

Lateral Nanoconcentrator Nanowire Multijunction Photovoltaic Cells

Investigators

Professor H.-S. Philip Wong (Department of Electrical Engineering)

Professor Peter Peumans (Department of Electrical Engineering)

Professor Mark Brongersma (Department of Materials Science)

Professor Yoshio Nishi (Department of Electrical Engineering)

Graduate researchers: Ms. Ying Chen, Mr. Jason Parker, Ms. Trudie Wang

Post-doctoral researcher: Dr. Aaron Hryciw

Senior Research Associate: Dr. Jim McVittie

Abstract

We have made progress in (a) simulation of metal nanostructures for light concentration and lateral solar spectrum splitting, (b) Ge and TiO₂ nanowire growth and device fabrication. The methodology developed for the simulation of metal nanostructure enables us to explore various designs for the light focusing structures in the coming months. The nanowire growth results established the ability to grow 20 – 40 nm nanowires for the fabrication of solar cells with a confined extent for light collection.

Introduction

The objective of this research project is to develop a novel type of multijunction photovoltaic cell that uses lateral arrays of semiconductor nanowires (NWs) of various bandgaps as the elements that convert optical energy into electrical energy.

In contrast to conventional multijunction cells, the NWs of varying bandgap will **not be connected in series** in our approach. Instead, a specially-designed nanostructured metal film is used to split the incident broadband solar spectrum and localize spectral energy in different lateral spatial locations (spectral splitting and concentration) coinciding with the location of the NWs of the optimized bandgap.

The same nanostructured metal film also allows for current extraction from each nanowire separately such that photocurrent matching is not required. This allows us to use a wide range of bandgaps (depending on the performance of the lateral metal spectral splitter and concentrator) without requiring current matching. This removes the most important efficiency bottleneck of multijunction cells such that efficiencies >45% may be achieved over a wide range of spectral conditions

The NWs can be grown by the vapor-liquid-solid (VLS) method and the sol-gel approach, both of which have the potential for low cost manufacturing since epitaxial growth conditions are easily met at moderate temperatures over the short length scale of a NW. To demonstrate the lateral multijunction principle, we will use nanowires of materials that span the solar spectrum, including Si, Ge, III-V materials and other abundant, non-toxic, low-cost elements, e.g., TiO₂.

Background

Multijunction cells are currently the photovoltaic technology with the highest demonstrated power conversion efficiency exceeding 40%. While successful, this approach has several inherent limitations. Efficiencies exceeding 45% are theoretically possible, but practically unachievable because it becomes impossible to match the photocurrents of the subcells such that efficient operation is achieved for the varying illumination conditions that occur, for example, over the course of a day. Our approach uses lateral arrays of **semiconductor nanowires** (NWs) of various bandgaps as the elements that convert optical energy into electrical energy. To achieve spectral splitting needed for efficient multijunction operation, the NWs are located on top of a specifically **designed metal nanostructure** that acts as (1) an array of electrodes to the nanowires, a (2) lateral spectral splitter, and (3) as a lateral concentrator.

Results

In the last few months of this project, we have made progress in selecting the basic methodologies for the project. In particular, the modeling of light concentration and spectral splitting by metal nanostructure has established preliminary results. The fabrications of nanowires of TiO₂ and Ge have made substantial progress. Nanowires of TiO₂ with 25 nm diameter were obtained using an innovative combination of the sol-gel process and the diblock copolymer self-assembly process. Individual nanowires of Ge with 40 nm have been grown using the vapor-liquid-solid mechanism. These nanowires have the appropriate diameter for wavelength selective absorption in a well-defined, small spatial location.

Electromagnetic Simulations of the Lateral Concentrator

As a preliminary step to designing the metal nanostructure that will be used to concentrate and laterally split the solar spectrum in the multijunction PV cell, finite element modeling was used to model the optical focusing effect of an archetypal tuned metal nanoantenna. Comparison of our models against experimental results of similar structures will allow us to calibrate our models and eventually design more complex structures for concentrating light.

Since the bowtie antenna is one of the more prominent and experimentally demonstrated geometries, the Finite Element Analysis (FEA) model focused on reproducing a metal bowtie deposited on a dielectric substrate in an air environment. The dimensions and material of the bowtie were chosen to follow Kino selected geometry [Sundaramurthy, Kino (2006)] such that our results could be compared. The modeled bowtie has a thickness of 20nm and a gap of 16nm. The bowtie material was modeled as Au and the substrate was SiO₂. In order to accurately model an incident plane wave hitting the bowtie antenna from the z-direction, perfectly matched layer (PML) boundary conditions were used to surround the substrate and air above and below the bowtie geometry. The meshed geometry is shown in 2-dimensions in Fig. 1.

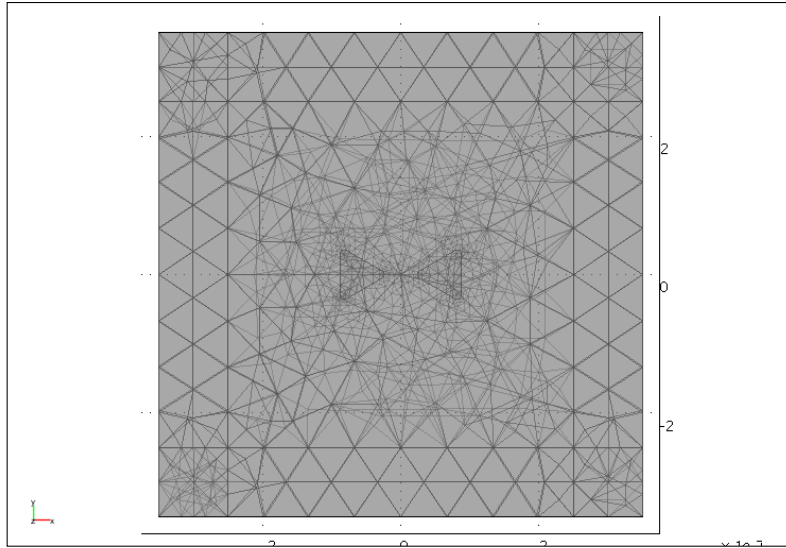


Fig. 1: Meshed bowtie geometry in 2-dimensions.

The intensity of the optical electric field ($|E|^2$) was evaluated in the center of the bowtie as a function of wavelength, as shown in Fig. 2a. The structure exhibits a resonant peak near 700nm in agreement with the resonance recorded by Kino and coworkers at 830nm after accounting for the difference in substrate index (Kino used ITO with $n_{ITO} > n_{glass}$ leading to a spectral red-shift in Kino's case). The optical electric field intensity profile for the bowtie excited by light at $\lambda=750\text{nm}$ is shown in Fig. 2b, agrees qualitatively with the results reported by the Kino group.

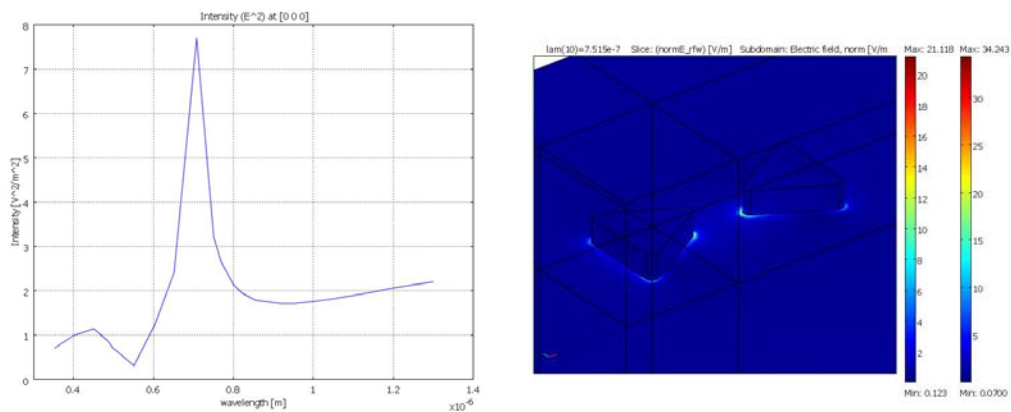


Fig. 2: (a) Intensity plotted against wavelength at the center of the bowtie gap on the substrate surface. (b) Optical electric field intensity profile.

The next stage of our modeling work will explore whether such metal nanoantenna structures can enhance the amount of energy absorbed by semiconductor nanowires placed in the location where there is maximum field enhancement. More complex geometries will also be looked at to see if different wavelengths can be spatially

separated and concentrated by metal nanostructures. We have made an important step in that direction by establishing a very fast electromagnetic field model based on the rigorous-coupled-wave-analysis (RCWA). This tool will give us the unprecedented ability to rigorously optimize photonic structures.

Ge Nanowire Growth and Device Fabrication

The basic Ge nanowire solar cell device structure and device fabrication process flow are shown in Fig. 3.

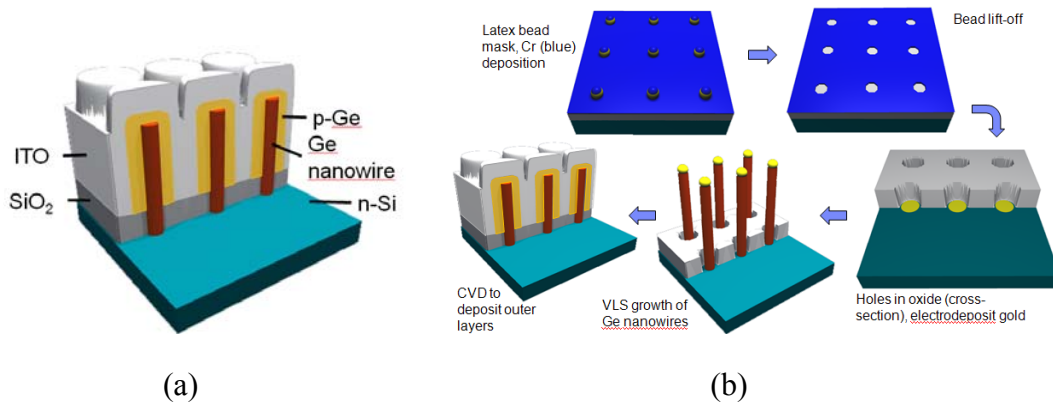


Fig. 3: (a) Ge nanowire device structure. (b) Device fabrication process flow.

In order to define the position of the nanowires, we utilize patterning techniques that employ packed latex beads. The latex beads (polystyrene) are spun coat onto a thermally grown SiO₂ surface (Fig. 4) and assembled in a close-packed geometry. The bead size is reduced with an O₂ plasma etch. The pitch between the latex beads is fixed by the original bead size, but the final bead diameter can be tailored using O₂ plasma etches.

A Cr layer is then deposited. The beads are lifted off, followed by etching of the underlying oxide to create holes in the oxide. Nanowires are grown via the VLS method, the gold is removed with a wet etch, and the p-type Ge layer is deposited using CVD.

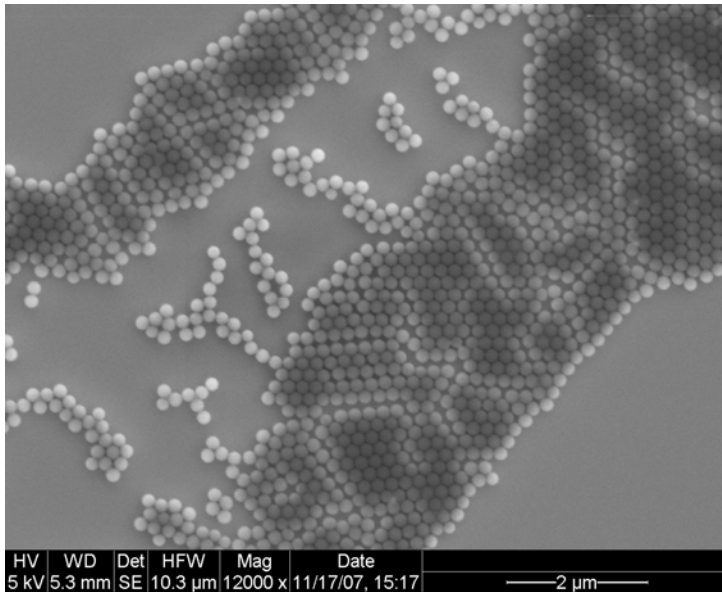


Fig. 4: Self-assembled latex beads

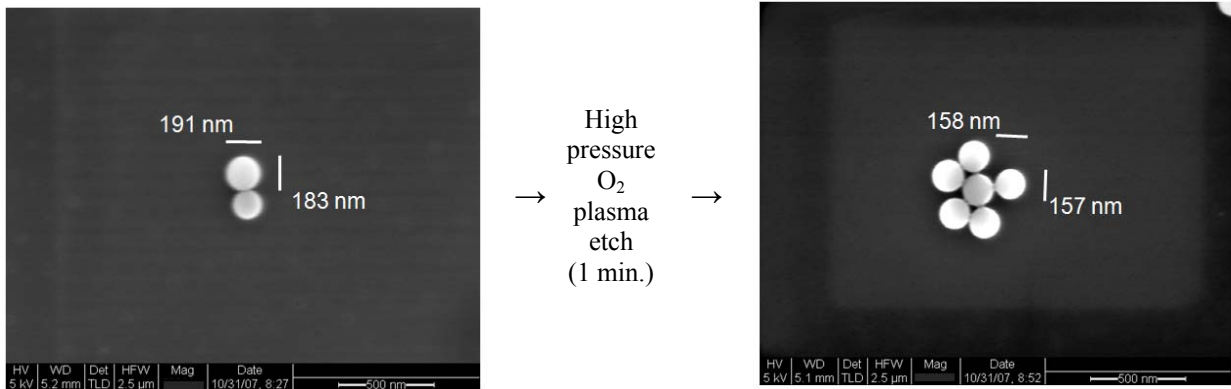


Fig. 5: Trimming of latex bead size.

For the sake of simplicity in the early processing of the nanowire p-i-n structure, sparse latex bead patterns are currently used for the nanowire processing. This decouples the steps creating the hole pattern and the subsequent nanowire processing steps.

Ge nanowires grown after Au electrodeposition in 50 nm holes is shown in the SEM picture in Fig. 6. The substrate is Si (111), as Ge nanowires have been shown to preferentially grow in the [111] direction on Si. Prior to VLS nanowire growth, electrodeposition must be done. We begin this process with a short 1% HF dip to etch away oxide at the bottom of the holes. The electrodeposition is then done using aqueous HAuCl_3 with either an applied voltage or electrolessly. Both methods have been successful. The thickness of the Au catalyst at the bottom of the holes depends on the electrodeposition time and hole density.

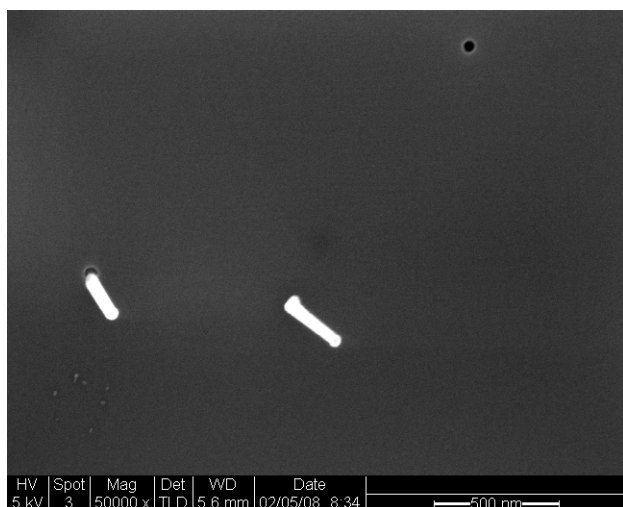


Fig. 6: Isolated, individual Ge nanowire grown in 50 nm holes.

An issue with the gold catalyst electrodeposition can be seen in the figure above. Gold is not deposited in some holes. This is related to the surface tension of the fluids used in the electrodeposition, which may not allow fluid to enter all small holes. To induce electrodeposition in all small holes, we are experimenting with adding surfactant to the electrodeposition solution.

Titanium Dioxide Dye-Sensitized Solar-Cells

During the past few months, we have investigated templated sol-gel growth of TiO₂ nanowires. We did sol-gel plating of polycrystalline TiO₂ thin film on a flat substrate, which has an average anatase crystallite grain size of as large as 52nm. Many experiments have been done and improvements have been made on sol-gel depositing of TiO₂ in porous anodic alumina (PAA) and diblock copolymer templates. So far the chemical composition of TiO₂ in the thus grown nanowires has been verified by XPS and Raman measurement is planned to verify the anatase phase in the nanowires.

TiO₂ Nanowire Array Growth with Porous Anodic Alumina (PAA) Template

During the past few months, we were able to deposit TiO₂ nanowires and nanotubes in porous anodic alumina (PAA) template by electrically induced sol-gel method, as shown in Figure 7 and Figure 8. We observed that the sol-gel TiO₂ morphologies depend on the concentration of KNO₃. A concentrated KNO₃ tend to generate wires and diluted KNO₃ results in tubes. The XRD spectrum of the thin films deposited on ITO and Au substrates showed high anatase TiO₂ concentration and a large average grain size of 52nm.

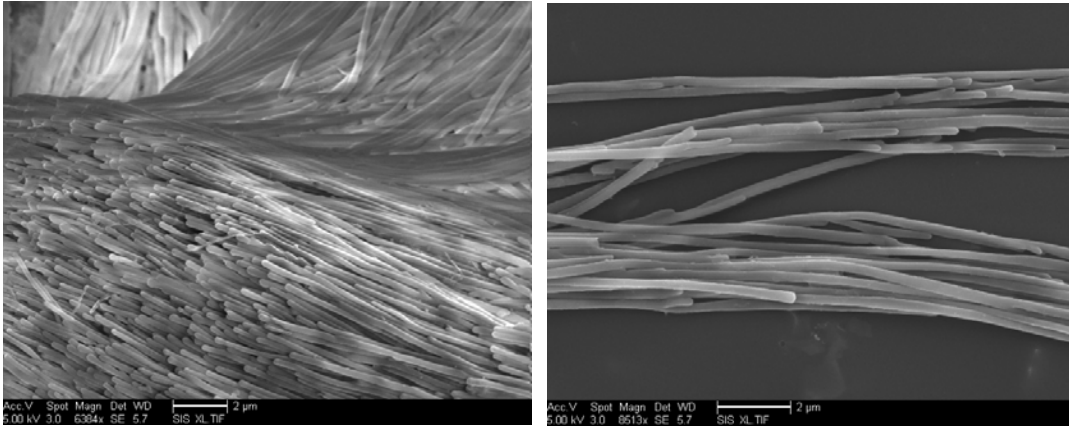


Figure 7: Nanowire growth in Whatman 200nm diameter pore PAA: Cathodical electrodeposition at -1.1V (vs. SCE) from an aqueous solution containing approximately 0.15M $\text{TiO}_x(\text{SO}_4)$, 0.07M H_2SO_4 (partially as $(\text{NH}_4)_2\text{SO}_4$ with $\text{pH} \approx 2.2$) and 0.39M KNO_3 , and subsequent heat treatment in air at 450°C for 24hrs. (Scale bars: $2\mu\text{m}$)

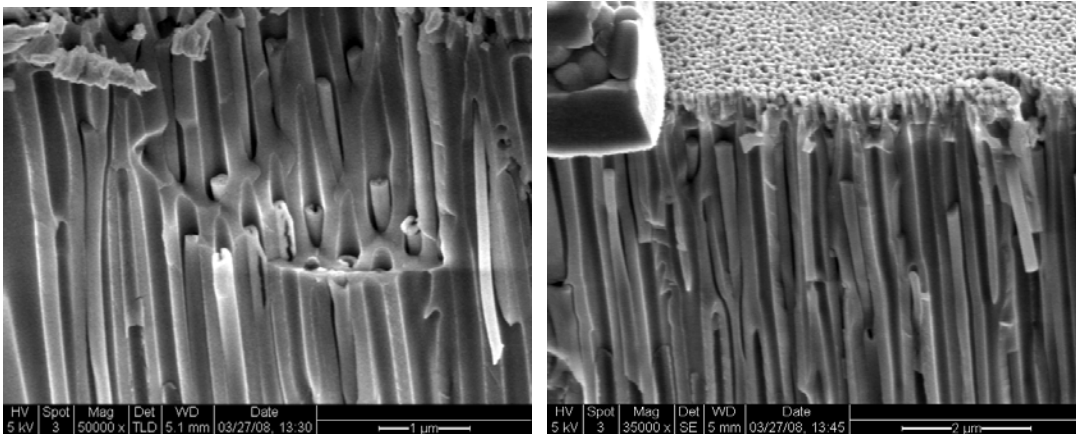


Figure 8: 200nm pore PAA template with ITO coating after sol-gel process: Cathodical electrodeposition for 8h at -1.1V (vs. SCE) from an aqueous solution containing 0.02M TiOSO_4 , 0.03M H_2O_2 and 0.1M KNO_3 , and subsequent heat treatment in air at 400°C for 1h. (Scale bars: Left: $1\mu\text{m}$; Right: $2\mu\text{m}$)

TiO₂ Nanowire Array Growth with Diblock Copolymer Template

We also used diblock copolymer as the sol-gel TiO_2 growth template. Compared to porous anodic alumina (PAA) templates, diblock copolymer templates have the following advantages:

- With the 20nm pore diameter and relatively low total thickness, it is more likely that the nanowire can stand on the substrate, which makes it easier to perform optical property measurement.
- There is no gap between the polymer template and the substrate, so all sol-gel processes will happen inside the pores of the template.
- The polymer template will not liftoff during TiO₂ nanowire annealing, which make the structure with individual nanowires standing on the substrate possible.
- Block copolymer can be easily removed by dry-etching, which eliminates the chemical etching step which can cause nanowires to collapse.

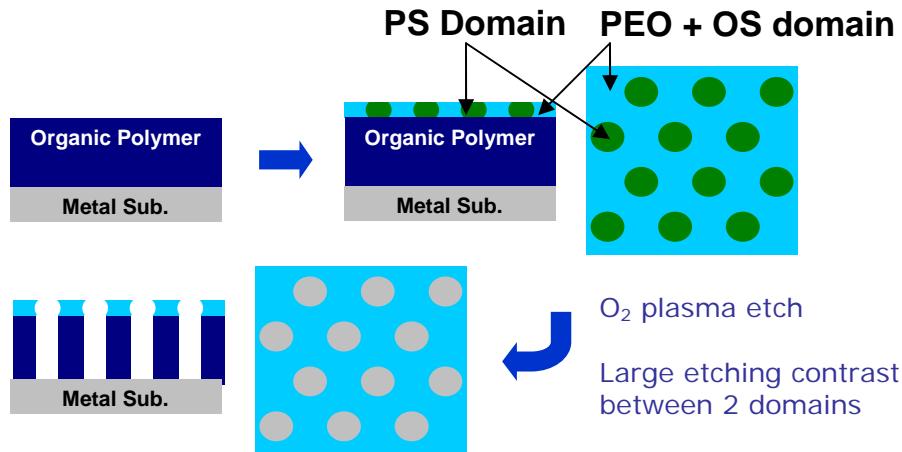


Figure 9: (Figure courtesy of Sung-Woo Kim, Stanford University) Preparation processes of diblock copolymer template.

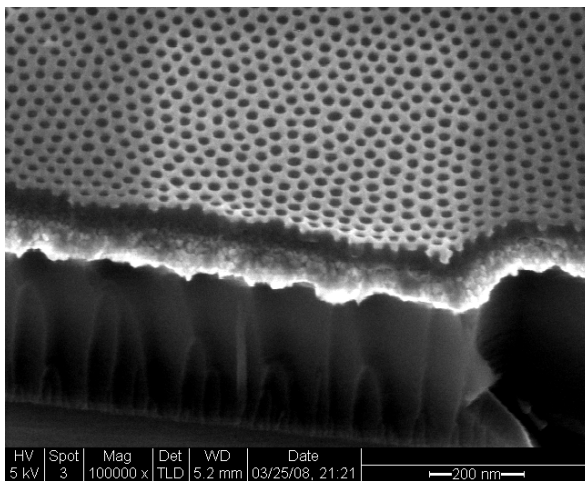


Figure 10: SEM picture of a diblock copolymer template with a pore diameter of 25nm and pore depth of 70nm. (Scale bar: 200nm)

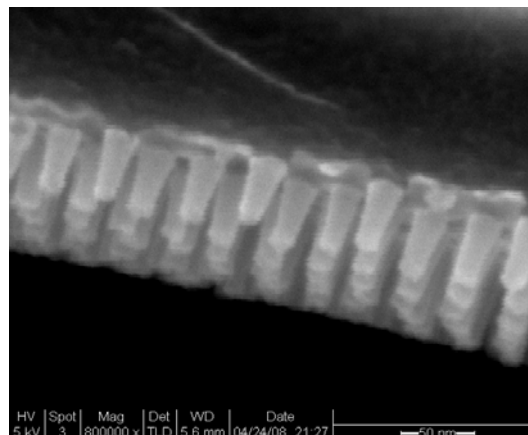
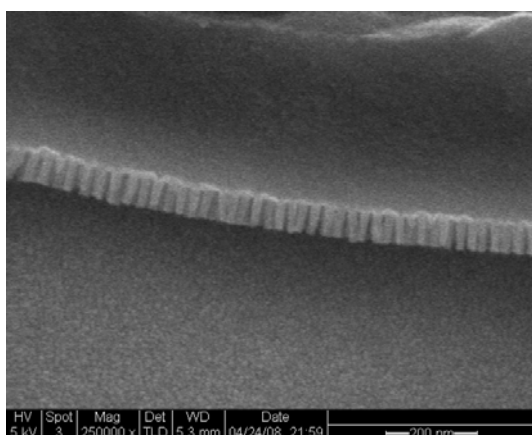
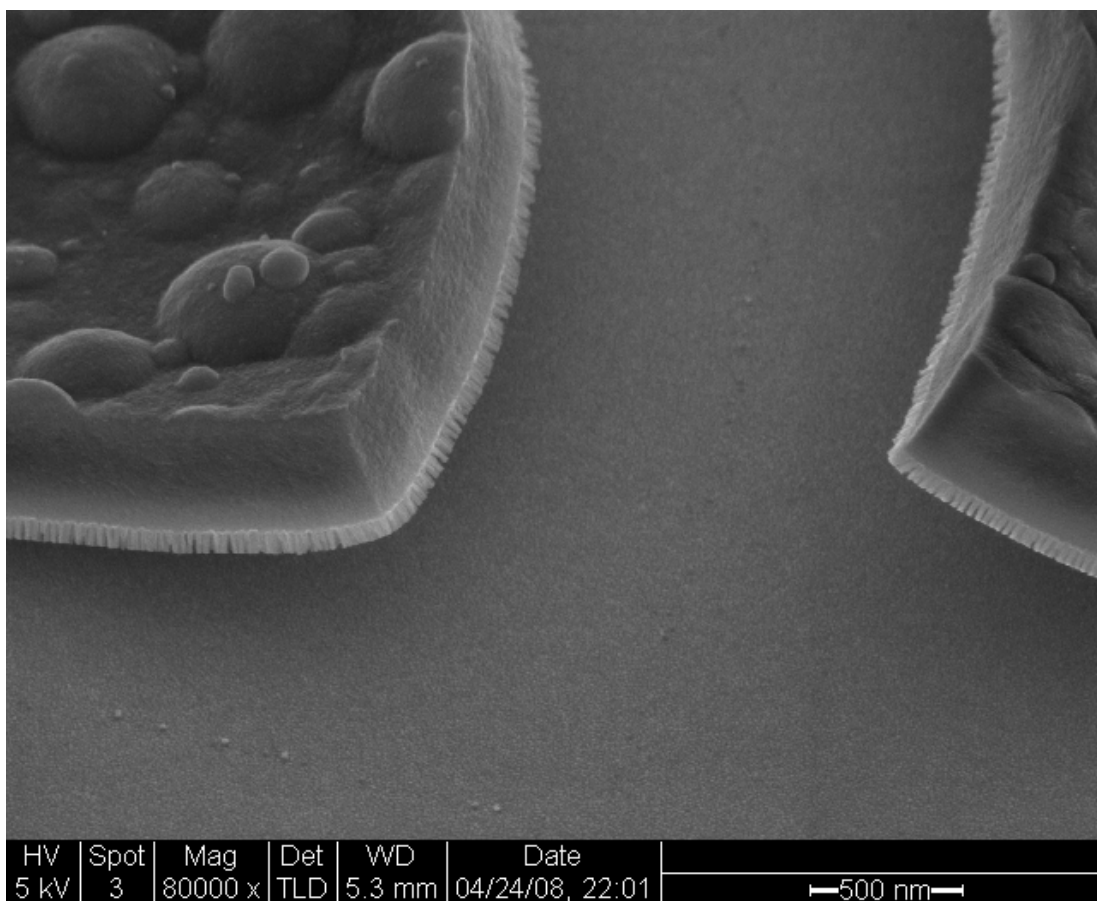


Figure 11: 25nm pore diblock copolymer template after sol-gel process: Cathodical electrodeposition at room temperature for 2min at -1.1V (vs. SCE) from an aqueous solution containing 0.02M TiOSO_4 , 0.03M H_2O_2 and 0.1M KNO_3 , and subsequently heat treatment in air at 110°C for 8h and 400°C for 1h. (Scale bars: Lower left: 200nm; Lower right: 50nm)

Figure 9 shows the process flow of making such a diblock copolymer template and Figure 10 shows the SEM picture of a thus made template with a pore diameter of 25nm and pore depth of 70nm. TiO₂ was deposited on a diblock copolymer template, as shown in Figure 11. It can be seen from the SEM pictures that after 400°C annealing, the thick overlayer on top of the template grabbed the nanopillars out from the pores of the template. The thick overlayer may be the result of a sol-gel process that was too fast, which can be resolved by using lower temperature. Our on-going research is to find an optimal condition to control the deposition thickness.

To summarize, we have grown TiO₂ nanopillars using electrically induced sol-gel method with diblock copolymer as the template. The growth is uniform as suggested by the SEM pictures. The next steps are to (1) find an optimal sol-gel process condition where the deposition thickness can be more precisely controlled and (2) fabricating diblock copolymer with pores having higher aspect ratios.

Progress

We have established the methodology to simulate and design metal nanostructures that can be used to concentrate and laterally split the solar spectrum in the lateral multi-junction solar cell. The fabrication of nanowires of TiO₂ and Ge have progressed steadily. We have successfully demonstrated growth of the nanowires and are poised to complete the first solar cell in the project in the coming months. Our team has established a bi-weekly team meeting which serves to integrate our learning.

Future Plans

We will refine our modeling of the light concentration by nanostructures by comparing our results with experimental data. After the modeling methodology is verified, we will begin to design metal nanostructures to achieve wavelength separation. Nanowire device fabrication will continue to incorporate the remainder of the process to form a complete solar cell. In the future we will focus on using the diblock copolymer templating method for TiO₂ nanowire growth. We expect to complete device fabrication in the next 6 months. We plan to move forward on the acquisition of a MOCVD tool for nanowire growth for materials with different bandgaps targeted for different parts of the solar spectrum.

Publications

None this period.

Contacts

Professor H.-S. Philip Wong: hspwong@stanford.edu

Professor Peter Peumans: ppeumans@stanford.edu

Professor Mark Brongersma: markb29@stanford.edu

Professor Yoshio Nishi: nishi@ee.stanford.edu

Graduate researchers:

Ying Chen: mihuhou@stanford.edu

Jason Parker: jaypark@stanford.edu

Trudie Wang: trudie@stanford.edu

Research Associates and Post-doctoral researchers:

Jim McVittie: mcvittie@cis.stanford.edu

Aaron Hryciw: ahryciw@stanford.edu