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Growth and characterization of type-II ZnO/ZnTe core-shell nanowire arrays for solar cell applications

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ARTICLE INFO

Article history:

Available online xxxx

Keywords:

ZnO

ZnTe

Nanowires

Core-shell nanostructure

ABSTRACT

Large area, well-aligned type-II ZnO/ZnTe core-shell nanowire arrays have been fabricated on an a-plane sapphire substrate. The ZnO nanowires were grown in a furnace by chemical vapor deposition with gold as catalyst and then were coated with a ZnTe shell on the ZnO nanowires surface by a metal-organic chemical deposition chamber. The morphology and size distribution of the ZnO/ZnTe core-shell nanowire arrays were studied by scanning electron microscopy (SEM) and the crystal structure was examined by x-ray diffraction (XRD). Transmission measurement was used to study the optical properties of the core-shell nanowires. The results indicated that the ZnO/ZnTe core-shell nanowire arrays have good crystalline quality. In addition, it was found that the nanowire arrays have good light absorption characteristics and these properties make it suitable for making photovoltaic devices.

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1. Introduction

Quasi-one-dimensional (quasi-1D) materials, such as nanowires, nanobelts and nanoneedles have attracted much attention recently for their potential application in making nanodevices [1–3]. As it retains the only needed conducting channel while having the advantage of the reduced dimensionality, the quasi-1D system might be the optimized choice for making opto-electronic devices. Among the optoelectronic devices, photovoltaic devices [4,5] are the most important ones as these devices can convert photon energy into electrical energy. Mixed organic–inorganic type-II band-alignment dye-sensitized solar cells have been fabricated by combining CdSe nanorods with poly (3-hexylthiophene) (P3HT) [6,7] or by combining CdTe nanorods with polymer (P3OT) [8]. As the all-inorganic core-shell structures have better carrier transport property, optical absorption profile,

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and device stability than the hybrid system, it has been proposed recently that the all semiconductor core-shell nanorods with type-II band alignment might be promising candidates for making solar cells [9]. In this paper we report our studies on the growth and characterization of the vertically aligned ZnO/ZnTe core-shell nanowires. Chemical vapor deposition and metal-organic chemical vapor deposition were used to grow a ZnO core and ZnTe shell and our results revealed that the ZnO/ZnTe core-shell structures are good crystalline quality and optical properties.

2. Experimental details

A two-step synthesis was used to fabricate the ZnO/ZnTe core-shell nanowires array on a-plane sapphire. For the growth of a ZnO core, gold was used as catalyst to grow the vertical ZnO nanowire arrays on sapphire substrates by chemical vapor deposition. ZnO and carbon powders mixed in the weight ratio of 7:1 were chosen as source materials. High-purity argon gas (99.99%) was introduced into the quartz tube at a constant flow rate of 50 sccm at a growth temperature of 930 °C. After the growth process, the furnace was cooled down and the sample was transferred to the MOCVD chamber for the deposition of the ZnTe shell on the ZnO nanowire surface. In the MOCVD chamber, the ZnO nanowires were annealed at 550 °C for 5 min and then the ZnTe shell was grown at the same temperature for 10 min. Dimethylzinc (DMZn) and Dimethyltelluride (DMTe) were used as precursors the molar flow rate of DMZn and DMTe is 1:2 and the reactor pressure was kept at 760 Torr during the growth. The morphology and size distribution of the ZnO/ZnTe core-shell nanowire arrays were studied by scanning electron microscopy (SEM), the crystal structure was examined by x-ray diffraction (XRD) and transmission spectroscopy was used to study the optical properties of the nanowire arrays.

3. Results and discussion

Fig. 1(a) shows the tilt-view SEM image of ZnO nanowire arrays on the sapphire substrate. This image revealed that the ZnO wires are vertically aligned, the length of nanowire is around 1–2 μm and the diameter is in the range of 70–100 nm. The SEM picture of the core-shell ZnO/ZnTe nanowires is shown in Fig. 1(b) and the inset is an enlargement of one of the nanowires. Comparing Fig. 1(a) with Fig. 1(b), it was found that the surface of ZnO wires became rougher after the growth of the ZnTe shell, and the diameter of the nanowire increased from 70–100 nm to 150–300 nm. From the images it can be observed that a ZnTe shell was successfully grown on the ZnO nanowires in a large area.

Fig. 2 shows the XRD patterns of ZnO nanowires and ZnO/ZnTe core-shell nanowire arrays. In Fig. 2(a) it indicated that the peak occurs at $2\theta = 34.2^\circ$, which is the diffraction peak from the (002) plane of the ZnO nanowires with a wurtzite structure ($a = 0.3253$ nm and $c = 0.5213$ nm) and it also indicated that the ZnO nanowires grown on substrates were oriented in the c -axis direction. The peak of ZnO (101) can be identified as originating from the thin layer of ZnO which was grown before the ZnO nanowires. In the XRD pattern it showed that the ZnO nanowires are of good crystalline quality. The XRD result of the ZnO/ZnTe core-shell structures is shown in Fig. 2(b). Although the (002) and (101) peaks from ZnO are observable in this figure, the spectrum is now dominated by the diffraction pattern from ZnTe. The diffraction peaks at 25.0° , 41.7° and 49.4° are attributed to the diffraction from the (111), (220) and (311) planes of ZnTe with a zinc-blende structure ($a = 0.610$ nm), respectively. As the diffraction peak from the (111) plane has much higher intensity than that from the (220) and (311) planes, the majority of the ZnTe layers are in the (111) direction. From the diffraction peaks the crystalline quality of the ZnTe shell is also of good quality. As the diffraction peaks of ZnTe shell are the same as the diffraction peaks of bulk ZnTe, the ZnTe layer is apparently fully relaxed. These results are consistent with the results obtained from the SEM image that a layer of ZnTe with a thickness of around 100 nm was coated on to the surface of the ZnO nanowires.

Light absorption properties are important for photovoltaic devices, and it was shown in a recent theoretical calculation that although ZnO is transparent to visible light, due to the type-II band alignment and the spatial proximity of the band edge wavefunction to the interface, ZnO/ZnTe core-shell structures could have light absorption not only in the visible range but could extend the range down to 1.17 eV [10]. The results on the transmission measurement of the ZnO nanowires and

Fig. 1. Tilt-view SEM images of (a) aligned ZnO nanowire arrays (b) aligned ZnO/ZnTe core-shell nanowires arrays. The inset is a higher-magnification SEM image of a single ZnO/ZnTe core-shell nanowire.

ZnO/ZnTe core shell nanowires are shown in Fig. 3. For the sample to consist of only ZnO nanowires we could see that it is indeed transparent in the visible range, and the most importance feature in the transmission curve is the strong increase of light absorption near and above the energy gap of ZnO. For the sample with the ZnO/ZnTe nanostructure, we could see that the transmission curve is quite different from that of the ZnO nanowire sample.

There are two sudden drops in the transmission curves of ZnO/ZnTe nanowires sample, one is near 375 nm and the other is near 550 nm. The result corresponds to the bandgap energy of ZnO and ZnTe, respectively, which confirm that the sample consists of ZnO/ZnTe nanowires of good quality. We also notice that the transmission intensity decreases gradually from 550 nm to 375 nm. For the staggered type-II band alignment, the band gap of the composite structure could be much smaller than the individual material that it was made of. In the case of ZnTe/ZnO the band gap is near 1.17 eV. Theoretical calculations taking the proximity effect of the electron and hole wavefunctions in the nanostructure into consideration predicted that for the type-II core-shell nanostructure [10], the light absorption will start from the band gap energy and increase gradually as the photon energy increases,

Fig. 2. XRD patterns of (a) ZnO nanowire array (b) ZnO/ZnTe core-shell nanowire arrays.

Fig. 3. Transmission spectra of ZnO nanowires (dashed line) and ZnO/ZnTe core-shell nanowires (solid line).

which is consistent with our results. In addition, we also found that the overall transmission intensity is much smaller for the ZnO/ZnTe sample than that of the ZnO sample, indicating that the ZnO/ZnTe sample has a light trapping effect. Much effort had been put into making structures to have a light trapping effect for making high efficiency solar cells. The core-shell structure with its rough surface and grains attached to the wires can apparently create multiple reflections and enhance the light absorption efficiency. Thus, this structure has the advantage that no additional light trapping design is needed when it is used for solar cell applications.

4. Conclusion

In conclusion, large area, vertically aligned ZnO/ZnTe core-shell nanowire arrays were successfully grown by using CVD and MOCVD for the growth of the ZnO core and the ZnTe shell and their structures and optical properties are examined in detail. SEM and XRD characterization indicate that for these nanowires, the ZnO core has a wurtzite structure, the ZnTe shell has a zinc-blende structure and both materials have good crystalline quality. As the core-shell nanowire absorbs light with energy well below the band gap energy of ZnO and the nanowire arrays appear to have good light trapping ability, the core-shell ZnO/ZnTe represent a novel structure for the fabrication of a stable and efficient system for generating electric power from sunlight.

References

- [1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 5 (2003) 15.
- [2] Y. Ding, X.D. Wang, Zh.L. Wang, *Chem. Phys. Lett.* 398 (2004) 32.
- [3] S. Bellucci, *Phys. Status Solidi C* 2 (2005) 34.
- [4] M. Law, L.E. Greene, J.C. Johnson, R. Saykally, P. Yang, *Nat. Mater.* 4 (2005) 455.
- [5] J.B. Baxter, E.S. Aydil, *Appl. Phys. Lett.* 86 (2005) 053114.
- [6] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, *Science* 295 (2002) 2425.
- [7] W.U. Huynh, J.J. Dittmer, W.C. Libby, G.L. Whiting, A.P. Alivisatos, *Adv. Funct. Mater.* 13 (2003) 73.
- [8] Y. Kang, N.G. Park, D. Kim, *Appl. Phys. Lett.* 86 (2005) 113101.
- [9] H. Zhong, Y. Zhou, Y. Yang, C. Yang, Y. Li, *J. Phys. Chem. C* 111 (2007) 6538.
- [10] J. Schrier, D.O. Demchenko, L.W. Wang, *Nano Lett.* 7 (2007) 2377.