

Controlled Growth of Zn₂GeO₄/ ZnO Heterojunction Nanowires

B.B. Cao, J.J. Chen, and W.L. Zhou

Advanced Materials Research Institute, University of New Orleans, New Orleans, LA 70148

Semiconductor nanowire heterojunctions have been strongly pursued because of their electrical and optoelectronic applications in nanodevices. In general, the nanowire heterojunctions fall into two categories: radial junctions and axial (longitudinal) junctions [1]. The latter ones are quite challenging due to stringent requirements of crystallographic relationships and reactant atmospheres during growth, especially for ternary/binary nanoheterojunction. In this work, we present the growth of axial Zn₂GeO₄/ZnO heterojunction nanowires via a chemical vapor deposition process. The length of binary segments ZnO, grown epitaxially along the ternary nanowires Zn₂GeO₄, can be tuned from several hundreds of nanometers to over ten micrometers. The morphologies and structures of the as-synthesized products were characterized by field emission scanning electron microscopy (FESEM, Carl Zeiss 1530 VP), and transmission electron microscopy (TEM, JEM-2010 at 200 kV).

In the first synthesis, the mixture of 0.8g ZnO, 0.06g and 0.01g graphite powder was located at the center of the tube furnace, and a Si substrate coated with 10 nm Au was placed at 20 cm from the tube center. The heating temperature was set as 1100°C, the tube pressure kept at 100-200 mTorr without any carrying gas. Fig.1 (a-b) shows the typical morphology of Zn₂GeO₄/ZnO heterojunction, length of ZnO around 500 nm. Fig. 1(c-e) are selected area electron diffraction (SAED) patterns collected from region C, D and E denoted in Fig. 1(b), revealing an orientation relationship of $(300)_{\text{Zn}_2\text{GeO}_4} // (-110)_{\text{ZnO}}$ and $(003)_{\text{Zn}_2\text{GeO}_4} // (110)_{\text{ZnO}}$.

According to above epitaxial relationship, the second synthesis was performed to intend to grow even longer ZnO nanowire by addition of a secondary ZnO source after 1 hour reaction of the first synthesis. Fig. 2(a) is a FESEM image of a number of heterojunctions grown from the second synthesis, indicated by white arrows in the highlighted circles. The yield of the heterostructures is roughly estimated to be 20% and the ZnO segment can grow even longer than 10 micrometers as shown in a single junction TEM micrograph marked by white arrow in Fig. 2(b). The Au catalyst, as shown in Fig. 2(c), can be seen at the tip of the nanowire, indicating the growth follows VLS mechanism, and Zn₂GeO₄/ZnO junction is enlarged as shown in Fig. 2(d), following the epitaxial growth relationships discussed above. This ultra-long heterostructure, consisting of two nanomaterials with different rigidities, may have a potential mechanical application in nanodevices fabrication.

References

- [1] L. J. Lauhon et al, Phil. Trans. R. Soc. Lond. A **362** (2004) 1247.
- [2] W. I. Park et al, Adv. Mater. **15** (2003) 526.
- [3] This work was supported by the DARPA Grant No.HR0011-07-1-0032, research grants from Louisiana Board of Regents Contract Nos. LEQSF(2007-12)-ENH-PKSFI-PRS-04 and LEQSF(2008-11)-RD-B-10, and American Chemical Society Petroleum Research Fund under PRF No 48796-DN110.

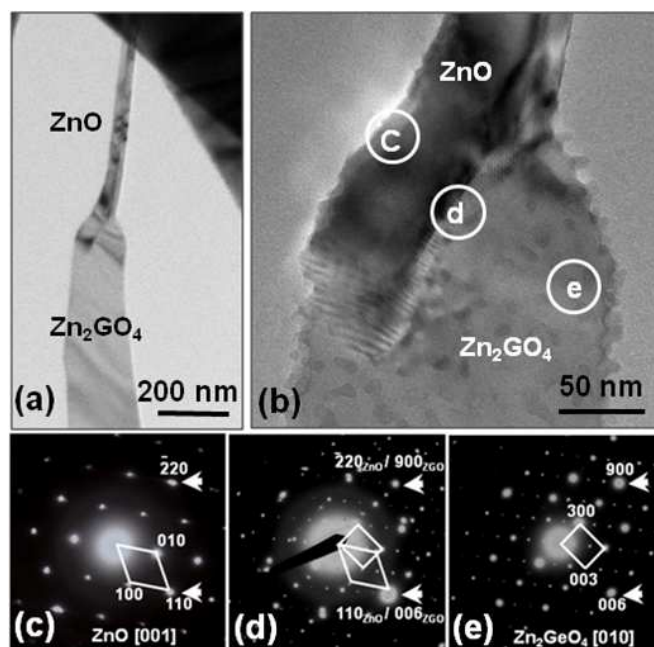


Fig. 1 (a) Typical morphology of a $\text{Zn}_2\text{GeO}_4/\text{ZnO}$ axial heterojunction. (b) Enlarged heterojunction area. (c) SAED pattern of ZnO [001] from region C. (d) Superimposed SAED pattern from interface (region D), where ZGO denotes Zn_2GeO_4 . (e) SAED pattern of Zn_2GeO_4 [010] from region E.

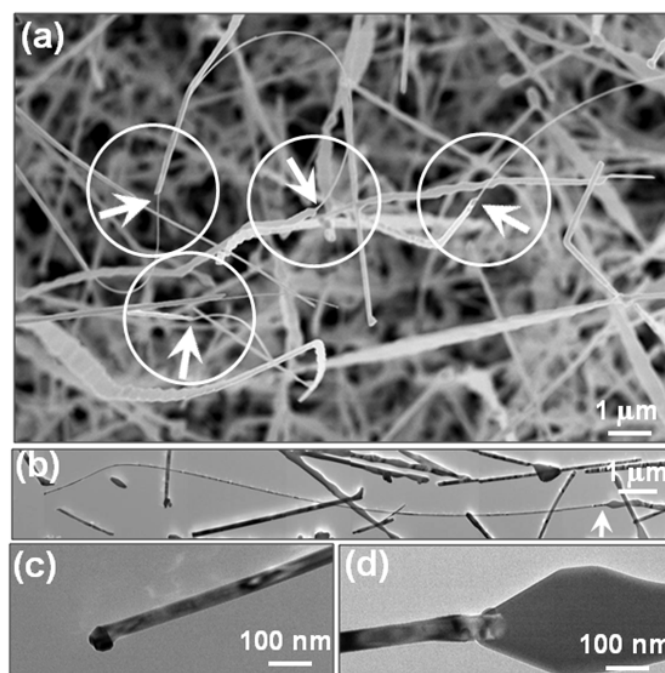


Fig. 2 Ultra-long $\text{Zn}_2\text{GeO}_4/\text{ZnO}$ axial heterojunction nanowires fabricated in the second synthesis. (a) FESEM image of a number of ultra-long heterostructures with their junctions indicated by white arrows. Note that the thin ZnO segments are much longer. (b) Bright field TEM image of a single $\text{Zn}_2\text{GeO}_4/\text{ZnO}$ axial nanowire with more than $10\ \mu\text{m}$ long ZnO . (c-d) The enlarged tip and junction area, respectively.