SYNTHESIS, BAND GAP ENGINEERING AND PHOTOVOLTAIC APPLICATIONS OF MULTINARY SEMICONDUCTOR NANOWIRE/NANOCABLE ARRAYS

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多元半導體納米線/納米電纜陣列的製備、帶隙工程及光伏應用

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Abstract

Band gap engineering provides semiconductors with tunable and controllable properties for their applications in optoelectronic and photovoltaic devices. The present work systematically investigates controllable synthesis of one dimensional (1D) multinary nanostructures through simple chemical methods, their band gap engineering via composition variation and their photovoltaic performances. New materials and device structures are explored to achieve efficient photovoltaic performance. Physical processes involved in the nanoscaled synthesis, including phase transformation, ions exchange, Kirkendall effect, and Ostwald ripening, and their implication to morphologies and properties of the nanomaterials have been studied.

Bundles of homogeneously alloyed \( \text{Cu}_2-\text{x}(\text{S}_y\text{Se}_{1-y}) \) nanowires with lengths of several hundreds of micrometers and diameters of 200–500 nm have been controllably prepared over the whole composition range of \( y \) (0 ≤ \( y \) ≤ 1) via a simple water-evaporation method. The nanowire bundles have similar copper contents (0.37 ≤ \( x \) ≤ 0.44), morphologies, and the same face centered cubic (fcc) crystal structure and growth orientation of [110] over the entire composition range of \( y \). This is the first report on fcc ternary \( \text{Cu}_2-\text{x}(\text{S}_y\text{Se}_{1-y}) \) phase. The lattice parameter of the fcc \( \text{Cu}_2-\text{x}(\text{S}_y\text{Se}_{1-y}) \) compounds changes linearly with the S content, which is consistent with that described by the Vegard’s Law. Both the direct and the indirect band gaps of the nanowire bundles are found to have quadratic relationships with the S content.


Using the fcc \( \text{Cu}_2-\text{x} \text{Se} \) nanowire bundles as sacrificial template, bundles of hexagonal \( \text{CuSe} \) and tetragonal \( \text{CuInSe}_2 \) nanowires as well as bundles of \( \text{CuInSe}_2/\text{CuInS}_2 \) core/shell nanocables are prepared by simple chemical approaches and demonstrated as a novel means for synthesis of I-III-VI chalcopyrite photovoltaic
materials. Mechanisms for the chemical conversions and phase transformations are investigated in detail. Formation of CuInSe$_2$/CuInS$_2$ core/shell nanocables with increasing shell thickness shifts x-ray diffraction (XRD) peaks of the CuInSe$_2$ cores to higher 20 degrees, and also enhances the optical absorption properties over the visible-near infrared region, which is obviously beneficial for their photovoltaic applications. (Publication: ACS Nano 2010, 4, 1845–1850)

Highly-ordered arrays of Cu-rich and Cu-deficient CuInSe$_2$ nanotubes as well as ZnO/CuInSe$_2$ core/shell nanocables have been synthesized on transparent glass substrates via a simple ions-exchange route using ZnO nanorod arrays as sacrificial templates. Chemical conversions and phase transformations from hexagonal ZnO to cubic ZnSe, hexagonal CuSe and tetragonal CuInSe$_2$ are demonstrated. Large differences in their solubility product constants ($K_{sp}$) are crucial for direct ions-exchange in the conversions. The absorption coefficient of the CuInSe$_2$ nanotubes in visible region is on the order of $10^4$ cm$^{-1}$. Arrays of ZnO based nanocables can serve as promising photoelectrodes for photoelectrochemical (PEC) solar cells. Power conversion efficiency of the ZnO/Cu$_{1.57\pm0.10}$In$_{0.68\pm0.10}$Se$_2$ cell is about double that of the ZnO/CuSe cell. (Publication: ACS Nano 2010, 4, 6064–6070)

Arrays of ZnO/Zn$_x$Cd$_{1-x}$Se (0 $\leq x \leq 1$) core/shell nanocables with composition-tunable shells have been synthesized via a simple ions-exchange route using ZnO nanowires as sacrificial templates. Through the effects of stoichiometry, and the type-II heterojunction, optical absorptions of the nanocable arrays can be controllably tuned to cover almost the entire visible spectrum. The lattice parameter and the band gap of the ternary Zn$_x$Cd$_{1-x}$Se shells show respectively linear and quadratic relationships with the Zn content ($x$). While the 1D ZnO/TiO$_2$ nanofiber based quantum dot sensitized solar cells (QDSSCs) have a typical efficiency below 4%, these ZnO/Zn$_x$Cd$_{1-x}$Se nanocables arrays are demonstrated to be promising photoelectrodes for PEC solar cells, giving a
maximum power conversion efficiency up to 4.74% and external quantum efficiencies (EQE) as high as 82%. (Publication: *Nano Lett.* **2011**, *11*, 4138–4143)

A novel architecture with dual hollow structures has been demonstrated by synthesis of highly-ordered array of Cu$_2$O nanotubes constructed from hollow nanospheres with diameters of 165–185 nm and shell thicknesses of 20–40 nm. Formation mechanisms are carefully investigated, revealing that formation of Cu$_2$O nanotubes is the results of the “Kirkendall effect”; while evolution of the Cu$_2$O hollow nanospheres in the walls is resulted from the “Ostwald ripening” process. Furthermore, the Kirkendall effect involved in the nanoscaled synthesis has been directly proved by introducing a Cu$_{2-x}$Se interlayer with thickness about 5–10 nm into the hierarchical Cu$_2$O nanotubes, resulting in formation of arrays of Cu$_2$O/Cu$_{2-x}$Se heterogeneous nanotubes, in which Cu$_2$O hollow semi-nanospheres are covered on both the inner and the outer surfaces of Cu$_{2-x}$Se shells. From the microstructures, the diffusion rate of copper ions through the Cu$_{2-x}$Se shells is estimated to be double that of ascorbic acid molecules. (Publication: *Cryst. Growth Des.* **2009**, *9*, 4524–4528)
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Figure 6.9 SEM images of the heterogeneous products prepared by using arrays of Cu(OH)$_2$/Cu$_{2-x}$Se core/sheath nanorods as precursors at different temperature for 60 min. (a) 25°C; (b) 40 °C; (c) 70 ºC, and (d) 80 ºC.
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Table 1.1 Recent deployment growth compared with clean energy targets.

Table 1.2 Record power conversion efficiency ($\eta$) of first and second generation solar cells and their corresponding modules.

Table 2.1 Compositions, lattice parameters and band gaps of Cu$_{2-x}$(S$_y$Se$_{1-y}$) nanowire bundles prepared with reactants of various S/Se ratios.

Table 5.1 Photovoltaic parameters obtained from the $J$–$V$ curves using the ZnO/Zn$_x$Cd$_{1-x}$Se nanocable arrays as electrodes.
# List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>ID</td>
<td>One Dimensional</td>
</tr>
<tr>
<td>CIS</td>
<td>Copper-Indium-Selenide, CuInSe&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>CIGS</td>
<td>Copper-Indium-Gallium-Selenide, Cu(In&lt;sub&gt;x&lt;/sub&gt;Ga&lt;sub&gt;1-x&lt;/sub&gt;)Se&lt;sub&gt;2&lt;/sub&gt;</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
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<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
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<td>FFT</td>
<td>Fast Fourier Transform</td>
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<tr>
<td>UV</td>
<td>Ultraviolet (light in the range of 200–400 nm)</td>
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<tr>
<td>Vis</td>
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<td>K</td>
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<td>K&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>Solubility Product Constant</td>
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<td>TEG</td>
<td>Triethylene Glycol</td>
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<td>Photovoltaic</td>
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<td>QDSSCs</td>
<td>Quantum Dot Sensitized Solar Cells</td>
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<td>J-V</td>
<td>Current Density-Voltage</td>
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<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
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