Project 09: Nanowire Photovoltaics
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Project Co-applicants: Zetian Mi (ZM) and Simon Watkins (SW)

Semiconductor nanowires are prime candidates for third generation solar cells with the potential for lower cost and greater energy conversion efficiency compared to conventional thin film devices due to less material utilization, enhanced photovoltage or photocurrent due to hot carrier or multi-exciton phenomena[1,2,3,4,5,6], enhanced light absorption[7], and freedom from lattice matching requirements due to strain accommodation at the nanowire surfaces, which provides greater freedom in bandgap engineering and substrate selection. Of particular interest are coaxial structures in which a doped nanowire core is surrounded by a shell of opposite doping type, forming a core-shell p-n junction[8,9,10]. A coaxial p-n junction enables carrier extraction across the radius of the nanowire, while the long axial length of nanowires permits high optical absorption due to light trapping effects. While various Silicon nanowire photovoltaic devices have been reported[11,12,13,14,15], III-V coaxial photovoltaic devices remain to be studied. Unlike Si, the alloy composition and therefore the bandgap of III-V nanowires may be tuned to better match the solar spectrum. Hence, GaAs and related III-V materials offer the highest energy conversion efficiency in photovoltaic devices.

Nanowires are grown using metal seed particles in a physical vapor deposition process which allows precise control of nanowire geometry (see Fig. 19). With this method, nanowires with lengths of several microns and diameters ~10 nm are possible. However, many fundamental aspects of nanowire PV are still not well understood including nanowire doping and surface passivation which will be addressed by this project.

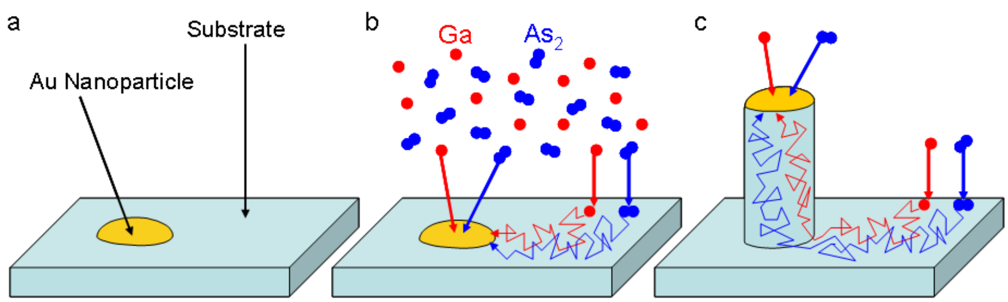
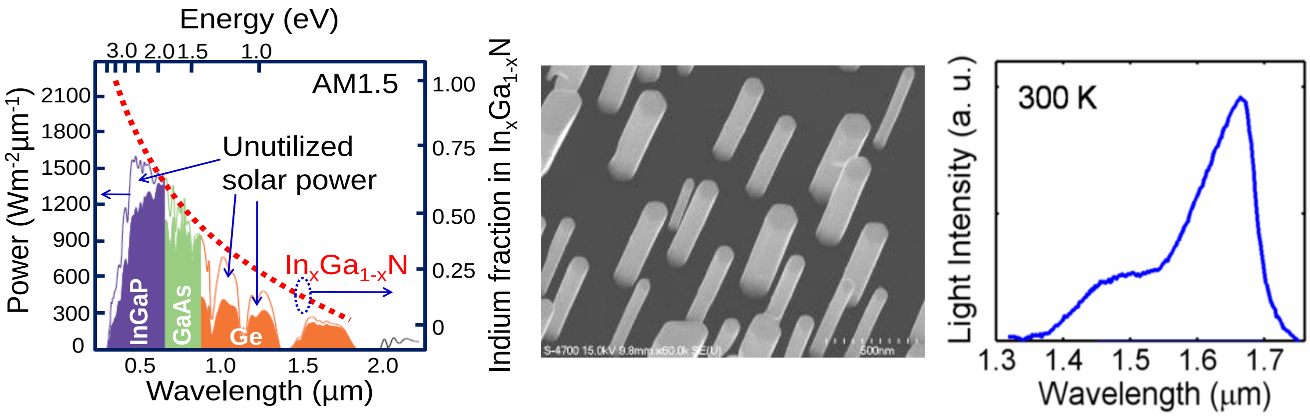


Fig. 19. Illustration of typical nanowire growth process. (a) Metal nanoparticles (typically Au) on a substrate surface. (b) Precursor gas atoms and/or molecules (e.g., Ga, As_2) are incident on the substrate surface, diffuse and become trapped by the metal particle. (c) Supersaturation of the metal particle results in the formation of a nanowire (GaAs in this case).

In(Ga)N-Based Nanowire Solar Cells
To date, solar cells with the highest efficiencies, ~32.0% and 40.7%, have been realized in III-V stacked cells and concentrators, respectively. Such devices are generally grown on GaAs or Ge substrates, which are prohibitively expensive and, as a result, their terrestrial applications have been very limited. Illustrated in Fig. 20 (a) is the solar power spectrum as well as the spectrum that is effectively absorbed by a state-of-the-art GaAs/InGaP/Ge triple-junction solar cell. It is evident that a large portion of the solar spectrum in the energy ranges of 1.0 – 1.2 eV and 2.5 – 3.4 eV has not been utilized. On the other hand, the energy bandgap or absorption spectrum of the $In_xGa_{1-x}N$ alloy can be continuously varied from 0.7 to 3.4 eV, providing an almost perfect fit to the solar spectrum. Unlike bulk material, high quality InGaN nanowires can be grown directly on Si substrates, which eliminate the use of expensive III-V or Ge substrates. Therefore, InGaN may lead to a new generation of solar cells with greatly improved efficiency and lower cost. The nitrides also exhibit many favourable photovoltaic properties, including

high carrier mobility, low effective carrier mass, and high absorption coefficients.



(a) **(b)** **(c)**

Fig. 20. (a) The utilized solar power spectrum of a triple junction Ge/GaAs/InGaP solar cell and bandgap energies of the InGaN alloy system that cover the entire AM1.5 solar spectrum; (b) SEM image of non-tapered InN nanowires grown directly on Si substrates; (c) photoluminescence emission spectrum measured at room-temperature.

The group of Z. Mi (McGill) has recently achieved, for the first time, superior quality InGaN nanowires grown directly on Si substrates with non-tapered morphology, shown in Fig. 20(b). They also exhibit photoluminescence at room temperature, illustrated in Fig. 20(c). To realize high efficiency heterojunction solar cells on Si, p-type InGaN nanowires will be first grown on n+ Si substrates. Insulating photoresist will then be used to fill the spacing between the nanowires. The nanowire tips are subsequently exposed for metal contact by partially dissolving the photoresist on top of the sample surface. Ni/Au and Ti/Al metal contacts will then be deposited on the InGaN nanowires and the n-type Si substrate, respectively. The processed InGaN/Si nanowire solar cells will be characterized, and iterations of the design, growth, fabrication and characterization will be performed. Our objective is to demonstrate such devices with efficiency > 10%, compared to the currently reported ~2.7% [16]. This goal will be achieved by collaboration between Z. Mi (McGill) and R.R. LaPierre (McMaster) to provide detailed studies of the InGaN nanowire crystal structure and the InGaN/Si interface using the high resolution transmission electron microscopy (HRTEM) facilities at the Canadian Centre for Electron Microscopy at McMaster. Subsequently, the photoluminescence (PL) of individual nanowires will be measured and correlated with the structural measurements and with the cell performance. In addition, InGaN coaxial heterostructures will be fabricated in which a larger bandgap (higher Ga content) shell surrounds a smaller bandgap (higher In content) core to act as a passivating layer to reduce carrier recombination on the nanowire sidewalls. These structures will also be studied by HRTEM and PL and correlated with cell performance for comparison to unpassivated nanowire cells. Similar device processing has been carried out by the group of R. R. LaPierre at McMaster using GaAs nanowires. Knowledge and results related to the device processing will be shared between the groups of Z. Mi and R.R. LaPierre through student exchanges during the second and fourth year of the proposal to determine the processing methods resulting in optimum PV efficiency.

GaAs-Based Nanowire Solar Cells

GaAs nanowire devices from the R.R. LaPierre group have been fabricated using the molecular beam epitaxy (MBE) facilities of McMaster, demonstrating PV efficiencies of several percent. This proposal will support a new collaboration to grow nanowires by metalloorganic chemical vapour deposition (MOCVD) using the facilities of S. Watkins at Simon Fraser. S. Watkins has recently begun a program to fabricate III-V and II-VI (ZnO) nanowires by MOCVD using Au and other catalysts. In comparison to MBE, the MOCVD process is a more industry-relevant process by enabling deposition over multiple wafers and is the process used for fabrication of concentrator cells. The MOCVD process also results in less parasitic thin film growth between the nanowires which is currently a limiting factor in the PV efficiency of MBE-grown devices. Finally, the group of R. R. LaPierre has found difficulties in dopant incorporation in MBE-grown nanowires, which may be resolved by MOCVD. For example, elemental Si may be amphoteric along the (111) growth direction of MBE-grown nanowires; i.e., Si may be either n-type[17] or p-type[18] depending on growth conditions. Te supplied by a GaTe source, is an alternative n-type dopant, but it is difficult to incorporate in MBE-grown nanowires due to surface segregation. Doping of nanowires and their characterization is therefore one of the big open challenges of nanowire research. This proposal will include an investigation of n- and p-type dopant incorporation in MOCVD-grown nanowires using metalloorganic sources of Te, S, C, Zn, and Mg. Doped nanowires will be fabricated at McMaster into individual nanowire field effect transistor devices and 4-point probe devices which enables the determination of dopant type, concentration and carrier mobility. These results will be correlated with the performance of cells fabricated from p-n junction core-shell nanowires for comparison with similar MBE-grown structures. Knowledge related to the growth of nanowires and PV device processing will be shared between the groups of S. Watkins and R. R. LaPierre through student exchanges during the first and third year of the proposal.

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