Supporting Information

Subwavelength photocathodes via metal-assisted chemical etching of GaAs for solar hydrogen generation

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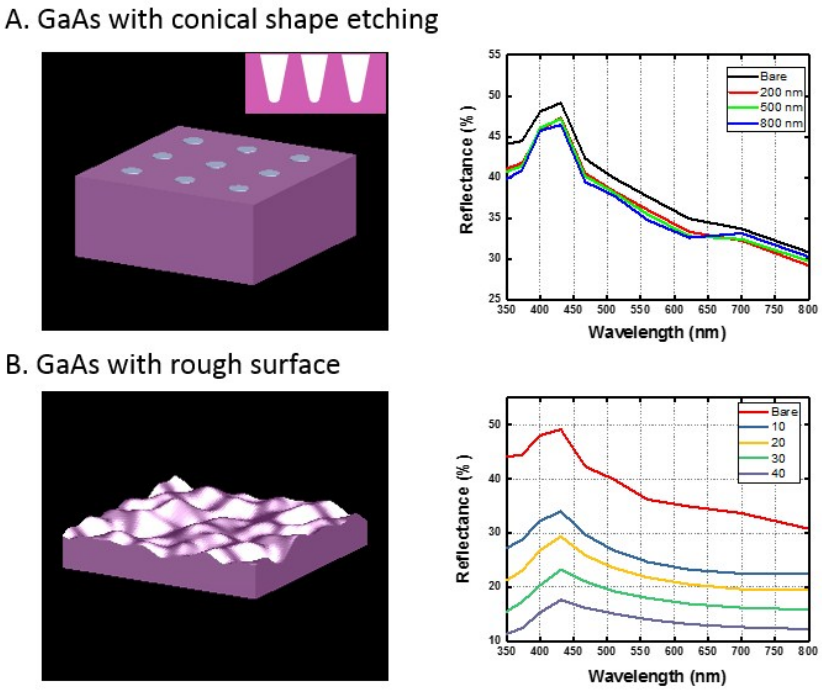

Figure S.1 (A) GaAs with conical shape etching (Upper diameter: 100nm, Bottom diameter 20nm, Etch depth: 200nm, 500nm, 800nm) and (B) GaAs with rough surface (RMS: 10, 20, 30, 40). In a structure like A, the reflectance decreases at the beginning of the etching process. However, after the initial etching, even if the etching depth is deepened, the reflectance is not affected. On the other hand, as the surface roughness increases, the reflectance decreases continuously.

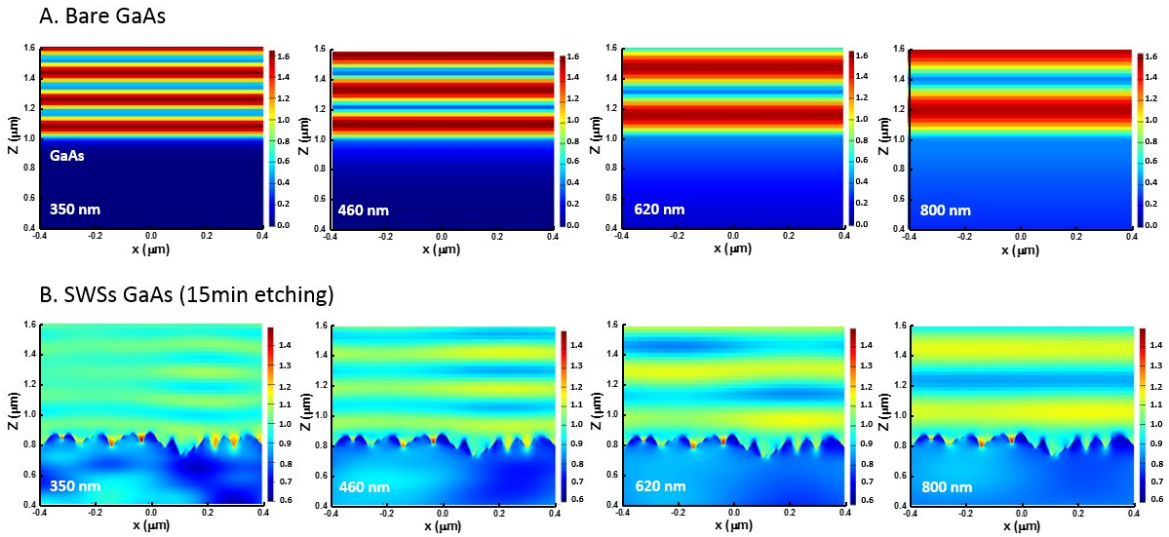

Figure S.2. Electric field simulation of (A) Bare GaAs and (B) SWSs GaAs at light incidence. In bare GaAs, the longer the wavelength of the incident light, the deeper the incident light penetrates the GaAs. In contrast, SWSs GaAs exhibits constant and high light absorption regardless of the wavelength of the incident light.

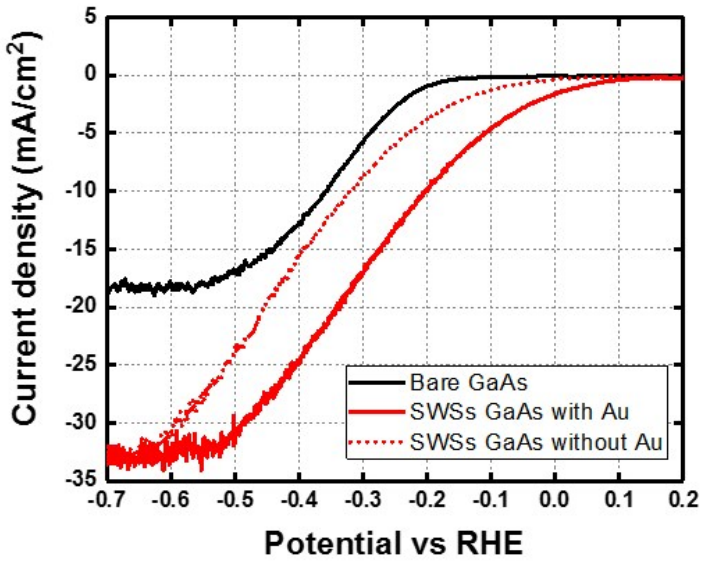

Figure S.3. LSV analysis of etched SWSs GaAs photocathode with and without gold. We fabricated PEC photocathodes using SWSs GaAs, and then the Au was removed using an Au etchant. From our LSV analysis results, we found no significant effect on the LLPCs, but the open circuit potential exhibited a positive shift of approximately 0.1 V.

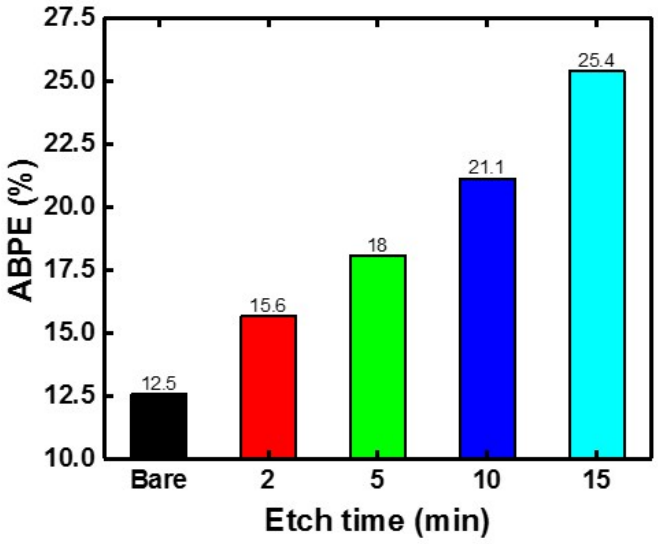

Figure S.4. Applied bias photon to current efficiency (ABPE) of SWSs GaAs photocathode. As the etching time increases, the ABPE also increases. (Bare: 12.542%, 2 min: 15.639, 5 min:18.044%, 10 min: 21.119%, 15 min: 25.374%) These were calculated assuming that Faradaic efficiency was 100%. when the 15-minutes etching SWSs GaAs was applied to a PEC cell, the ABPE was improved by approximately 100% over the bare GaAs PEC cell.

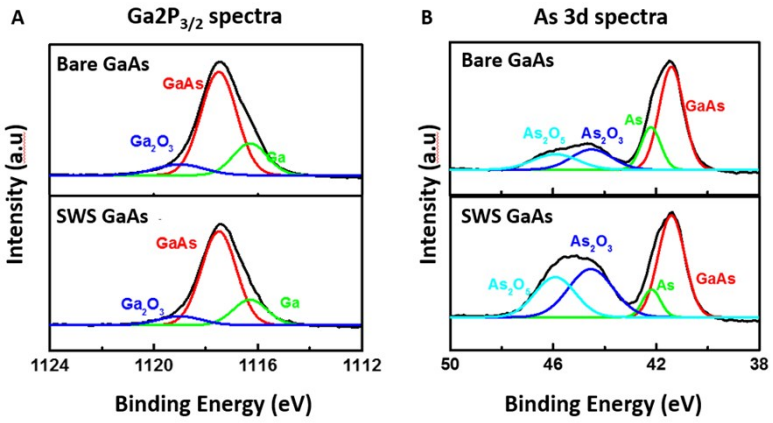

Figure S.5. XPS spectra of the (A) $Ga2P_{3/2}$ and (B) As 3d. After the formation of SWS GaAs, As oxide was formed. Since As oxide has higher chemical stability than Ga oxide, only As oxide is observed on GaAs surface after MacEtch.