THE SYNTHESIS AND PHOTOVOLTAIC APPLICATIONS OF SILICON AND II-VI SEMICONDUCTOR NANOWIRE ARRAYS

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The Synthesis and Photovoltaic Applications of Silicon and II-VI Semiconductor Nanowire Arrays
硅和 II-VI 族半導體納米線陣列的合成以及光伏應用

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Abstract

Renewable and green energies have attracted intensive research effort due to the energy crisis as a result of the rapid depletion of fossil fuel. Alternative energy sources such as fuel cell, hydrogen fuel, methanol, geothermal energy, tidal energy, and wind energy, fusion power, and solar energy, are presented. Among these sources, solar energy technology has been well accepted as one of the most feasible and sustainable technologies. Various kinds of novel solar cells (SCs) with different architectures and working mechanisms have been developed; and it has been demonstrated that the efficiency of the SCs strongly depends on the light-harvesting areas and effectiveness of charge collection by the electrodes. The development of nanoscience and nanotechnology opens new routes for the further advancement of solar cell techniques.

The thesis starts with the synthesis and doping of ZnSe nanowires (NWs) by the chemical vapor deposition (CVD) method. The effects of As-doping on the electrical and transport properties of NWs were firstly studied by characterizing single-NW field effect transistors (FETs). We also employed the hydrothermal method to synthesize ZnO NW arrays on Zn foils. The field electron emission (FEE) characteristics of the ZnO NW arrays were revealed to be comparable to the FEE properties of carbon nanotube (CNT) arrays. In addition, various kinds of ZnO array structures such as vertical NW arrays, pyramidal bundle arrays, dendrite arrays, SiO$_2$ coated dendrite arrays, and ZnO NW/silicon microwire (MWs) hierarchical structure were also fabricated. The performance of different ZnO nanostructures in dye-sensitized solar cells was evaluated. Furthermore, the conversion efficiencies are
comparable to the present reported results.

In the first section, As-doped ZnSe (ZnSe:As) NWs were synthesized the first time by introducing zinc arsenide as the dopant during the growth of ZnSe NWs. Studies on the FETs fabricated from individual ZnSe NWs revealed the p-type behavior of As-doped ZnSe NWs. It was observed that further rapid thermal annealing (RTA) significantly enhanced the p-type transport properties and greatly improved the conductivity. The enhancement was attributed to activation of As acceptors from the passivated states of As-H bonding. Guided by the x-ray photoelectron spectroscopic analysis and electrical properties of ZnSe:As NW FETs, the formation of $\text{As}_2\text{Zn}-2\text{V}_{\text{Zn}}$ complex and $\text{AsSe}$ were suggested to originate the p-type conduction in ZnSe NWs.

In the second section, ZnO NW pyramidal bundle arrays were grown on zinc substrates at a low temperature without the assistance of catalysts and templates. The bundle arrays were shown to form by sticking of NWs at their tips. FEE characterization of NW bundle arrays revealed a very low turn-on electric field of about 2.3 V/$\mu$m and a threshold electric field (corresponding to the field electron emission current density of 10 mA/cm$^2$) of 6.8 V/$\mu$m, which are comparable to those observed in CNT arrays. The bundle arrays also show pronounced long-term field electron emission stability at a high current density. In addition, the formation mechanism of the pyramidal bundled arrays and the origin of peculiar field electron
emission properties were discussed.

In the third section, various ZnO NW array structures including vertical NW arrays, pyramidal NW bundle arrays and dendrite NW arrays were synthesized by a solution method. These NW arrays were applied in DSCs and their morphology-dependent performance was evaluated. The work shows that dendrite NWs have a better performance than the other two structures due to the larger surface area for dye adsorption. In addition, the instability of ZnO in the present commercial dyes (N3 or N719) which contain the carboxyl groups resulting in the generation of Zn\(^{2+}\)/dye complexes was also considered. In this work, dendrite ZnO NW arrays were coated with SiO\(_2\) in order to limit the recombination and shield the ZnO surface. The efficiency of the solar cells can be further improved by about one quarter.

In the fourth section, 3D ZnO NW/silicon MW hybrid architectures with the controlled geometry were fabricated by combining the bottom-up and top-down methods. Silicon MW arrays chemically etched from patterned silicon wafers were used as 3D scaffold for the ZnO NW growth. The geometry of silicon microwires was controlled by varying the size of mask dots and etching time. In contrast to the top-down approach to fabricate Si scaffolds, the sequential growth of radial ZnO NWs conformally on the Si scaffolds follows a bottom-up method by employing a modified carbon-assisted self-catalytic growth via CVD. The method is expected to be applicable to the synthesis of 3D hybrid structures of other nanomaterials. The
construction of such a hybrid system opens the door to the practical application of functional low dimensional semiconductors. For the application of the novel structure in DSCs, a thin ITO layer was inserted between Si MWs and ZnO NWs for the collection of electrons. It was demonstrated that the 3D structures of Si/ZnO indeed showed an improved performance in DSCs; the capability for energy conversion was increased by about 5 fold as compared to the counterpart device made of ZnO NW grown on a planar substrate.

In addition to the above work, the final section also describes future work based on the present experiments. The remaining work will focus on the improvements of 3D ZnO NW/Si MW heterojunction SCs, core-shell structure SCs based on Si MW array and Si NW arrays based photoelectrochemical (PEC) SCs.
Chapter 1 Review of the methodologies, characterizations and solar cell applications of Si and II-VI semiconductor nanowires

1.1 Overview

1.2 Methodologies to synthesize Si and II-VI semiconductor nanowires

1.2.1 Top-down approach

1.2.2 Bottom-up approach

1.3 Characterizations of NWs

1.3.1 Scanning electron spectroscopy

1.3.2 Transmission electron microscopy and high-resolution transmission electron microscopy

1.3.3 X-ray photoelectron spectroscopy

1.3.4 X-ray diffraction

1.3.5 UV-Vis spectroscopy

1.4 Dye-sensitized solar cells and photoelectrochemical solar
Chapter 2 p-type conduction in arsenic-doped ZnSe NWs

Chapter 3 Field electron emission of ZnO NW pyramidal bundle arrays
Chapter 4 DSCs of ZnO/SiO$_2$ dendrite NW arrays........................................88

4.1 Overview........................................................................................................88
4.2 Experimental section.....................................................................................90
  4.2.1 Synthesis of aligned ZnO arrays and pyramidal bundle arrays.................90
  4.2.2 Synthesis of ZnO dendrite NW arrays.....................................................90
  4.2.3 SiO$_2$ coating to dendrite ZnO.................................................................91
  4.2.4 Fabrication of ZnO NW array DSCs.........................................................91
4.3 Results and discussion..................................................................................92
  4.3.1 Characterizations....................................................................................92
  4.3.2 Dye-sensitized solar cell performances................................................94
4.4 Conclusion......................................................................................................96
4.5 References.....................................................................................................97

Chapter 5 Controllable fabrication of 3D radial ZnO NW/Si MW hybrid architectures for DSCs.................................................100

5.1 Overview.......................................................................................................100
5.2 Synthesis of 3D radial ZnO NW/Si MW hybrid architectures.....................102
Chapter 6 Conclusion and future work

6.1 Conclusion

6.2 Future work

6.2.1 CdS:In/Si NWs hybrid photovoltaic cells

6.2.2 Si MW core-shell photovoltaic cells

6.2.3 Si nanostructures based PEC cells

6.3 References

Appendix: Publication list