II.G.3  Oxidatively Stable Nanoporous Silicon Photocathodes for Photoelectrochemical Hydrogen Evolution

Abstract
Stable and high-performance nanoporous “black silicon” photoelectrodes with electrolessly deposited Pt nanoparticle (NP) catalysts are made with two metal-assisted etching steps. Doubly etched samples exhibit >20 mA/cm² photocurrent density at +0.2 V vs. reversible hydrogen electrode (RHE) for photoelectrochemical hydrogen evolution under 1 sun illumination.

We find that the photocurrent onset voltage of black Si photocathodes prepared from single-crystal planar Si wafers increases in oxidative environments (e.g., aqueous electrolyte) owing to a positive flat-band potential shift caused by surface oxidation. However, this beneficial oxide layer becomes a kinetic barrier to proton reduction that inhibits hydrogen production after just 24 h. To mitigate this problem, we developed a novel second Pt-assisted etch process that buries the Pt NPs deeper into the nanoporous Si surface. This second etch shifts the onset voltage positively, from +0.25 V to +0.4 V vs. RHE, and reduces the charge-transfer resistance with no performance decrease seen for at least two months.

Progress Report
Recently, nanostructured Si photocathodes have been developed for hydrogen production due to their advantages of low reflectivity and a higher surface area compared to bulk planar Si, which improves charge collection, exchange current density, and hydrogen gas surface-desorption. Our group and others have focused on the metal-assisted solution etching of planar Si to prepare nanostructured Si—a process that is suitable for large-scale manufacture and has been applied to make high-efficiency Si solar cells.

But the performance of Si electrodes used in any aqueous PEC system normally deteriorates from surface oxidation, an effect that appears to be unavoidable because of the high reactivity of Si with O₂, especially in the presence of water. In a deployed PEC hydrogen production system, surface oxidation might be expected during the night and at other times when photoelectrons are not providing cathodic protection against surface oxidation. Although the deposition of a surface-adsorbed catalyst such as Pt can help reduce the kinetic barrier for proton reduction, the PEC properties of Pt-deposited Si photoelectrodes are also found to degrade significantly upon surface oxidation.

Here we find that our black Si photoelectrodes with electrolessly deposited Pt NP catalysts (Pt/b-Si) exhibit improved PEC hydrogen production performance relative to...
to planar Si (pl-Si) electrodes. In particular, the deleterious effect of air exposure for more than 1 h on pl-Si or catalyst-free black Si (b-Si) electrodes are not observed in Pt/b-Si at aging times greater than 24 h. Instead, the nanoporous Pt/b-Si electrode exhibits a positive onset potential shift (by ~200 mV) upon aging for 24 h that improves its PEC performance. To explore the mechanism for the positive onset potential shift of nanoporous b-Si after exposure to air, Mott-Schottky (MS) plots of the pl-Si, b-Si, and Pt/b-Si electrodes were measured in 0.5 M H$_2$SO$_4$ after different aging times. The MS data confirm that oxide growth results in a positive flat-band potential shift for the Si photocathodes, which initially improves PEC performance but eventually degrades it with further oxide growth.

To address this issue, we have developed a novel re-etching process as described in Fig. 1A. This process results in high PEC performance despite the presence of surface oxide. These black Si photoelectrodes with buried Pt NP catalysts (B-Pt/b-Si) exhibit an ~300 mV positive shift for hydrogen evolution compared to a Pt-modified planar Si photoelectrode and are stable even after months of air exposure (Fig. 1B). Electrochemical impedance studies reveal that the second etch leads to a considerably smaller interfacial charge-transfer resistance than samples without the additional etch, suggesting that burying the Pt NPs improves the interfacial contact between the black Si surface and the Pt catalysts.

Future Directions

We plan fundamental experiments to probe the nature of the interface between Pt and b-Si using high-resolution transmission electron microscopy, scanning tunneling microscopy, x-ray absorption spectroscopy, and related techniques. Utilizing this secondary etching treatment with buried p-n junction photocathodes may reduce the overpotential for hydrogen evolution and make possible tandem overall water splitting devices using this photocathode and an appropriately matched photoanode such as bismuth vanadate.

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