Chemistry Letters Vol.37, No.8 (2008)

Spontaneous Multiple Heterostructure Formation in Cadmium–Tellurium Nanowire Arrays and Its Optical Properties

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The high quality CdTe/Te multiple heterostructure nanowire arrays were successfully fabricated by a nano-confined precipitation process. The optical properties of the as-obtained CdTe/Te heterostructure nanowires are systematically investigated, which demonstrate the strong coupling of electronic bands in CdTe/Te heterojunction.

One-dimensional (1-D) semiconductor nanostructures have attracted great interest because of novel physical and chemical properties compared with bulk materials.[1] Up to now, much effort has been made for the fabrication of heterostructure nanowires and corresponding device applications, and some progress has been achieved. For example, by the vapor–liquid–solid (VLS) process,[2] GaAs (direct gap)/GaP (indirect gap) heterostructure nanowires can be obtained to serve as optical nanobarcodes. On the other hand, porous anodic alumina (PAA) template-assisted electrochemical deposition provides a simple and versatile route to assemble uniform heterostructure nanowire arrays with controllable diameter and period,[3] which is widely used for fabricating giant magnetoresistance[4] and thermoelectric superlattice nanowires.[5] Thus, owing to the more and more unique and important properties of semiconductor heterostructure nanowires, it is quite significant to explore various new 1-D heterostructure materials, which may be helpful for finding many potential applications in the field of electronic, thermoelectric, and optoelectronic devices.

Cadmium telluride (CdTe, direct energy band gap of 1.45 eV) exhibits advanced photovoltaic properties and plays important role in photoelectron devices and solar cells.[6] Here, using a convenient nanoconfined precipitation method,[7] we successfully fabricate the CdTe/Te multiple heterostructure nanowire arrays by a simple post-annealing process of the supersaturated Cd–Te nanowire arrays and systematically investigate the corresponding optical properties.

It was reported[8] that the stoichiometric CdTe nanowire arrays can be electrodeposited from the electrolyte solution containing 1 M Cd^{2+} and 3×10^{-4} M $HTeO_2^{+}$. From the Cd–Te phase diagram,[9] one can see that a slight increase of Cd or Te content could induce the formation of supersaturated Cd–Te alloy. Thus, the Te-rich supersaturated $Cd_{0.28}Te_{0.72}$ nanowire arrays can be obtained by an electrodeposition process within the PAA template at −0.65 V with a solution consisted of 1 M $CdSO_4$ and 0.04 M TeO_2, which was confirmed by the energy dispersive spectroscopy (EDS) result (Figure S1).[14] For studying the growth of CdTe/Te heterostructure nanowire arrays, powder X-ray diffraction (XRD), and differential scanning calorimetry (DSC) techniques were employed. The microstructures and compositions were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and EDS, respectively.

As shown in Figure 1a, the XRD pattern of the as-prepared Cd–Te nanowire arrays with broad peaks can be indexed to the hexagonal Te phase (JCPDS 04-0554). With steadily increasing the annealing temperature, two series of patterns can be distinguished above 200 °C, which can be indexed to the hexagonal Te phase and the cubic CdTe phase (JCPDS 15-0770). Finally, only pure CdTe phase can be observed after annealing the sample at 450 °C. This phase transformation process was confirmed by DSC results, which indicates the crystallization of Te-rich supersaturated Cd–Te alloy occurs around 125 °C and the decomposition of the heterostructure nanowire arrays around 410 °C (Figure S2).[14]

The morphologies of the Cd–Te nanowires annealed at 300 °C for 5 h show that the nanowires are of large scale and straight with high-aspect ratios, see Figure 2. From the close-up image of a single nanowire in Figure 2c, two kinds of segments can be easily distinguished by obvious heterogenous contrast. The length of each segment ranges from 50 to 100 nm, and the segments appear alternately and orderly, which indicates the uniform periodicity in these heterostructure nanowires. Each segment was characterized to be of a single crystal by HRTEM, and the upper pattern of segment I can be indexed to the (111) plane of cubic CdTe phase while the lower pattern of segment II can be indexed to the (102) plane of hexagonal Te phase, as shown in Figure 2e (detailed structure information of separated segments is presented in Figure S3),[14] which is consistent with the XRD results. The corresponding EDS results in Figure 2f also demonstrate that segment I consists of about 49% Cd and 51% Te which is quite close to stoichiometric CdTe as the equilibrium phase, and segment II is pure Te.

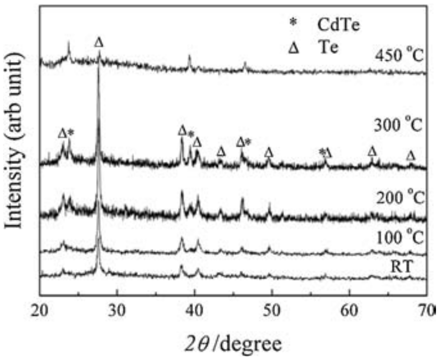

Figure 1. XRD patterns of supersaturated Cd–Te nanowire arrays annealed at different temperatures.

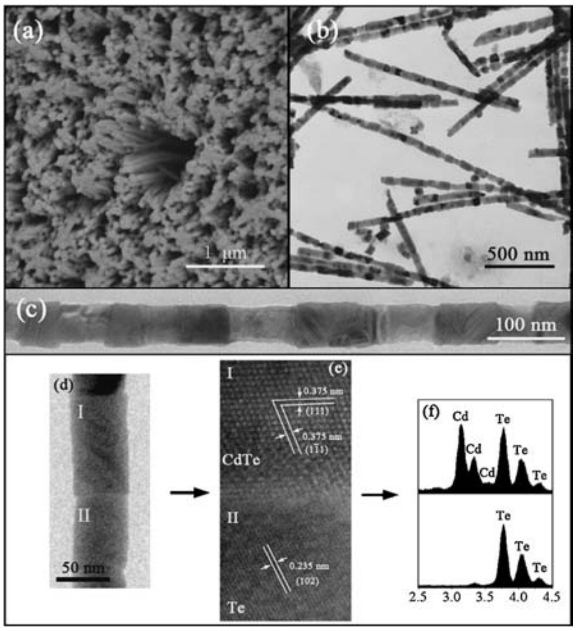

Figure 2. a) and b) SEM and TEM images of the CdTe/Te nanowires, c) TEM image of a single nanowire, d) and e) close-up and HRTEM image for a couple of segments, and f) the corresponding EDS results.

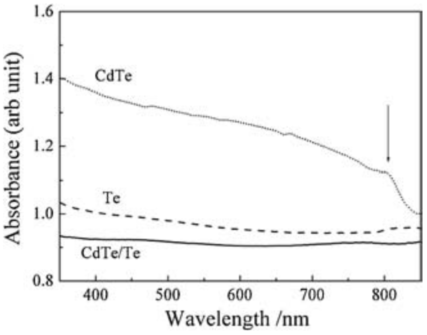

Figure 3. Absorption spectra of nanowires. From top to down: CdTe, Te, and CdTe/Te nanowires.

These results strongly demonstrate that the supersaturated Cd–Te alloy decomposes into CdTe and Te, as follows:

$$\mathrm{Cd}_x\mathrm{Te}_{1-x}(x < 0.5) \xrightarrow{\Delta} x\mathrm{CdTe} + (1-2x)\mathrm{Te} \qquad (1)$$

The UV–vis absorption spectra of the CdTe/Te multiple heterostructure nanowires as well as the pure CdTe and pure Te nanowire arrays were carefully studied. As shown in Figure 3, the absorption spectrum of the pure CdTe nanowires illustrates the slight blue shift of band edge (800 nm) as compared with that of the bulk counterparts. Be different from the CdTe nanowires or nanocrystals with tunable absorption band edge around 700 nm,[10] here the appearance of absorption band edge with longer wavelength in our work is reasonable because of its larger diameter (60 nm). The absorption spectrum of the pure Te nanowires does not show any peak in this region, which is consistent with other reports because of its narrow band gap (0.35 eV).[11] It is interesting that the absorption spectrum of the CdTe/Te multiple heterostructure nanowires is similar to that of the pure Te nanowires, no obvious absorption band edge could be found. This quenching effect of absorption band edge strongly indicates the coupling of electronic bands in the CdTe/Te heterostructures.[12] Since the electron affinity of Te $= 1.97\,\mathrm{eV}$ and that of CdTe $= 4.28\,\mathrm{eV}$,[13] the band alignment of the CdTe/Te heterosystem could be obtained (see Figure S4).[14] In this case, the incident photon with energy larger than the band gap of Te will be absorbed. It implies that the narrow band gap of the Te segments perhaps dominates the absorption property which results in quenching of the absorption band edge.

In summary, high-quality CdTe/Te multiple heterostructure nanowire arrays were successfully fabricated by a nanoconfined precipitation method. The as-prepared CdTe and Te segments are confirmed to be single crystals, and the heterostructure interface is clear and perpendicular to the axial direction. Compared with the absorption properties of pure CdTe and Te nanowires, the quenching of absorption peak of CdTe/Te nanowires supports the coupling of electronic bands between the CdTe and Te segments. The above results are very important for the design of optoelectronic device.

The work was supported by the National Natural Science Foundation of China (No. 50721061) and the National Basic Research Program of China (No. 2006CB922005).

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Published on the web (Advance View) July 5, 2008; doi:10.1246/cl.2008.848