# Origin of the Electrical Barrier in Electrolessly Deposited Platinum Nanoparticles on p-Si Surfaces

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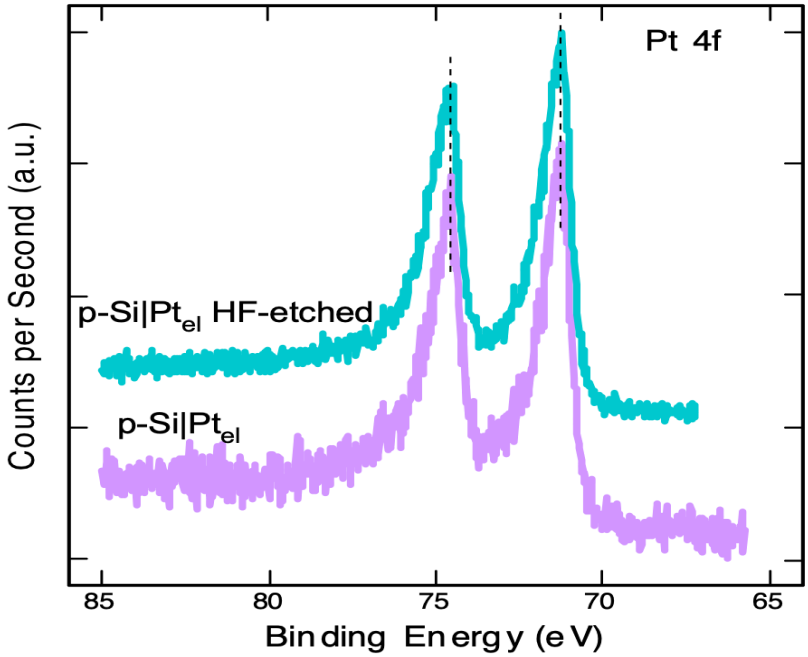


**Figure S1.** XPS data of Pt 4f core levels for a p-Si/Pt$_{el}$ electrode before, purple, and after, cyan, etching in HF(aq).

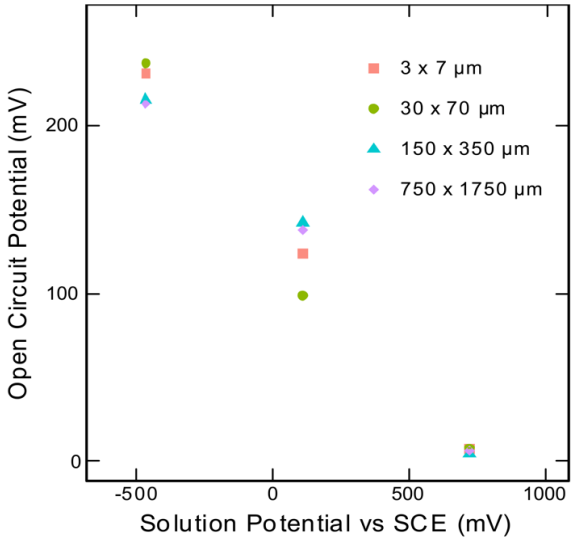


**Figure S2.** Electrochemical open-circuit potential measurements of p-Si/$SiO_x$/$Pt_{EB}$(nxm) electrodes having various catalyst diameters with constant coverage. Values were measured against various solution potentials and compared to electrodes that contained electroless Pt deposits. The diameter of the Pt deposits did influence the measured open-circuit potential, and the electrodes showed similar levels of performance to that exhibited by the electrode coated with electrolessly deposited Pt.

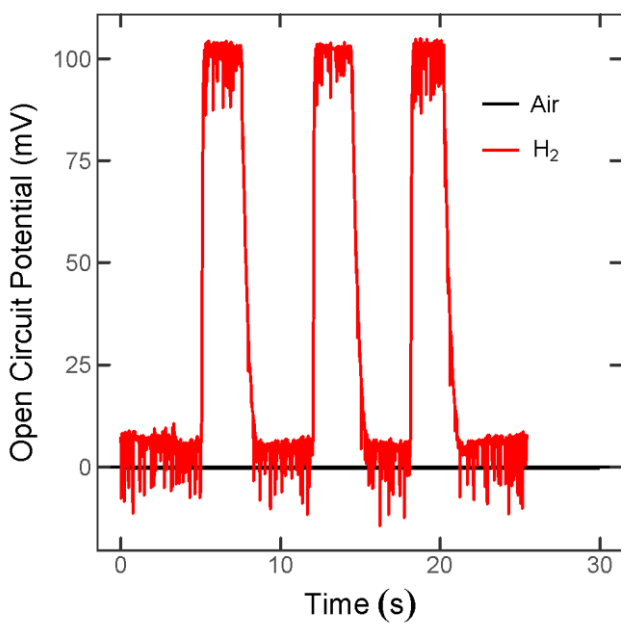


**Figure S3.** Open-circuit potential ($E_{oc}$) of a p-Si/$SiO_x$/$Pt_{EB}$(TF) solid-state device under 1 Sun of illumination in $H_2$ and air atmospheres. Under air, the device produced no photovoltage while under hydrogen, band bending was generated, resulting in $E_{oc}$ ~100 mV.

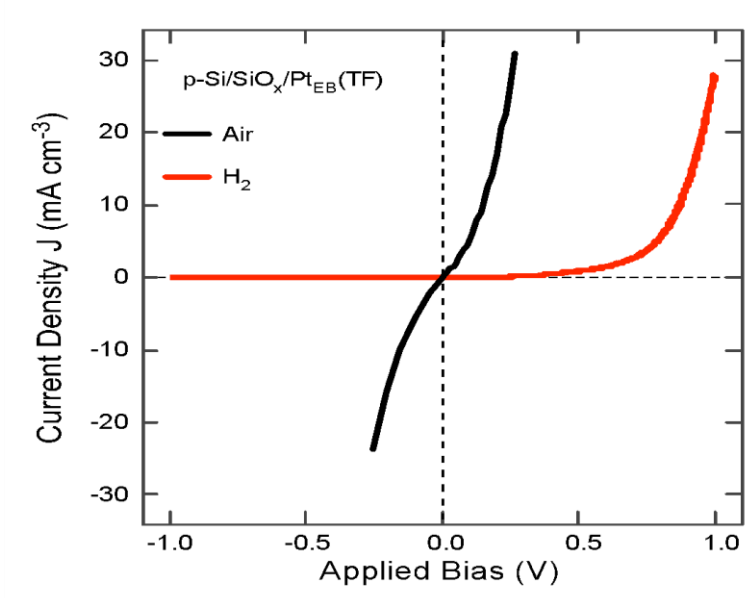


**Figure S4.** Expanded scale of the *J-V* characteristics of a p-Si/$SiO_x$/$Pt_{EB}$(TF) solid-state device before vs during exposure to $H_2$(g).

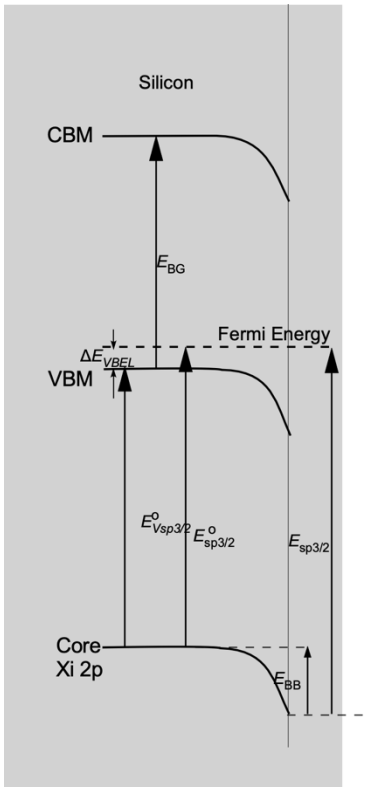


**Figure S5**. Band-bending diagram for p-Si/Pt devices in vacuum.[1] $E_{BG}$ is the band gap of Si, 1.12 eV, $E^{o}_{V2p3/2}$ is the bulk binding energy of the Si $2p_{3/2}$, $E^{o}_{2p3/2}$is the energy of the Si $2p_{3/2}$ signal relative to the VBM, 98.68 eV[1], $\Delta E_{VBFL}$ is the energy difference between the VBM and the Fermi level, 0.25 eV (from doping of 1.5 x $10^{15}$ $cm^{-2}$), $E_{2p3/2}$ is the measured binding energy of the p-Si $2p_{3/2}$ signals, 99.24 to 99.53 eV (Figure 2), and $E_{BB}$ is the calculated band-bending energy, 0.26 to 0.55 eV.

(1) Hunger, R.; Fritsche, R.; Jaeckel, B.; Webb, L. J.; Jaegermann, W.; Lewis, N. S. High-resolution photoemission studies of the interfacial reactivity and interfacial energetics of Au and Cu Schottky barriers on methyl-terminated Si(111) surfaces. *Surf. Sci.* **2007**, *601*, 2896-2907; https://doi.org/10.1016/j.susc.2007.04.249.