Nanowire Photovoltaics in Photoelectrochemistry and Plasmonic Ring Structures

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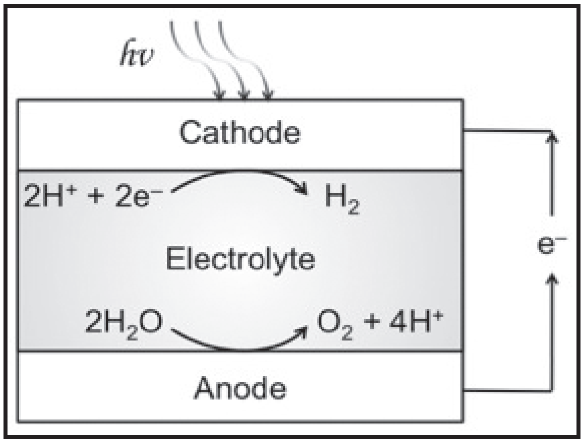

Figure 1: Schematic of a photoelectrochemical cell.

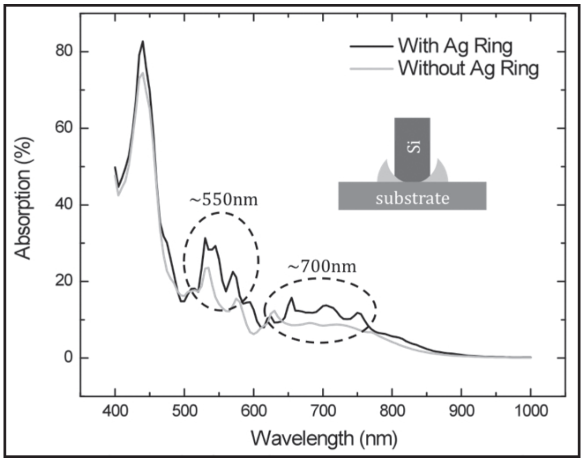

Figure 2: Simulation results of 90 nm diameter nanowires in 200 nm outer diameter silver rings.

Introduction:

Advances in solar technology using nanowires include improved photoelectrochemical cells and photovoltaics with integrated plasmonic structures. The high aspect ratio of nanowires can improve efficiency in the solar cell because they provide increased surface area and increased extraction of photogenerated charge carriers.

In the application of photoelectrochemical cells, light energy is used to split water by combining solar photovoltaics and water electrolysis into one device. As shown in Figure 1, light energy absorbed by the semiconducting electrode excites electrons to drive two half-reactions, ultimately producing hydrogen. Photoelectrochemical cells based on III-V semiconductors have higher efficiencies than devices separately producing electricity and splitting water [1]. III-V materials are ideal because their bandgap can be tailored for both efficient light absorption and water splitting. This study employs the use of gallium phosphide (GaP) nanowires as the semiconducting cathode in a photoelectrochemical cell.

In plasmonics, plasmons are light waves at a metal-dielectric interface bound to oscillating charges. Their properties have led to research in subwavelength optics, microscopy, bio-photonics, and light enhancement [2]. Resonating plasmons within metallic nanoring structures can enhance electric fields at geometry-dependent wavelengths. To harness the energy from plasmons, nanowires were incorporated into silver rings because simulations show increased visible light absorption in such a structure (Figure 2). This study implemented and optimized the fabrication of nanowires in silver (Ag) rings for future use in solar applications.

Methods:

Nanowires were grown on silicon substrates by chemical vapor deposition using the vapor-liquid-solid mechanism with gold (Au) colloid catalysts.

Photoelectrochemistry. In this study, GaP was chosen as the III-V material because of its 2.26 eV band gap, sufficient to drive the 1.23 eV electrolysis of water. Trimethylgallium and tertbutylphosphine were source gases of gallium and phosphorus in metal-organic chemical vapor deposition. The wires were grown at 460°C, 76 torr, and with a V/III ratio of 30:1. After growth, the nanowires were assessed with a 3-electrode photoelectrochemical compression cell using 0.1 M H_2SO_4 electrolyte. Approximately 0.5 cm^2 of the sample was exposed to the electrolyte.

Plasmonic Ring Structures. The process to fabricate germanium (Ge) nanowires in Ag rings began with a deposition of 200 nm Au colloids on silicon. A 5 nm coating of aluminum oxide using atomic layer deposition was applied for electrical isolation. Ag was sputtered and subsequently plasma-etched to form Ag rings around the Au colloids. Then, the Au was wet-etched to the desired diameter. Finally, nanowires were grown via chemical vapor deposition with germane source gas. This study optimized the Au wet etch and nanowire growth. The Au etch used consisted of 17% sodium iodide, 2% iodine, and 81% water.

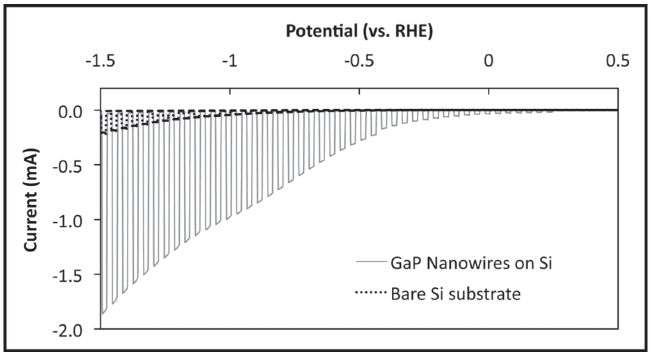

Figure 3: Photocurrent generated with changing potential. Light chopping occurred every one second.

Results and Discussion:

GaP nanowires in photoelectrochemical cells showed improved performance over bare silicon control samples and Ge nanowires in silver rings were successfully fabricated.

Photoelectrochemistry. In the GaP nanowire cells, photocurrent was measured with a potentiostat and the nanowire cells were compared to a control, bare silicon substrates. As shown in Figure 3, the nanowires generated up to 3 mA more photocurrent than bare silicon substrates under light illumination. Moreover, gas bubbles were observed at the interface, indicating the production of hydrogen. Photocurrent generated by the GaP nanowires on silicon was measured over one hour and the current remained stable, although scanning electron microscope (SEM) images indicate some roughness on the wires after testing.

Plasmonic Ring Structures. In the nanowire-in-a-ring structure, the Au colloids were etched smaller for proper nanowire growth to occur. The optimal Au wet etch process consisted of two steps: one longer etch of low concentration Au etch and one shorter etch of high concentration Au etch. Typical etch times and concentrations for one sample were 15 seconds in 1.25% Au etch followed by one second 100% Au etch. The lower concentration etch decreased the volume of Au colloids to desirable size while the higher concentration etch removed any unwanted Au surrounding the silver rings.

Nanowire growth times were also explored and the nanowires grew successfully with a longer nucleation step, in comparison to nanowires grown without rings. Nucleation occurred at 370°C and growth occurred at 310°C. With this recipe, up to 50% of rings with Au colloids grew a wire. A successful germanium nanowire grown in a silver ring is shown in Figure 4.

Conclusions:

In photoelectrochemical cells, water splitting by III-V nanowires is a promising approach to produce hydrogen for energy. Gallium phosphide nanowires can generate photocurrent and split water. Future work will increase density of nanowires, further tune the band gap with the addition of indium, and explore alternative non-photoactive substrates such as indium tin oxide, fluorine tin oxide, or Au. The plasmonic ring structures studied provide experimental insight into the field of plasmonics and germanium nanowires were successfully grown in silver rings.

Future work includes; further fabrication optimization to increase yield, reflectance measurements, and fabrication of a solar cell with integrated rings. Ultimately, nanowires are versatile for a number of applications. For the advance of solar technology, the use of nanowires can decrease cost, improve light absorption, and increase cell efficiency.

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References:

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[2] W. L. Barnes, A. Dereux and T. W. Ebbesen; "Surface Plasmon Subwavelength Optics"; Nature, Vol. 424, p. 824-830 (2003).

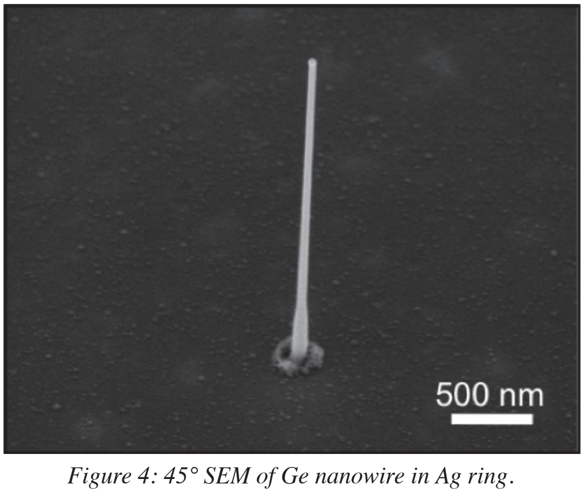

Figure 4: 45° SEM of Ge nanowire in Ag ring.