Synthesis of Vertically-aligned ZnO/ZnS Core/shell Nanowire Array for Photovoltaic Application

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The synthesis and organization of quasi one-dimensional (1D), vertically aligned nanostructures to construct three-dimensional architectures, boosting charge transport and collection and/or enhancing the light absorption, have demonstrated advantages over conventional planar devices.[1] Of particular interest is the use of nanowire array in geometry of core/shell as the active layer and carrier transport medium, which takes full advantage of the proposed quasi 1D system in light absorption, charge separation and transport, and the elimination of recombination loss.[2] Here, we report the successful synthesis of vertically aligned ZnO/ZnS nanowire array, together with comprehensive structural and material characterizations for this unusual nanoheterostructure.

The vertically aligned ZnO nanowire array was firstly grown on an ITO substrate at 600°C and further served as a template for further ZnS coating by pulsed-laser deposition (PLD). A Carl Zeiss 1530 VP field-emission scanning electron microscope (SEM), and a FEI Tecnai F20-UT high-resolution transmission electron microscope (FETEM) equipped with a nanoprobe energy-dispersive X-ray spectroscope (EDS) were used to characterize structure, morphologies, and compositions of the nanowires.

Fig.1(a) shows a typical SEM image of an as-synthesized ZnO nanowire array, revealing perpendicular growth of ZnO nanowires on the ITO glass with an average length of ~7 µm and diameters in the range of 50~120 nm. SEM images of the nanowire array after the pulsed-laser deposition of ZnS are presented in Fig.1(b). Compared to the bare ZnO nanowire, we found a noticeable increase in the diameter and rough surface for the ZnO/ZnS nanowires, which implies that ZnS is successfully deposited over the ZnO nanowire. Fig. 1(c) shows a typical low-magnification TEM image of a ZnO/ZnS core/shell nanowire. The sharp interface between the core and shell clearly shows that the ZnO nanowire is fully sheathed by a ZnS layer along the entire length. The ZnS layer is ~12 nm thick and has a rough surface. Fig. 1(d) is a high-resolution TEM image of the rectangular area d in Fig. 1(c) that shows the detailed interface structure between the ZnO core and ZnS shell. To achieve more precise information about the growth relationship, the magnified HRTEM image of the core and shell taken from rectangles e and f areas in Fig.1(c) and their corresponding fast Fourier transform (FFT) patterns are shown in Figs.1(e) and 1(f), respectively. The marked inter-planar d spacings of 0.31 and 0.52 nm correspond, respectively, to the (111) lattice plane of zinc-blende ZnS with the [011] zone axis and the (0001) lattice plane of wurtzite ZnO with the $[2\bar{1}\bar{1}0]$ zone axis. Thus, the core and shell are determined as epitaxial growth with the growth relationship of $[0001]_{ZnO}//[\bar{1}1\bar{1}]_{ZnS}$ and $[01\bar{1}0]_{ZnO}//[21\bar{1}]_{ZnS}$, in contrast to that for the previously studied ZnO/ZnSe system, where [0001]_{ZnO}//[001]_{ZnSe} was observed.[3] The fabrication of photovoltaic device will also be discussed.

References

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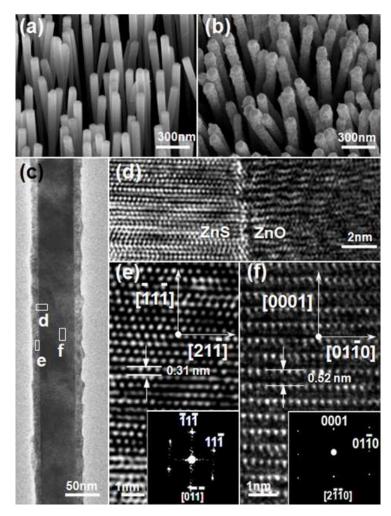


FIG 1. (a) and (b) show representative SEM images of bare ZnO and ZnO/ZnS core/shell nanowire arrays, respectively. (c) Low-magnification TEM micrograph of a ZnO/ZnS core/shell nanowire, showing a thin layer of ZnS coated on the ZnO nanowire. (d) High-resolution TEM image of the interface of the core/shell heterostructure, enlarged from the rectangular area in (c), showing the epitaxial growth relationship of ZnO wurtzite core and ZnS zinc-blende shell. (e) and (f) Atomic images of the core and shell areas taken from the rectangular areas in (c), respectively. The insets in (e) and (f) represent the corresponding fast Fourier transfer patterns.