially in the planar process for device fabrication.

Fig. 1 shows the schematic diagram of a typical method developed for fabricating devices with vertically-grown nanorods. As illustrated, the process is difficult to control in terms of the number and orientation of the NRs or NWs grown on the substrate, hence devices fabricated from these nanomaterials have large variations in uniformity and properties, and poor reliability. Moreover, additional back-filling and planarization processes are typically required for making the top-sitting electrodes, followed by the removal of the fillers if necessary. The whole process is complicated and presents significant handling difficulties, thereby leading to devices with poor uniformity and unreliable properties. Therefore, it is crucial and appealing to develop vertically aligned and densely packed nanorods which would resemble a continuous thin film. Also, it is necessary that these nanorod thin films can be used to fabricate devices (Fig. 1(b) and (c)) for mass production using the conventional planar processing techniques. Although vertically-aligned carbon nanotubes (VA-CNTs) have been used to develop similar thin films, these VA-CNT structures are not continuous solid but possess voids and gaps between the individual components, making them unsuitable for the planar processing.

ZnO possess unique properties suitable for fabrication of electronic, optoelectronic and particularly piezoelectric devices such as surface and bulk acoustic wave (SAWs and BAWs) resonators, piezoelectric transducers for microfluidics and lab-on-a-chip, as well as various physical and biochemical sensors. ZnO nanorods have also attracted great attention for the development of nano-generators in recent years, but this application requires a special scheme to make non-contact electrodes above the discrete nanorods. The difficulty of achieving such complicated structure has hampered the widespread application of these nano-generators. Successful synthesis of smooth and continuous ZnO thin films consisting of vertical ZnO nanorods by a chemical solution method is reported in this work. Moreover, it was found that the as-grown nanorod films have stronger photoluminescence emissions than the discrete ZnO nanorods. SAW devices made from these films also show Sezawa wave resonances, indicating a great potential of using the nanorod films for fabricating large area optoelectronic and piezoelectric devices.

The smooth and continuous ZnO nanorod films were grown on (100)-oriented SiO2/silicon (Si) substrates with a ZnO seed layer. The seed layers were deposited via a high target utilization sputtering (HiTUS) system at room temperature using a metallic Zn target in Ar and O2 gas mixture. This technique yields high quality films with very low stress and defect density, with...
The growth of ZnO nanorods was carried out at temperatures between 50 and 95 °C in sealed glass beakers in which the pretreated seed-containing substrates were immersed in the precursor solution for a certain duration. Detailed information of the synthesis and characterization can be seen in the Supplementary Information (SI).

Process temperature was found to have a significant effect on the morphology and structure of the nanorods. At lower temperatures (50-70°C), while the growth of ZnO nanorods could be achieved, the nanorods were discrete and well separated from each other with a radial size less than 20 nm. The growth rate increased with the increase of temperature, and a smooth and dense nanorod film was obtained at ~90°C. With a further increase of temperature to 95°C, an increase in the surface roughness was observed with the presence of voids thereby indicating that there exists only a narrow temperature window for the growth of continuous nanorod films.

Beside the influence of temperature, the morphology of the films is also affected by the thickness of seed layer, and the concentrations of the starting precursors. A correlation was observed between the thickness of the seed layer and the surface of nanorod films. The thicker seed layers (50 ~ 70 nm) produces smoother films. The smoother the surface of ZnO seed layer, the smoother the ZnO nanorod films with typical root mean square (RMS) roughness less than 10 nm for a film thick round 4 µm measured by atomic force microscopy (AFM), better than most ZnO layers of the thickness deposited by sputtering (Figure S11).

_X-ray diffraction (XRD) analysis indicated that both the discrete nanorods and the continuous nanorod films have wurtzite crystal structure with a strong diffraction peak at 2θ = 34.4°, corresponding to the (002) ZnO planes (Fig. S12). Although similar solution synthesis techniques have been reported before for the growth of ZnO nanorods, the resultant materials were typically discrete nanorods, not continuous and smooth films. X-ray photoelectron spectroscopy (XPS) measurement showed spectrum peaks corresponding only to Zn and O elements with no additional peak from others (see Fig. S13 for details), implying the high purity of the ZnO material synthesized._

The photoluminescence properties at room temperature were investigated for both discrete nanorods and nanorod films as shown in Fig. 3. Apart from the strong luminescent peak centred at 378 nm, several weak emissions were observed at 422, 450 and 484 nm. The dominant emission at 378 nm (3.3 eV) can be assigned to the band-to-band emission of ZnO. As compared to discrete nanorods, the emission intensity of ZnO thin films is much stronger. This suggests that the nanorod films possess a higher crystallinity and improved surface/interface properties in addition to the high density. Few weak emission peaks in the region between 420 and 540 nm were also detected and ascribed to the presence of point defects such as oxygen vacancies and zinc interstitials. The presence of the defects indicates that the nanorods are slightly oxygen-deficient and rapid crystal growth may have contributed to more defects in the crystal when compared to other slow deposition process.

SAW devices were fabricated by using the nanorod films to demonstrate their suitability for large-area planar device applications (See SI for fabrication details). Figs. 4(a) and 4(b) show the SEM images of the SAW device with the interdigitated transducer (IDT) electrodes on ZnO/Si substrate. It can be observed that the device has a smooth surface and is free from voids or particles. The reflection characteristic of the SAW...
devices clearly showed two resonant peaks at ~120 MHz and ~240 MHz (Fig. 4(c)), corresponding to acoustic velocities of 7744 m/s and 15360 m/s, respectively. ZnO/Si is a bilayer structure, and the acoustic velocity depends on the thickness of the ZnO layer. As ZnO has a lower acoustic velocity (2724 m/s) than that of the Si-substrate, it generally generates a Rayleigh wave of low phase velocity and high velocity Sezawa wave. The obtained wave velocity of 7744 m/s for the first peak is much higher than that of the Rayleigh wave (~4200 m/s) for the normalized thickness of \( hk = 0.39 \) (\( h \) being the thickness of ZnO; \( k = 2\pi/\lambda \) wave vector), but compatible to that of the Sezawa wave of ~6800m/s. Therefore, the first peak observed is attributed to be the Sezawa wave and the second one, to the harmonic mode of the Sezawa wave.

**Fig. 4** SEM images of the fabricated SAW device: (a) a IDT transducer, (b) details of the IDT pattern. (c) is a reflection spectrum of the SAW device on a 4 µm thick ZnO nanorod film.

In summary, we have successfully grown continuous ZnO films composed of densely packed (002) ZnO nanorods via a chemical solution method. The as-grown ZnO nanorod films have films composed of densely packed (002) ZnO nanorods via a chemical solution method. The as-grown ZnO nanorod films have 40 Sciences Research Council (EP/F06294X/1 and EP/F063865/1), Carnegie Trust Funding and Royal Society of Edinburgh, UK and the National Natural Science Foundation China (60936002, 61150110485, 61150110487). X-ray photoelectron spectra were obtained at the National EPSRC XPS User’s Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility.

**Notes and references**

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