

Project 06: Polymer/Nanostructured Silicon Heterojunction Solar Cells

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Silicon is far from ideal as a material for photovoltaic power generation from sunlight. Silicon's indirect bandgap necessitates the use of relatively thick layers to absorb a significant fraction of the spectrum. The minority carrier lifetime in these layers must be high to allow photogenerated carriers to reach the collecting junction, in turn placing stringent requirements on material purity and crystallinity. The bandgap of Silicon is 1.1 eV, while the optimum bandgap for solar energy conversion in a mono-junction inorganic device is known to be closer to 1.3 eV. However, Silicon is abundant, non-toxic, and technologically well understood, which justifies continued research to attempt to overcome its drawbacks. Hydrogenated amorphous Silicon (a-Si:H) has long been known to provide at least a partial solution to these drawbacks. The lack of long-range order in a-Si:H produces a quasi-direct gap, and also increases the bandgap to a near-ideal 1.6 eV, allowing thin films of this material to be used to produce commercial solar cells with very low cost and reasonable efficiency. It can also form the basis for inexpensive thin film photovoltaic devices that can be incorporated in building materials, which appear to offer the best opportunity for solar power generation in areas already served by the grid. However, there are drawbacks. Maintaining acceptable carrier lifetime-mobility products in a-Si:H is critically dependent on the passivation of dangling bonds with hydrogen. It has long been known that the Si-H bond is unstable¹, leading to degradation under illumination through the Staebler-Wronski effect (SWE)².

Nanostructuring of inorganic films can enable band-structure modifications that are highly desirable for photovoltaic energy conversion. In theory, the band structure modifications observed in a-Si:H can also be obtained in nanostructured crystalline material. In Silicon, and other narrow-gap, inorganic semiconductors such as germanium, nanostructuring can widen the bandgap, better matching the solar spectrum, and can give a quasi-direct band structure, improving the absorption coefficient. In nanostructured *c*-Si it may also be possible to obtain these advantages without Staebler-Wronski degradation. To avoid light-induced degradation, the implementation of a practical solar cell will require careful attention to passivation of all interfacial bonds, blocking pathways for electron-hole recombination at these surfaces. Minority carrier diffusion lengths in inorganic thin films are likely to be very short, making it highly desirable to place the collecting junction close to the surface. Both issues argue for the use of heterojunctions.

In seminal work M. A. Green, *et al* demonstrated that nearly ideal p-n junction-like properties could be obtained by depositing metals on Silicon surfaces carefully passivated by the growth of ultra-thin oxide layers through which electrons could readily tunnel³. The available technology of the time led to application of these concepts in Schottky barrier-like Metal-Insulator-Semiconductor (MIS) solar cells. Naturally, the presence of the top metal layer limited the amount of light that could reach the semiconductor, restricting efficiency.

In recent years there have been enormous advances made in the technology of conducting polymers⁴. Indeed, recent research has revealed great potential for two or more layer thin-film organic polymer photovoltaic devices⁵, but efficiencies have so far been limited by tight binding of excitons⁶. These results lead to the question of whether heterojunction organic/inorganic devices could provide better performance than existing thin film technologies, which has led very recently to reports of polymer-semiconductor heterojunctions⁷. Unlike metal layers in early Schottky barrier and MIS devices, the conductive polymers can be nearly transparent to much of the solar spectrum, allowing light to reach the semiconductor underneath. Work to date has been cursory, concentrating on initial demonstrations rather than detailed investigation.

This project will experimentally characterize photovoltaic devices incorporating a heterojunction(s) between structured inorganic semiconductor layers and coated organic layers. The three main components in this investigation will be:

- 1) structured inorganic layer(s)
- 2) interfacial passivation of inorganic material(s)
- 3) conformal organic layer(s)

Structured Inorganic Layer(s)

At least initially, the focus will be on Silicon as the inorganic semiconductor material component. It is our intention to carry out experiments using several forms:

- single crystal Silicon (c-Si)
- amorphous Silicon (a-Si)
- “black Silicon” nanostructured by reactive ion etching (RIE)
- glancing angle deposition (GLAD) templated nanotube or nanorod Silicon
- nanoparticulate Si

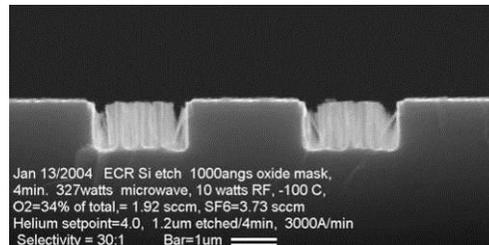


Fig. 14 Nanostructured silicon produced in Carleton Microfab

The purpose of examining the single crystal and amorphous materials is to provide end-points in the crystallinity continuum for comparison purposes and as a benchmark to determine progress. Black Silicon has been previously generated by many groups using a number of methods. A method has been developed in the Carleton Microfab (Fig. 14) and is a result of self-templated etching during ECR-RIE with careful control of etching parameters and sample temperature.

The GLAD-templated nanotube/nanorod growth will draw on recent results out of M. Brett’s group at the U. of Alberta⁸. In this work he has shown the ability to create dense arrays of robust Si nanotubes having wall thicknesses of less than 20 nm as shown in Fig. 15. Preliminary results in the lab have indicated that it should be possible to achieve wall thicknesses of ~4 nm, and this size range should provide the required bandgap alterations for improved photovoltaic response. Tailoring and analysis of the properties of these films to optimize their use for solar cells will be a major effort in this project.

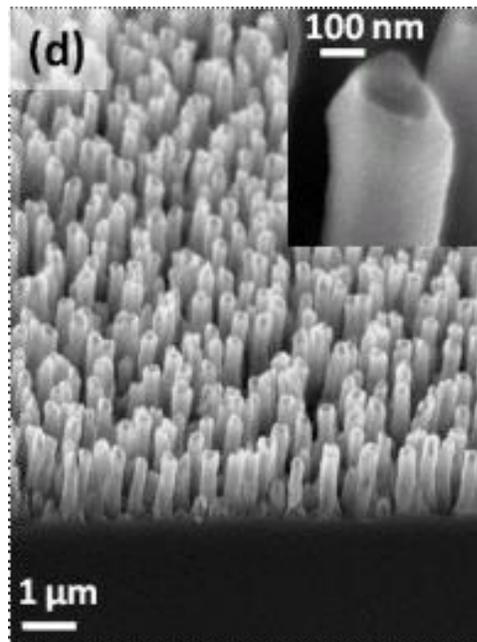


Fig. 15

Interfacial Passivation of Inorganic Material(s)

We propose to insert ultra-thin interfacial dielectric layers in polymer/Silicon heterojunctions to passivate the interface, with the goal of obtaining p-n junction behaviour. As indicated above, we will first develop this technology on crystalline bulk Silicon, but then investigate its extension to nanostructured Silicon surfaces and then eventually to nanostructured nanocrystalline Silicon thin films. It is our intention to investigate both grown oxide layers and other dielectrics formed by well-controlled conformal deposition techniques such as atomic layer deposition (ALD). The ALD growth and

characterization will be undertaken in collaboration with S. Barry's group in Carleton's Department of Chemistry.

In addition to the dielectric tunnel layer, a method to tie up the free Silicon bonds in the various nanostructured materials will undoubtedly be required. Hydrogenation will first be attempted with the hope that the SWE can be better managed than in the case of a-Si:H based devices. If operational testing shows optical degradation of the devices then additional methods of passivation will be undertaken.

Conformal Organic Layer(s)

In all cases a conformal coating using a conducting polymer (CP) or small molecule organic (SMO) will be required to complete the heterostructure. Initially, a commercially available conducting polymer such as poly(3,4-ethelenedioxythiophene) (PEDOT) will be used. This material has been reasonably well characterized and can be used as a hole conductor with a conductivity of up to 750 S/cm. In addition, the work function is appropriate to allow its use as a quasi-metal with Silicon in the Schottky barrier type solar cell of interest. M. Brett's group has recently reported a technique to improve the uniformity and conductivity of PEDOT layers⁹. Other polymers and organics will be used if changes in the energy levels of highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) are needed. A change may also be undertaken if exciton generation in the organic side of the heterojunction is deemed useful.

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