One-Year Exploratory Project: Nanowire-Nanocrystal Multiexciton Solar Cells

Investigators

Yi Cui, Assistant Professor, Materials Science and Engineering and Geballe Laboratory for Advanced Materials; Jia Zhu, Stephen T. Connor, Graduate Researchers, Stanford University.

Abstract

Multiexciton generation (MEG) is promising towards high-efficiency solar cells. Lead chalcogenide nanostructures are good potential candidates for applications in MEG solar cells. We have been successfully synthesized hyperbranched PbSe nanowire networks. Hyperbranched PbSe nanowire networks are synthesized via a vapor-liquid-solid (VLS) mechanism. The branching is induced by continuously feeding the PbSe reactant with the vapor of a low-melting point metal catalyst including In, Ga and Bi. The branches show very regular orientation relationships: either perpendicular or parallel to each other. The diameter of the individual NWs depends on the size of the catalyst droplets, which can be controlled by the catalyst vapor pressure. Electrical measurements across single branched NWs show the evolution of charge carrier transport with distance and degree of branching. Multiexciton generation is currently under investigation.

Introduction

The goal of this project to synthesize PbSe nanowires and nanocrystal sand study their MEG towards high efficiency solar cells.

Background

MEG solar cells utilize the impact ionization process to create multiple electron-hole pairs for every photon absorbed. Impact ionization has been shown to be greatly enhanced in quantum dots [1, 2]. Theoretical power conversion efficiency corresponding to 0.3eV bandgap is expected to be as high as 65%. However, separating and collecting electrons and holes for practical solar cell devices remains challenging in quantum dots due to the lack of charge separation interfaces and collection pathways. The objective of this project is to exploit nanowires as scaffolds to separate and collect charge carriers, which provide an efficient mean to separate and collect charge carriers for high efficient and low-cost solar cells.

Lead chalcogenides (PbE, E=S, Se, Te) are a special class of IV-VI narrow-bandgap (0.2-0.4 eV) semiconductors [3]. Quantum confinement of charge carriers in PbE can be much stronger than in most II-VI and III-V semiconductors. The energy level spacing can be even larger than the bulk bandgap. The similar and small effective masses of both the electrons and the holes imply that this strong confinement effect is split equally between electrons and holes so that the electronic structure is simple. In this project, PbE is the materials of choice for making nanowires.

Results

With GCEP's one-year project support, we have obtained synthesized PbSe branched nanowires (NWs). We have measured the electrical property of branched nanowires .

The synthesis of hyperbranched PbSe NW networks is initially realized by co-evaporation of PbSe with a small amount of In_2Se_3 powder in a tube furnace. Figure 1 shows the SEM images of as grown products on a <001> Si substrate surface with intrinsic oxide at different times and indicates the formation process of the hyperbranched NW networks. At the initial stage of growth (5 min, Fig. 1a), some NWs have reached lengths of 10-20 μm while others have just nucleated. At 10 min (Fig. 1b), there are no visible particles as at 5 min, suggesting that all the particles have nucleated NWs. Each nanostructure shows at least one generation of branching, i.e. three NW branches, and some have a couple of generations of branching resulting in a hierarchical structure. At 30 min, NWs show many generations of branching, resulting in the hyperbranched NW networks. There are several key characteristics which can be identified from SEM studies: first, the diameters of most NW branches are ~100 nm and do not change significantly over the course of the growth process. Second, the maximum length of each NW branch is limited to ~10-20 μm and does not increase significantly with the growth process. Third, the branches within the same NW network show a preferred orientation and appear to be perpendicular or parallel to each other, implying crystallographic registry.

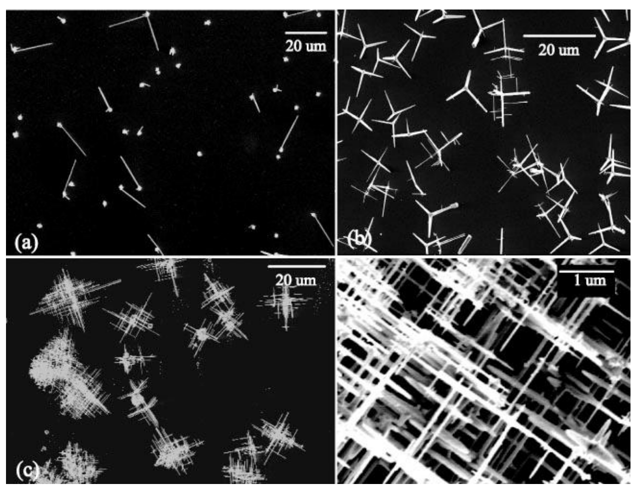

Figure 1. SEM images of PbSe NW network on Si <100> substrate grown for (a) 5 min. (b) 10 min. (c) 30 min. (d) High-resolution SEM image of PbSe NW network from (c).

The composition and structure of NW networks are studied using EDX and TEM. The EDX data show that NW networks consist of Pb and Se with an atomic ratio of ~1:1. Figure 2a shows a TEM image of a NW with three branches just nucleated. The directions of the main and branched NWs form a 90º angle, consistent with SEM observation. The high resolution TEM (HRTEM) images taken on the main NW (Fig. 2d) show that it is single-crystalline and the spacing of the lattice planes parallel or perpendicular to the NW long axis is 3.06 Å, consistent with the (200) planes of the PbSe rock-salt structure. HRTEM at the branching interface (Fig. 2c) gives the same lattice spacing and shows the single crystalline nature of branches extending from the main NW.

These data suggest that the main and branched NWs belong to the same single crystal. The single-crystalline nature of the whole NW network is further confirmed by selected-area electron diffraction (SAD) taken at the interface of main and branched NWs (Fig. 2b). The SAD shows a square lattice, which can be indexed as the diffraction patterns along the <001> zone axis. The long axis of the main and branched NWs is along the same crystallographic direction of <100>, consistent with HRTEM studies.

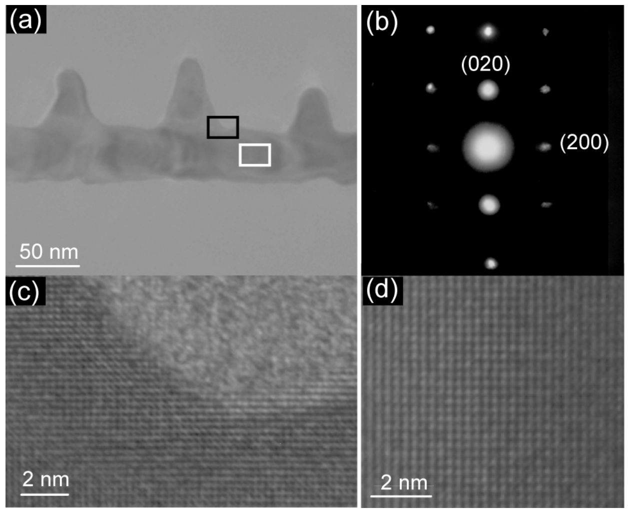

Figure 2. (a) TEM image of a branched PbSe NW. (b) and (c) SAD pattern and HRTEM image of the PbSe NW obtained at the branching interface (black rectangular in (a)), respectively. (d) HRTEM image of the main PbSe NW (white rectangular in (b)).

To study the electrical properties of these hyperbranched PbSe NW networks, we have carried out electron transport measurements on a single network. Since the branches extend out three-dimensionally to tens of micrometers, it is challenging to pattern the metal contact electrodes by lithography methods. Here we exploit in-situ nanoscale tungsten probes as contact electrodes in a Hitachi N-6000 Nanoprober instrument. The probe tips have sizes below 100 nm which is comparable to the size of the NWs and the probe positions are controlled by piezoelectric actuators with a nanometer precision. Right before contacting the NWs, the probes were shorted (<100 Ω resistance) to ensure that the tungsten oxide layer on the probe surface is thin enough. The leakage current through the substrate was immeasurably small (the dashed curve in Fig. 3f). The contact formation betweens probes and NWs can be monitored with in-situ SEM before during and after electrical measurements. Figures 3a to 3c are the SEM images showing the three cases: first, single NW branch is contacted (Fig. 3a); second, a junction locates between the two probes, i.e., two NW branches are contacted (Fig. 3b); third, electrons transport through many junctions or NW branches (Fig. 3c). In the first case, current (I) measured against voltage (V) (Fig. 3d curve a) shows nonlinear characteristics with resistance ~1 MΩ at low (Fig. 3e curve a) and ~40 kΩ at high voltage, suggesting there are energy barriers along the transport pathway. In the second case, IV curves (Fig. 3d and e curve b) indicate that the resistance increase significantly to 30 MΩ at low and ~400 kΩ at high voltage. In the third case, the resistance increases to very high values: ~10 TΩ at low and 5 GΩ at high bias. Careful data analysis indicates the following important facts: 1) Resistance at low bias increases with the length of electron transport pathway much faster than at high bias. By a rough estimation, the resistance at high bias increases linearly with the pathway length. 2) The high resistance region at low bias is widened with the pathway length increase, suggesting that the energy barrier also increases. This energy barrier may have a contribution from the metal probe-NW contact and from the branched NW themselves because of the mechanical bending of NWs forced by metal probes and the multiple intra NW p-n junction formation. It is well known that PbSe can be p- or n-type, depending on the stoichiometry. The variation of stoichiometry in the large branched NW networks can cause the formation of many p-n junctions. These possible explanations require future study.

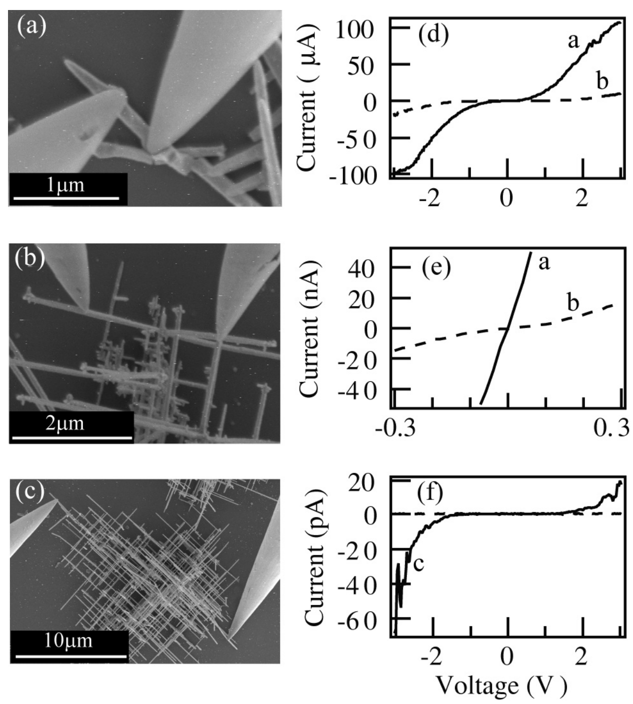

Figure 3 (a) to (c) are SEM images of hyperbranched NW networks contacted by two tungsten probes. (d) is I-V data with curve a and b corresponding to the cases in (a) and (b), respectively. (e) is the low bias region of (d). The solid line in (f) is the I-V data for (c) and the dashed line is the I-V data through the substrate.

Progress

The progress reported here on synthesis, characterization and electrical measurements is the basis for further MEG solar cell fabrications. We are continue out study on the MEG effect in these nanowires.

Future Plans

This one-year project has ended.

Publications

1. J. Zhu, H. Peng, C. K. Chan, Yi Cui "Hyperbranched Lead Selenide Nanowire Networks" *Nano Lett. 7,* 1095-1099 (2007).

2. Jia Zhu, Hailin Peng, Ann Marshall, David M. Barnett, William D. Nix and Yi Cui "Formation of Chiral Branched Nanowires by the Eshelby Twist" *Nature Nanotechnology* (in press).
3. Y. Cui (*Invited talk*) "Solar Cells and Batteries with Inorganic Nanowires" ACS spring meeting, One-dimensional Nanomaterials Symposium, Division of Inorganic Chemistry, Chicago, Illinois, Mar. 28, 2007.
4. Y. Cui (*talk*) "Lead Chalcogenide Nanowires and Hyperbranches for Multiexciton Generation Solar Cells" MRS Spring meeting, Symposium DD, San Francisco, California, Apr.12 , 2007.

References

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Contacts

Yi Cui: yicui@stanford.edu