

II.K.22 Photoelectrochemistry of Semiconductor Nanowire Arrays

Thomas E. Mallouk¹ and Joan M. Redwing²
(Primary Contacts), Sarah M. Eichfeld,²
Adrian P. Goodey,¹ Emil A. Hernandez,¹
and Rui Xiao¹

The Pennsylvania State University
Departments of Chemistry¹ and Materials Science
and Engineering²
University Park, PA 16802
Phone: (814) 863-9637; Fax: (814) 863-8403
E-mail: tom@chem.psu.edu, jmr31@psu.edu

DOE Program Officer: Mark Spitler

Phone: (301) 903-4568
E-mail: mark.spitler@science.doe.gov

Objectives

The primary goal of this project is to explore the use of semiconductor nanowires and nanowire arrays as components of liquid-junction photoelectrochemical cells and water splitting systems. Our first objective was to control the chemical purity of nanowires grown by the vapor-liquid-solid method so as to demonstrate simple liquid-junction photoelectrochemistry with one semiconductor doping type. A more ambitious goal has been to study photochemical charge separation in axial and radial nanowire p-n junctions and heterostructures. Learning to control the composition, structure, and surface chemistry of the nanowires is an important prerequisite realizing these goals.

Technical Barriers

Efficient photoelectrochemical cells and water splitting systems have been demonstrated with semiconductors Si, InP, and CdSe as large single crystals, but the cost of single crystals is too high for practical use in solar hydrogen generation. Nanowires of the same materials can be grown as single crystals and as epitaxial heterostructures by several techniques, including chemical vapor deposition and electrodeposition. In principle, arrays of nanowires can be used to make high efficiency, low cost liquid junction solar cells and multi-bandgap electrodes for overall water splitting.

Abstract

This project has investigated the photoelectrochemical properties of p-Si and p-InP nanowires grown by vapor phase techniques on p-Si substrates, and has developed an electrochemical method for growing crystalline nanowire arrays of

CdSe nanowires in anodic alumina templates. With p-Si and p-InP nanowire photocathodes in non-aqueous electrolytes, we observe low dark currents and photovoltages in the range of 100-230 mV. Our current efforts are focused on controlling nanowire dimensions (length and diameter), surface chemistry, and bulk composition in order to improve the photoelectrochemical properties of the nanowire arrays.

Progress Report and Future Directions

Photoelectrochemistry of p-Silicon Nanowire Arrays. Our initial work on silicon nanowire (SiNW) arrays employed porous alumina membranes as templates, and used electrodeposition methods to grown Au catalyst nanowire segments on top of Co back contacting wires. Under vapor-liquid-solid (VLS) growth conditions, we were able to obtain crystalline Si nanowire arrays as a brush on the outer surface of the membrane, with the Co back contact buried in the alumina matrix. The nanowire diameter corresponded well to the pore size of the membranes. These experiments used SiH₄ as the silicon source, and trimethylboron (TMB) or phosphine as p- and n-type doping gases, respectively. Four-point probe measurements on individual nanowires showed that they were heavily p-doped even without addition of TMB. Attempts to fabricate photoelectrochemical cells resulted in identical light and dark currents, consistent with the overdoping of the nanowires.

Because the most likely source of adventitious p-type doping was Al from the alumina membrane, we later used crystalline p-Si substrates. Under these conditions, dense crystalline nanowire arrays were also obtained, as illustrated in Figure 1. The nanowires that were not intentionally doped had resistivities in the range 10⁴-10⁵ Ω-cm and could be doped p- and n-type

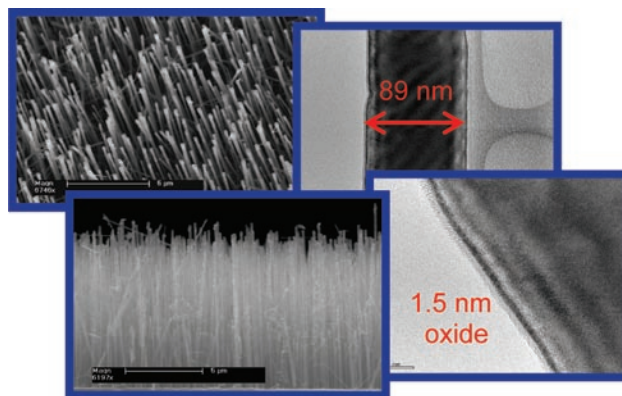


FIGURE 1. p-Si nanowire arrays grown by VLS.

by mixing TMB or phosphine with the silane source. After appropriate etches to remove the gold catalyst tips and superficial oxide layer, these nanowire arrays gave photovoltages of 200-230 mV in nonaqueous $[\text{Ru}(\text{bpy})_3]^{2+}$ solutions. Under identical conditions, p-Si single crystal electrodes had photovoltages of ~500 mV and lower dark current. The scan rate of the photocurrent established that the photocurrent came from the nanowire array and not the (dark) p-Si substrate. This result is very encouraging because it shows that VLS-grown nanowire arrays function as photodiodes in liquid junction cells. It also underscores the need to understand and minimize bulk and surface recombination in these systems in order to realize efficient semiconductor nanowire array solar cells.

Growth and characterization of Si nanowires.

Our initial studies demonstrated that SiNW fabricated by vapor-liquid-solid (VLS) growth using SiCl_4 as the silicon precursor on gold-coated (111) Si substrates had a high resistivity (400-6000 $\Omega\text{-cm}$) indicating a background impurity level less than $5 \times 10^{14} \text{ cm}^{-3}$ assuming bulk Si hole mobility. However, the surface of the SiNWs was found to be rough suggesting that HCl produced from the reaction of SiCl_4 and H_2 may be etching the wires during growth. In order to investigate this, nanowire growth experiments were carried out to study the effect of temperature and SiCl_4 partial pressure (P_{SiCl_4}) on the growth rate and structural properties of the nanowires. The SiNW growth rate was found to be strongly dependent on the SiCl_4 partial pressure (P_{SiCl_4}). As the P_{SiCl_4} was increased from 1.6 to 3.6 Torr, the SiNW growth rate increased linearly with P_{SiCl_4} reaching a maximum of 7 $\mu\text{m}/\text{min}$ at $P_{\text{SiCl}_4}=4$ Torr. As the P_{SiCl_4} was increased further, however, the growth rate dropped significantly. The experimental results were compared to the predicted mass of solid silicon formed as a function of P_{SiCl_4} using a gas phase equilibrium model of the SiCl_4/H_2 system at temperatures ranging from 1050-1100°C. The thermodynamic model predicted a similar maximum in Si solid phase formation and revealed that at high P_{SiCl_4} , the SiCl_4/H_2 gas phase equilibrium transitions into an etching regime where the formation of gaseous SiCl_x species becomes thermodynamically favored. These results also suggest that gas phase thermodynamics controls the growth of Si nanowires in the SiCl_4/H_2 system.¹

Structural characterization of the Si nanowires grown using SiCl_4 revealed that there was no gold catalyst present on the SiNW tips suggesting that gold diffusion was occurring at 900°C during nanowire growth and/or cool-down from the growth temperature. Subsequent studies determined that the Au diffusion was occurring primarily during the cool-down step. Field emission scanning electron microscopy (FESEM) revealed that samples slowly cooled (15°C/min) had small amounts of Au or no Au present on the SiNW tip, while a fast cool-down (50°C/min) left a larger portion

of the Au tip intact. Transmission electron microscopy (TEM) of the SiNWs revealed the absence of a native oxide layer on the nanowire surface suggesting that the surfaces are passivated by either hydrogen or chlorine during growth. These results are consistent with *in-situ* studies of Kodambaka *et al.*² where significant gold diffusion was observed to occur during nanowire growth on hydrogen-passivated SiNW surfaces at low growth rates under ultra-high vacuum conditions. Our results reveal that substantial gold diffusion can also occur after growth for SiNWs grown at much higher pressures and growth rates.³

Electrodeposition of CdSe Nanocrystal Arrays.

We have also developed a topochemical cation exchange route to obtain vertical arrays of crystalline CdSe nanowires (CdSeNW). The process begins by electrodeposition of amorphous Se in the pores of alumina membranes. The membranes are then partially etched with to expose the wires for reaction with $\text{Cd}(\text{NO}_3)_2$. Currently, the problem we have is that the polysulfide electrolyte used for CdSe photoelectrochemistry is basic and etches the membrane. We have recently initiated a collaboration with Dr. Alvin Compaan at the University of Toledo to sputter a thick layer of CdSe onto the membranes for back contact. Once we have addressed the back contact problem we will study the photoelectrochemical properties of the nanowire arrays in liquid- and polymer-junction cells.

Photoelectrochemistry of p-InP Nanowires. p-type InP is a very interesting photoelectrode material because it has a nearly ideal bandgap (1.4 eV). Single-crystal p-InP electrodes can attain photovoltages in the range of 0.8 V in liquid-junction cells, and can be catalyzed to act as photocathodes for hydrogen evolution from water. We have collaborated with Robyn Woo and Prof. Robert Hicks at UCLA, who have developed a metal-organic vapor phase epitaxy (MOVPE) method for growing InP nanowires on p-Si(111) surfaces from trimethylindium and tri-*t*-butylphosphine. Under the right growth conditions, dense arrays of single crystal

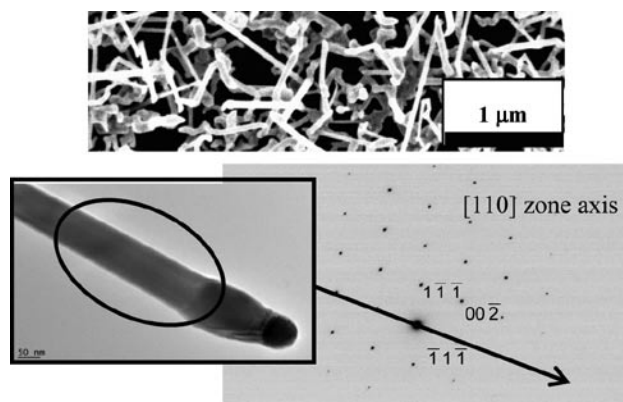


FIGURE 2. p-InP nanowires grown on p-Si(111).

nanowires can be obtained (Figure 2). Our preliminary photoelectrochemical measurements gave promising results in non-aqueous methylviologen electrolytes, as shown in Figure 3. The nanowire arrays have relatively low dark current, and in the light show photovoltages in the range of 100 mV. Again, this is an encouraging preliminary result because the growth conditions, nanowire dimensions, and surface chemistry are not yet optimized.

Our future work with these nanowire systems will concentrate on understanding and minimizing bulk and surface carrier recombination. One parameter that is readily controllable is the nanowire diameter. Recent studies by Kayes et al.⁴ suggest that the diffusion length of minority carriers in p-SiNW should be large relative to the diameters we have studied to date.

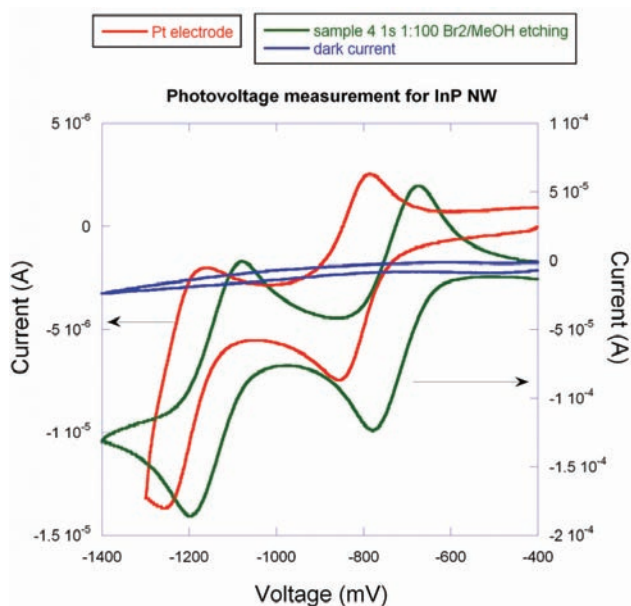


FIGURE 3. Cyclic voltammetry (50 mV/s) of a Pt disk electrode and an InP NW array photocathode under white light illumination and in the dark.

Increasing the diameter should decrease the surface-to-volume ratio and thereby affect the rate of surface recombination. Following up on our results in the p-Si (SiH₄/TMB) system, we are also studying the effect of doping and nanowire composition (as determined by choice of VLS catalyst) on dark current density and photoelectrochemical properties.

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