Project 09: Project Scientific Progress – Fall 2009 to Fall 2015

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We have divided the technical summary into three parts for each of the groups involved in nanowire solar cell development.

Ray LaPierre Group (McMaster University):

Nanowire Growth and Yield: The size, position, composition, impurity doping and dimensions of semiconductor nanowires can be controlled by the vapour-liquid-solid process. In this process (Figure 1), the bottom Si sub-cell is first covered in SiO_2, which also passivates the Si cell surface. Holes are patterned in the oxide by lithography. Next, III-V material is deposited using standard deposition equipment such as molecular beam epitaxy (MBE) or metalorganic chemical vapour deposition (MOCVD). Metal seed particles (e.g., Ga) are formed in the oxide holes during growth, and nanowire growth is seeded by these Ga particles. In this NSERC SNG project, we developed this process such that the nanowires can be deterministically positioned with greater than 80% yield of vertical nanowire growth and with no parasitic film growth between the nanowires. Our simulations have shown that the cell efficiency is optimized for a direct bandgap of 1.7 eV for the top nanowire cell and 1.1 eV (i.e., Si) for the bottom cell. The 1.7 eV nanowire bandgap can be achieved using $GaAs_{0.77}P_{0.23}$ material.

Optical Absorption: Experimental measurements and optical modeling has shown that semiconductor nanowires funnel and concentrate light due to an optical antenna effect, such that a sparse nanowire array will absorb nearly all incident light with very little material (Figure 2). The nanowire array also acts as a very effective anti-reflection coating with reflectance below 5% across the entire visible spectrum. As a result, our experimental and theoretical results have demonstrated high internal quantum efficiency over much of the solar spectrum using an optimum nanowire diameter of 180 nm and period (spacing) of 360 nm.

Carrier Collection: Impurity dopants can be incorporated into the nanowire during growth to control their electronic properties; specifically, to create the p-n junction diode that is necessary for a solar cell. The control of the doping in nanowires is therefore of fundamental importance in achieving high PV efficiency. Figure 3 shows a coaxial nanowire structure consisting of a p-type core and an n-type shell. The main advantage of a radial nanowire solar cell is the orthogonal direction of light absorption and carrier collection: optical absorption occurs along the nanowire length, while carrier collection occurs radially along the built-in electric field of the core-shell p-n junction. Since the nanowire diameter is much less than the carrier diffusion length, nearly all photogenerated carriers can be separated and collected at their respective junction before recombination occurs.

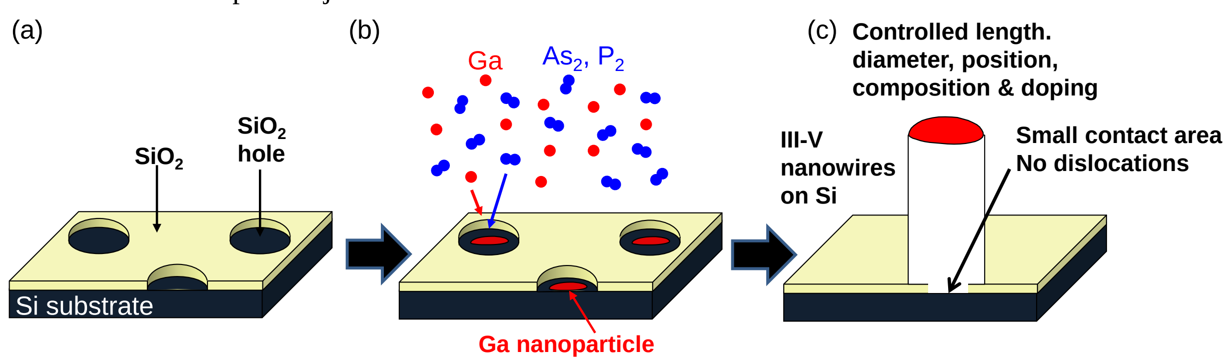


Figure 1. Illustration of nanowire growth process. (a) SiO_2 mask with holes on Si substrate. (b) During III-V material deposition, group III material (Ga) accumulates in the holes forming seed particles. (c)

Each seed particle become supersaturated with group V material (As_2, P_2) and crystallizes a III-V nanowire (e.g., GaAsP). Note that the diameter of the nanowire may be much larger than the oxide hole, but the small contact area to the substrate ensures no dislocations.

Current-Matching and Tunnel Junction: The highest efficiency occurs when the current from the bottom Si and top nanowire sub-cells are equal. A tunnel junction is used to electrically connect the top nanowire cell with the bottom Si cell.

Ohmic Contact Formation: A method of planarizing the nanowire array and contacting the top of nanowires was developed. The nanowires are planarized for contacting by a spin-on cylotene polymer, and indium tin oxide (ITO) is deposited on top of the nanowires. We have already demonstrated a process to achieve a high transmittance (89% over a wavelength range of 400 to 900 nm), low ITO sheet resistance (13 □/□), and low contact resistance to nanowires (<0.09 □cm^2), which are suitable for our PV device.

Figure 2. Optical simulations and experiments show that nanowires funnel and concentrate incident light due to an optical antenna effect, such that nearly all incident light is absorbed in very little material.

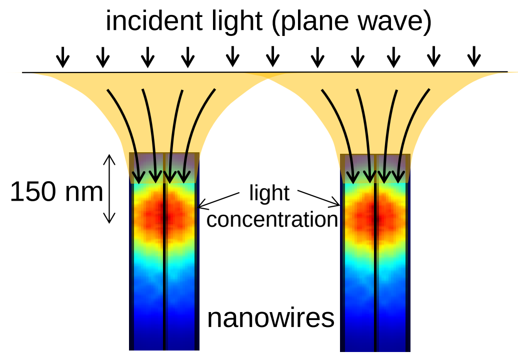
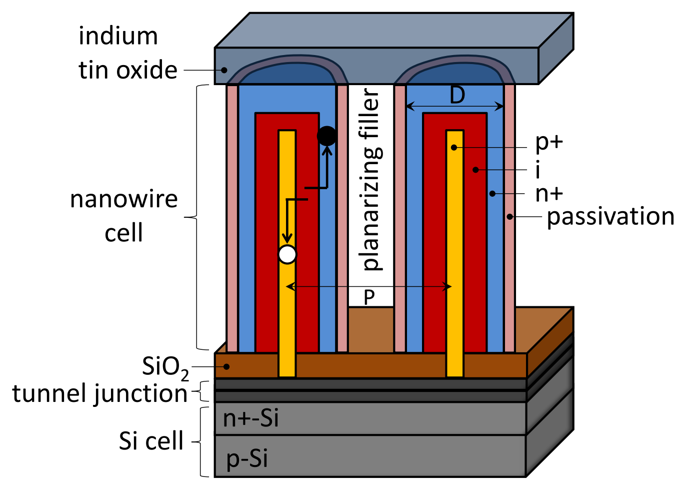


Figure 3. Cross-sectional view of a nanowire-on-Si solar cell (not to scale). Electron (filled circle) and hole (open circle) carrier flow are indicated in the left-hand nanowire. Nanowire diameter, D, and period (spacing), P, are indicated.



Surface Passivation: Nanowires require surface passivation to decrease the density of surface (trap) states on the nanowire sidewalls which lead to detrimental carrier depletion, carrier recombination, and lower charge carrier mobility. We developed a complete analytical model of surface depletion in PV devices, and have demonstrated effective nanowire passivation using AlInP. Our model of nanowire core-shell p-n junctions indicates that our surface passivation should be adequate for achieving high PV efficiency.

The world's highest efficiency for III–V on Si nanowire solar cells, achieved by us, is 2.5% (Figure 4).

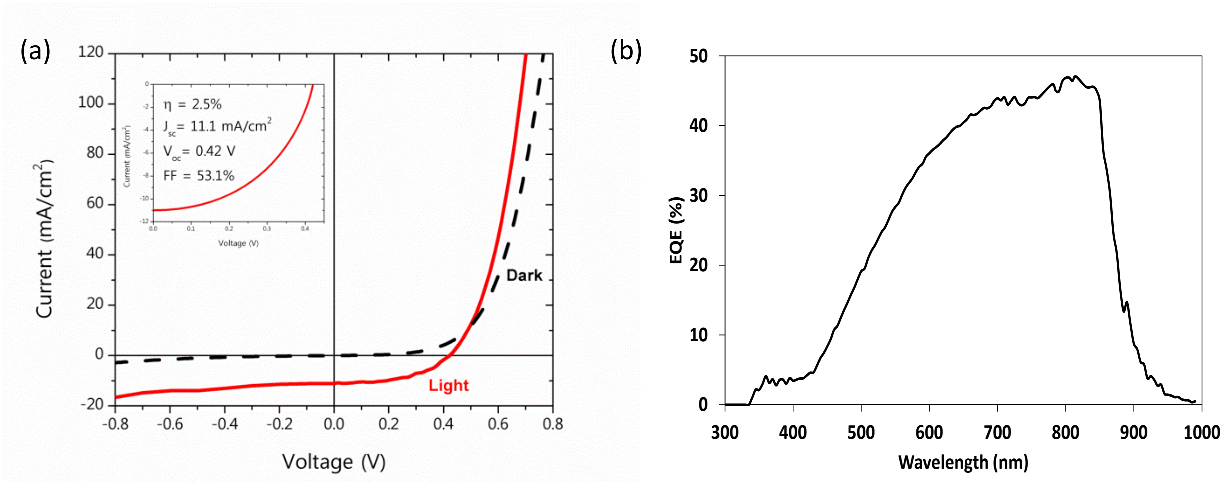


Figure 4. (a) Recent PV results. Dark and illuminated (AM1.5G) current-voltage characteristic of nanowire-on-Si solar cell, showing 2.5% efficiency. Inset shows the illuminated I-V curve in the fourth quadrant with efficiency (η), short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF). (b) External quantum efficiency of the cell.

Simon Watkins Group (Simon Fraser University):

The effort at SFU focussed on developing the technical ability to grow advanced nanowire (NW) structures by metalorganic vapour phase epitaxy (MOVPE). Prior to this award, the SFU team focussed exclusively on planar thin film growth. During the 5 year period of the award, SFU has developed world class expertise in the study and fabrication of semiconductor nanowire structures. Much of the credit for our success can be attributed to the very high productivity of PhD student Omid Salehzadeh who was first author on 7 refereed journal publications and coauthor on another 3 during the course of this project. Student Ali Darbandi has subsequently taken over as the lead student on this project and is also making excellent progress. Highlights of the 5 year project are listed below.

Control of growth mode of III-V nanowires using MOVPE, by means of precursor chemistry: The primary role of SFU in this collaboration was to provide expertise using the metalorganic vapor phase epitaxy (MOVPE) growth technique. This is considered to be a complimentary technique to molecular beam epitaxy (MBE) which is employed at McMaster. In principle, MOVPE has the potential for improved lateral growth around nanowires due to the fact that it occurs at much higher pressures. Our first major contribution was to demonstrate lateral growth of various III-V materials, primarily GaAs. We discovered early on that changing the precursor chemistry has a striking effect on the growth mode of III-V nanowires. Precursors with relatively strong bonds can be catalyzed by the Au nanoparticle at low temperature, at temperatures where direct vapor-solid growth is not possible, resulting in purely axial growth. Use of a different precursor with a lower decomposition temperature results in primarily lateral growth, which enables fabrication of core-shell structures. This was the main result of two early papers [1,2].

Development of nanoprobe technique for characterization of electrical properties of III-V nanowires: In order to fabricate advanced photovoltaic devices based on nanowires, control of doping in the various segments is extremely important. Knowledge of quantitative doping concentrations is challenging and many groups use overly simplistic assumptions, such as basing the doping estimates on data from Hall measurements on planar films where the doping mechanism is totally different. As part of this project we developed the capability to perform measurements of the current-voltage characteristics of single nanowires without removal from the substrate using a tungsten nanoprobe in a scanning electron microscope. This led to a series of studies of the quantitative dependence of resistivity and carrier concentration on various dopants in GaAs, include Te for n-doping [3,4,5], and carbon and Zn for p-doping [6]. The reproducibility of the technique is aided by the existence of a highly conductive metal nanoparticle at the tip of the NW. In addition, our McGill collaborator, Zetian Mi sent a student to SFU to perform nanoprobe measurements on their InN nanowires. This led to a successful joint publication which confirmed the high electrical quality of their InN [7]. Samples of GaAs NWs grown using Ga catalyst were also provided by McMaster, however we were unable to measure electrical properties in this case, presumably due to low doping resulting in carrier depletion. The nanoprobe work has been widely recognized and resulted in numerous invited talks at various conferences.

Development of quantitative model for determining relaxation in strained core-shell NW structures: Related to the passivation studies is our effort to establish accurate quantitative models for the estimation of critical thicknesses in various III-V heterojunction combinations. The reduced dimensionality of NWs means that they can more readily accommodate strain that their planar counterparts. Student Omid Salehzadeh developed a quantitative model for estimating critical thicknesses of strained core-shell heterostructures including most of the common III-V materials combinations. His model was based on the methods of LaPierre's group and others. This was validated experimentally by growing a series of core-shell structures of materials such as GaAs/GaP, InAs/GaAs, GaAs/GaSb, and InAs/InP. Careful validation of the model was achieved by comparison with transmission electron microscopy measurements of dislocation formation for various core-shell dimensions [8,9].

Demonstration of quantitative passivation of GaAs NWs using GaP: One of the keys to successful implementation of NWs in solar devices must be the elimination or reduction of surface state recombination. Since NWs have very large surface to volume ratio, this is a particularly acute issue. PhD candidate Ali Darbandi has explored the use of the wide bandgap material GaP to passivate surface states in GaAs n-type NWs. Using the nanoprobe method he was able to conclusively demonstrate a strong reduction in the surface depletion width of GaAs NWs with a GaP shell thickness of several nm. Surprisingly, the improvement was still observed even when large densities of dislocations were present on the GaP shell. Photoluminescence measurements performed at McMaster confirmed the significant reduction of surface traps. This work led to a joint publication with McMaster [9].

Demonstration of core-shell tunnel diodes for advanced heterojunction PV devices: Ali Darbandi has been working for about a year now to develop methods to use the nanoprobe to measure the electrical properties of single NW core-shell pn junctions. One of the most striking results of this work has been the observation of radial core shell tunneling in a GaAs n-p core shell diode structure. Clear negative differential resistance has been observed together with very high peak current densities. In addition to potential applications in high speed transistors, tunneling junctions could eventually find application to couple multiple junction core-shell devices, similar to the approach used in advanced planar PV. This work has been submitted to Nano Letters [10].

Demonstration of PV effect in single core-shell NWs: Ali Darbandi's thesis will continue to focus on the fabrication and electrical characterization of single NW PV devices. In the final months of the project this main goal is to demonstrated efficient photodiode action in a core-shell structure by putting together all of the pieces that have been developed so far. A calibrated optical fiber has been mounted within the scanning electron microscope used for the nanoprobe measurements.

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Zetian Mi (McGill University):

Although large surface to volume ratio of nanowire structures is advantageous for photovoltaic application, the large surface area is a prime cause of surface state related non-radiative recombination. This results in poor open circuit voltage and poor fill factor, which eventually leads to poor efficiency. To circumvent this problem, in Year 4, we have designed core-shell InGaN/GaN/AlGaN heterostructures where higher bandgap material AlGaN surrounds the InGaN/GaN core nanowire structures and effectively reduces the surface non-radiative recombination. The growth techniques were described in Year 4 report in detail and a significant improvement in the PL intensity of the core-shell structure compared to the non-core-shell structure was also reported.

The large area InGaN/GaN/AlGaN dot-in-a-wire core-shell solar cell devices were fabricated using the following process. First, nanowire arrays were spin-coated with polyimide resist for planarization and passivation, followed by O_2 dry etching to reveal the top region of the nanowires. Subsequently, the top AlGaN segment was etched by a Cl_2: Ar reactive ion etching process. Ni (5 nm)/Au (5 nm)/indium tin oxide (ITO) and Ti(10 nm)/Au(100 nm) layers were then deposited on the exposed GaN:Mg surface and the backside of the Si substrate to form p- and n- metal contacts, respectively. The fabricated devices with Ni/Au and Ti/Au metal contacts were first annealed at ~500 °C for 1 minute in nitrogen ambient. Upon the deposition of the ITO transparent contact, a second annealing step was performed at 300 °C in vacuum for ~1 hour. Multiple metal grid patterns were deposited on the device surface to facilitate the hole transport and injection process.

The current-voltage (I-V) characteristics were measured for a core-shell and non-core-shell structure and are presented in Fig. 1. The photovoltaic effect is clearly evident from the I-V curve of the InGaN/GaN/AlGaN core-shell solar cell. An improvement in the short circuit current density is also observed in the core-shell structure compared to the non-core-shell structure [1]. However, it should be mentioned here that this is only at 1.5 sun illumination and the device fabrication techniques need to be optimized to achieve enhanced performance from the core-shell solar cell.

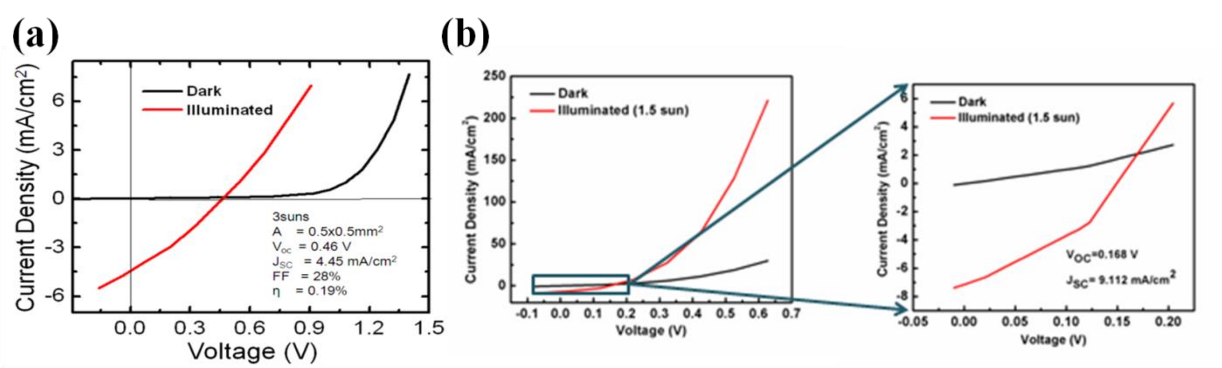

Figure 1 Current voltage characteristics of nanowire solar cell under 1.5 sun illumination: (a) non-core-shell, and (b) core-shell [1].

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