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

Investigators

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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. Significantly, the hyperbranched networks can be grown epitaxially on NaCl, a low-cost substrate for future device array applications. 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

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.

Background

This project was funded by GCEP since Jan. 1, 2007. By attending conferences and private communication in the last five months, I have discovered that MEG stimulates a

great deal of interest in many institutions. Using nanostructures for MEG enhancement has been the focus. Although most of the published data with nanostructures were conducted in quantum dots systems, attention has just been attracted to nanowires. It is expected that some breakthroughs might take place in nanowires.

Results

The results in this report are on synthesis, characterization and electrical measurements of PbSe nanowires (NWs).

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.

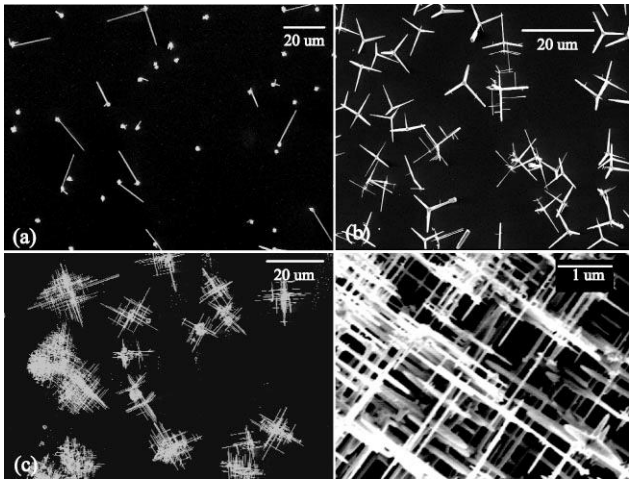

Figure 1. SEM images of PbSe NW network on Si <100> substrate grown for (a) 5 min. (b) 10 min. (c) 30 min. (d) High-resolution SEM image of PbSe NW network from (c).

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.

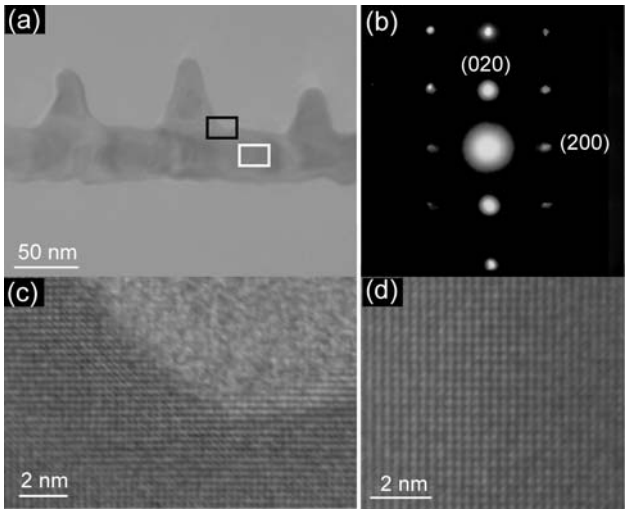

Figure 2. (a) TEM image of a branched PbSe NW. (b) and (c) SAD pattern and HRTEM image of the PbSe NW obtained at the branching interface (black rectangular in (a)), respectively. (d) HRTEM image of the main PbSe NW (white rectangular in (b)).

We believe that the formation of hyperbranched NW networks is through a metal-catalyzed VLS mechanism. The participation of In_2Se_3 during growth is necessary for growing NWs and inducing branching. The growth without In_2Se_3 does not produce NWs but only gives large size PbSe crystals. Indium vapor from the evaporation of In_2Se_3 may condense to form nanoscale liquid droplet for PbSe NW nucleation and growth due to the low melting temperature of In. The existing In vapor in the subsequent growth process continuously supplies nanocatalysts onto the pre-formed NWs to nucleate and grow the new branches. If this conjecture is true, we should be able to produce PbSe branched NWs with In metal precursors. Indeed, by placing In powder upstream at the temperature ~400°C during PbSe vapor transport, we are able to produce branched NWs (Fig. 3a) with morphology similar as using In_2Se_3 powder. Interestingly, other high vapor pressure metals such as Ga and Bi metals can also function as efficient catalysts for PbSe hyperbranched NWs (Fig. 3 b and c, respectively). It is challenging to predict the VLS growth conditions from the complex ternary phase-diagrams in Pb-Se and -In, -Ga, or -Bi, although it seems generally true that these low melting point metals can function as good VLS catalysts or solvents to dissolve the PbSe vapor and nucleate and grow PbSe NWs.

An important phenomenon in VLS growth is the appearance of metal catalyst particles at the tips of NWs. However, the majority of the PbSe NW branches usually show a tapered shape at the tip (Fig. 2a) without the presence of metal catalyst. We think that the absence of catalyst nanoparticles on most branches after synthesis might be due to the shrinkage and disappearance of catalysts through evaporation since they have a high vapor pressure. Another possible mechanism is through diffusion, which has recently been suggested in tapered Si NW grown using Au nanoparticles as catalysts. However, some NW branches do preserve their catalysts at the tip. Fig. 3d shows a TEM image of a Bi particle at the tip of a PbSe branch. Under the 200 keV electron beam, the Bi particle disappears within 30s and leaves behind only the PbSe NW branch (Fig. 3e). The observation is consistent with the volatility of low-melting point metal catalysts and confirms the VLS growth mechanism.

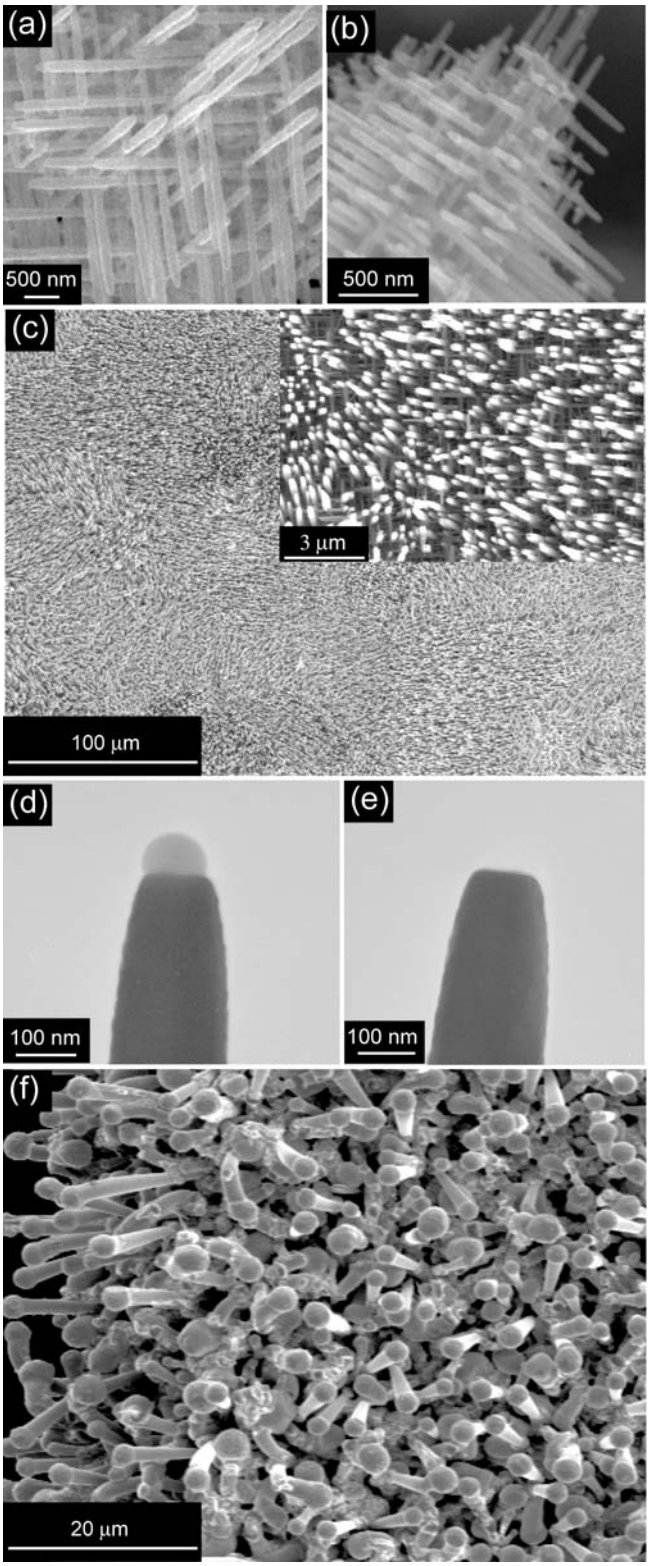

Figure 3. (a) (b) SEM images of PbSe NWs using Indium, Gallium as catalyst, growth for 60 min; (c) SEM image of PbSe NWs using Bismuth as catalyst, growth for 120 min, inset is a zoomed in picture; (d) (e) TEM image of PbSe NWs with and without Bi particles; (f) SEM image of PbSe NWs with Bi particles at the end.

The metal catalyst should be preserved if the collecting substrate temperature is lowered. To study this temperature effect, we also collected the synthesis product at the furnace's downstream edge, where the temperature is only 200^{o}C. SEM images on as-grown samples show that high density NWs are grown and each has a catalyst particle clearly seen at the tip although there is no regular branched NW formation (Fig. 3f). Branched NWs are not observed at low temperatures because branching involves new nucleation events, which require some activation energy. Insufficient thermal energy is available at the lower temperature to overcome this activation barrier. However, low temperature growth does preserve the catalyst particles. This observation provides further important evidence that the growth of PbSe NWs and their branches is via a VLS mechanism.

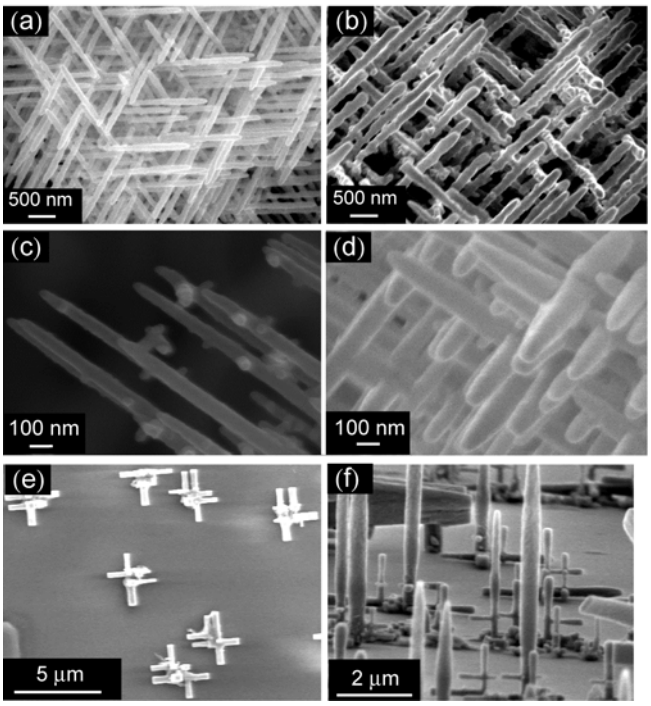

Figure 4 (a) (b) SEM images of PbSe NWs with different growth temperature: 650^{o}C and 700 ^{o}C, respectively, (c) (d) SEM images of PbSe NWs with different Indium temperature: 350^{o}C and 400 ^{o}C respectively, (e) and (f) top-view and cross-section SEM images of epitaxial growth of PbSe NWs on NaCl <001> substrate.

In the VLS mechanism, the catalyst size control can be used to control the size of hyperbranched NWs. Fig 4 a and b show the In metal source catalyzed PbSe NWs obtained from different furnace set temperature. It is shown clearly that decreasing the temperature from 700°C to 650°C will cause the reduction of the diameter of NWs from 150 nm to 100 nm. In fact, decreasing the set temperature is expected to decrease the In vapor pressure as well as the In-PbSe alloy particle size. Alternatively, the furnace temperature can remain unchanged while the temperature of the metal powder is changed by placing it at a different location in the tube furnace. For example, Figure 4c and d shows that the In powder was placed at locations with temperatures of 350°C and 400°C, respectively. The lower temperature resulted in thinner NWs (~60 nm) than the higher temperature NWs (~100 nm).

PbSe hyperbranched NW networks grown on Si substrates with intrinsic amorphous oxide do not show orientation registry between different networks (Fig. 1c). Because the capability of orientation control is important for device applications, we studied the orientation control by using the concept of NW epitaxial growth on a crystalline substrate surface. PbSe has a rock-salt structure with a lattice parameter of 6.124 Å. We choose a NaCl <001> substrate, which has a lattice parameter of 5.65 Å. Despite the large lattice mismatch of 8.4%, PbSe NW networks can still be epitaxially grown onto the NaCl substrate. Top-view SEM images as that in Fig. 4e show that all the NW branches in different networks orient only in two perpendicular directions, suggesting that NW networks have a perfect registry with respect to each other. These two preferred directions are parallel to the NaCl [100] and [010] directions, respectively. Side-view SEM images (Fig. 4f) taken by tilting the substrate indicate that the third orientation is perpendicular to the substrate surface, i.e., along the [001] direction, consistent with the growth direction of PbSe NWs. We emphasize the significance of using NaCl substrates for orientation control since NaCl is a low-cost substrate for device fabrication.

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. 5f). The contact formation betweens probes and NWs can be monitored with in-situ SEM before during and after electrical measurements. Figures 5a to 5c are the SEM images showing the three cases: first, single NW branch is contacted (Fig. 5a); second, a junction locates between the two probes, i.e., two NW branches are contacted (Fig. 5b); third, electrons transport through many junctions or NW branches (Fig. 5c). In the first case, current (I) measured against voltage (V) (Fig. 5d curve a) shows nonlinear characteristics with resistance ~1 MΩ at low (Fig. 5e curve a) and ~40 kΩ at high voltage, suggesting there are energy barriers along the transport pathway. In the second case, IV curves (Fig. 5d 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.

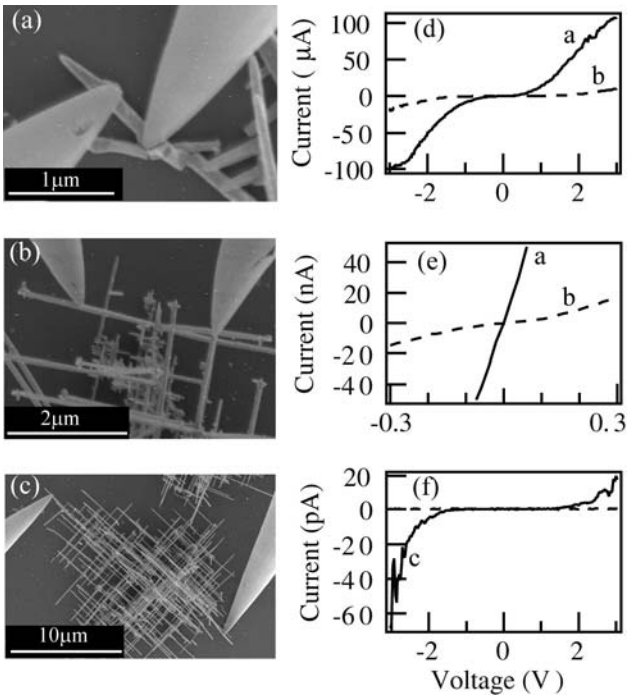

Figure 5 (a) to (c) are SEM images of hyperbranched NW networks contacted by two tungsten probes. (d) is I-V data with curve a and b corresponding to the cases in (a) and (b), respectively. (e) is the low bias region of (d). The solid line in (f) is the I-V data for (c) and the dashed line is the I-V 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 believe that if it is successful, our research on multiexciton solar cells has the potential to significantly reduce the global greenhouse gas emissions over the long term.

Future Plans

We plan to carry out the following studies: 1) Ultrafast laser spectroscopy studies of MEG in nanowires 2) MEG electrical measurements on single nanowires 3) Fabrication of MEG solar cells.

Publications

1. J. Zhu, H. Peng, C. K. Chan, Yi Cui "Hyperbranched Lead Selenide Nanowire Networks" *Nano Lett. 7,* 1095-1099 (2007).
2. 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.
3. Y. Cui (*talk*) "Lead Chalcogenide Nanowires and Hyperbranches for Multiexciton Generation Solar Cells" MRS Spring meeting, Symposium DD, San Francisco, California, Apr.12 , 2007.

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