

Supporting Information

Electrochemical Vapor Deposition (E-CVD) of Semiconductors from Gas Phase with a Solid Membrane Cell

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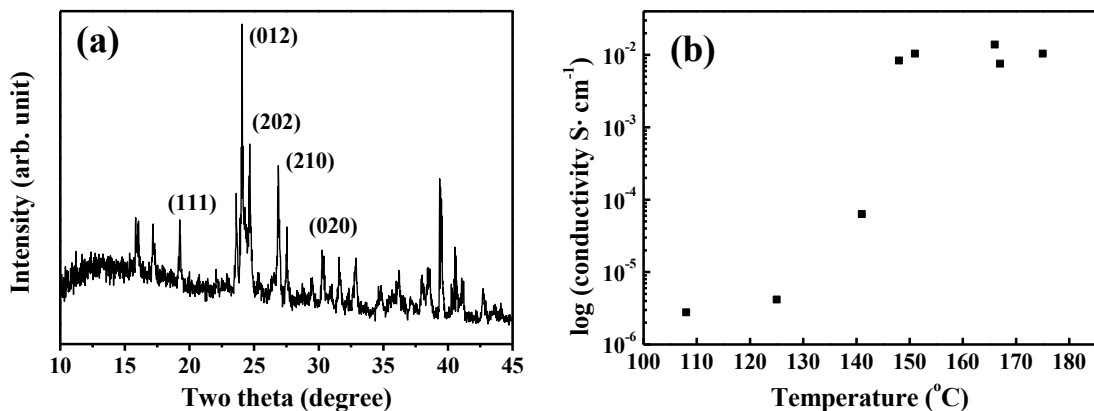


Figure S1. (a) Powder X-ray diffraction pattern and (b) the conductivity of synthesized CsHSO₄.

The membrane powder was pelletized (1.32 cm², 1 mm thick, 0.5 g) by pressing at 340 MPa with a mechanical press (uniaxial). Ag electrodes were fabricated on both sides of pellet by adding Ag paste. The conductivity of membrane pellet was determined by AC impedance spectroscopy (0±5 mV AC voltages, change in the frequency from 1 to 10⁵ Hz) at different temperature.

Cyclic voltammetry on CsHSO₄ membrane without any reactant gas

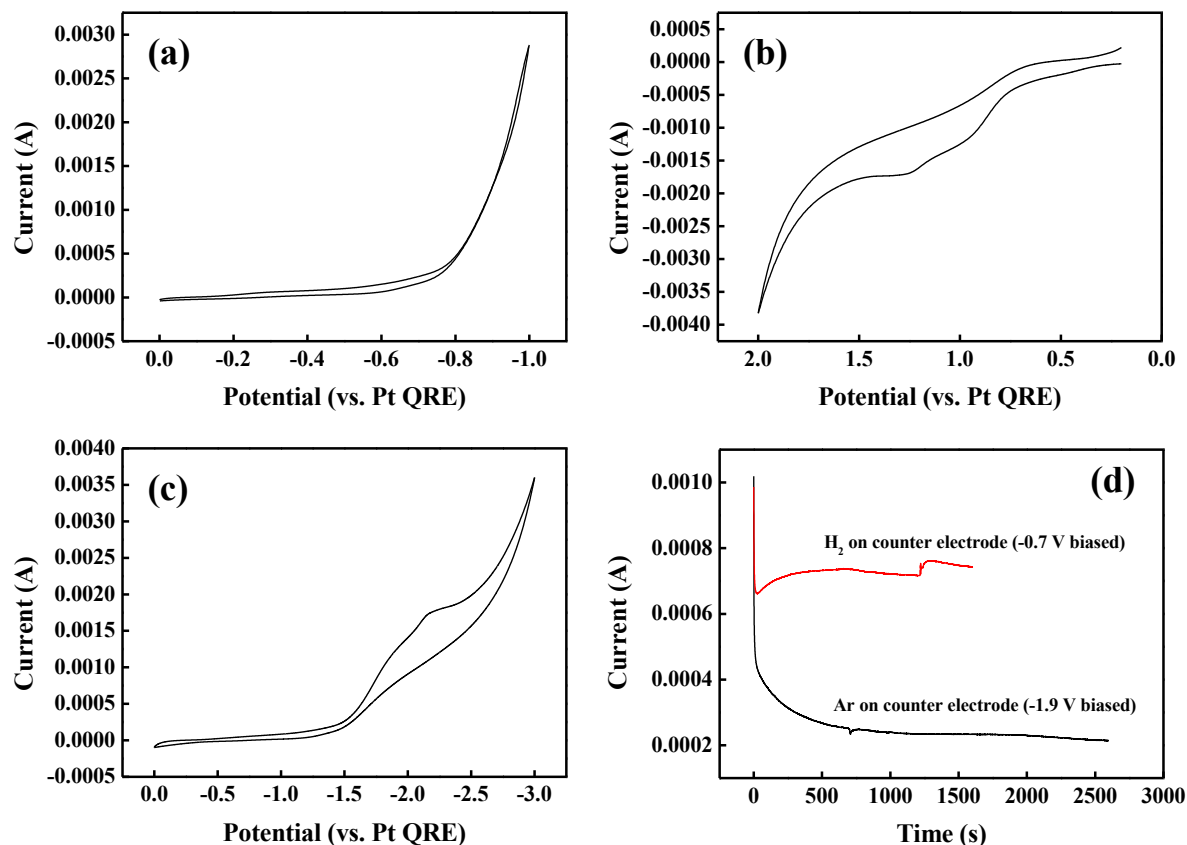
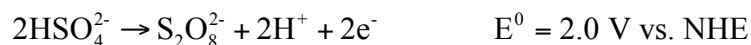


Figure S2. CVs on CsHSO₄ membrane with (a) negative potential and (b) positive potential scans (in the absence of H₂ flow) with respect to Pt quasi-reference electrode (three electrodes system); (c) Current response with the potential biased between two electrodes on each side of membrane (two electrodes system); (d) chronoamperometric curves with or without H₂ flow.

With all membrane-based electrochemical systems, current flows only by the transport of

conducting ion which is a proton in the case of CsHSO₄. Therefore, the reactions on both electrodes are considered at the same time, and those reactions should generate and consume protons to maintain a constant proton flow in the membrane during metal electrodeposition. Figure S2 showed cyclic voltammograms (CVs) on both electrodes under Ar gas flow, which means the absence of the reactant gas. As the potential of Pt electrode was swept negatively with reference to the other Pt electrode (three electrodes system), which acted as a Pt quasi-reference electrode, a big reduction curve was evolved and it must be the reduction of proton in CsHSO₄ (Fig. S2a). With the positive scan, two oxidation reactions were observed. First peak was assumed to be contributed from the oxidation of carbon paper presumably due to the presence of trace amount of water in CsHSO₄. The other was the oxidation of bisulfate (HSO₄²⁻) to S₂O₈²⁻ (Fig. S2b).



The proton reduction curve rises sharply in the negative potential region in which its slope is governed by the IR drop associated with the membrane resistance (~80 Ω) whereas the oxidation curve is sluggish. Accordingly, when a potential was swept negatively without Pt quasi-reference electrode (two electrodes system), the shape of i-V curve was very similar to that of oxidation reaction curve, indicating the current passing through the membrane was determined by the oxidation reaction (Fig. S2c). However, this oxidation reaction did not supply the proton to membrane, so that eventually the proton inside the membrane will be depleted. Accordingly, the current under Ar flow did not maintain and it decayed with time as shown in Fig. S2d.

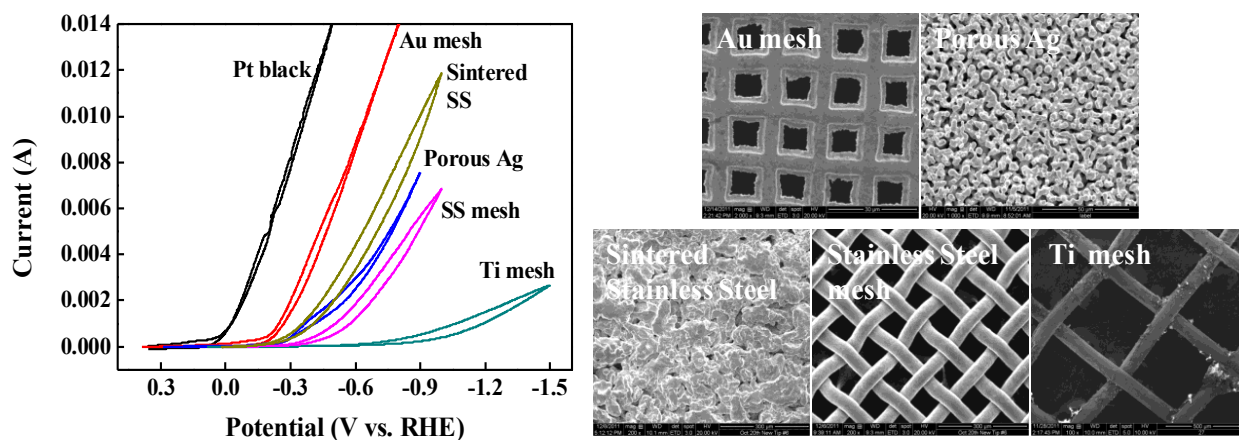


Figure S3. Cyclic voltammograms from various metal electrodes on CsHSO₄ membrane by applying negative potentials (in the presence of H₂ flow) with respect to reference electrode which can be regarded as a reversible hydrogen electrode. Small currents of SS and Ti meshes were due to the small surface areas which were associated with mesh size.

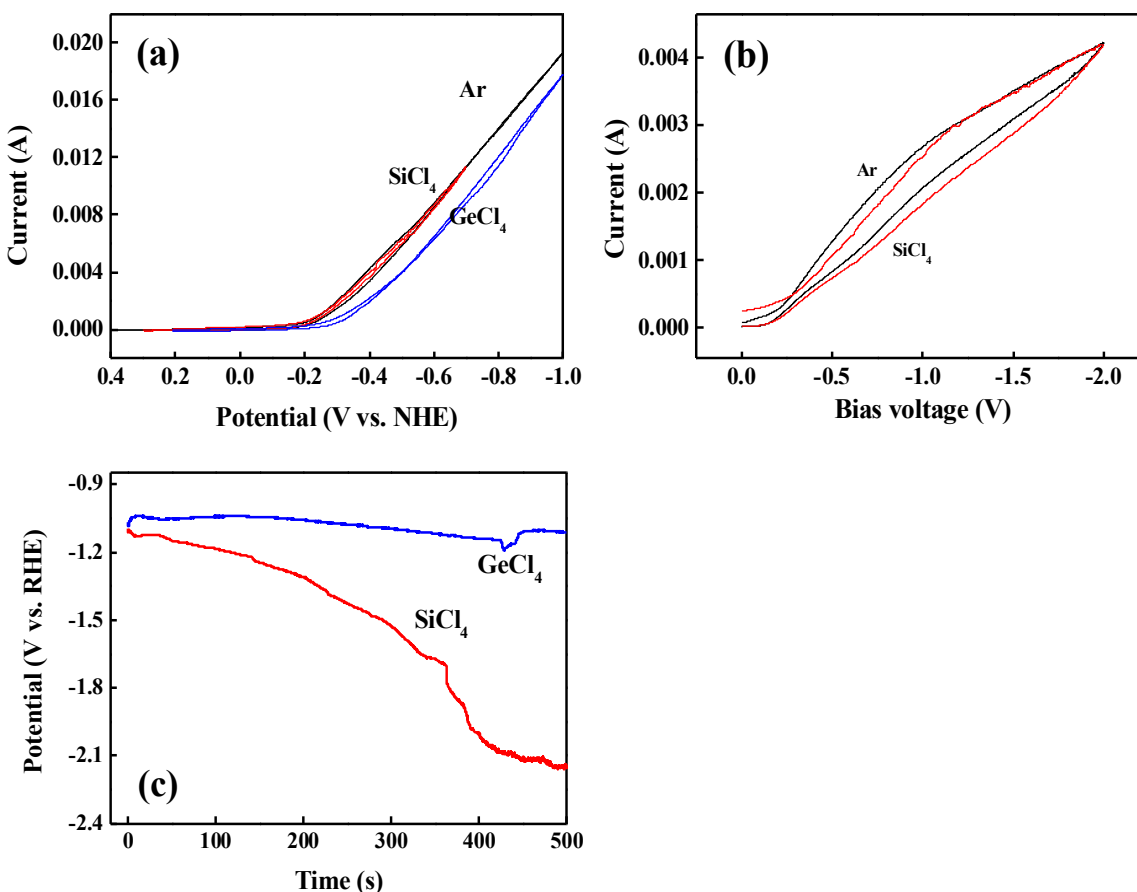


Figure S4. (a,b) CVs and (c) chronopotentiometry (10 mA) on CsHSO₄ membrane with Ar, SiCl₄, and GeCl₄ flowing in (a, c) three electrode and (b) two electrode systems. (a, c) The small difference with and without metal chloride gas flow shows the competition between proton and metal chloride reduction, and accordingly low current efficiency for the deposition process. We speculate that the increase in the potential of (c) chronopotentiometry arises from surface change and subsequent hydrogen evolution activity. In the case of silicon deposition, the increase is significantly larger and it might be due to the surface passivation of silicon, which is commonly observed in silicon electrodeposition process. (Munisamy, T.; Bard, A. J. *Electrochim. Acta* 2010, 55, 3797-3803.)

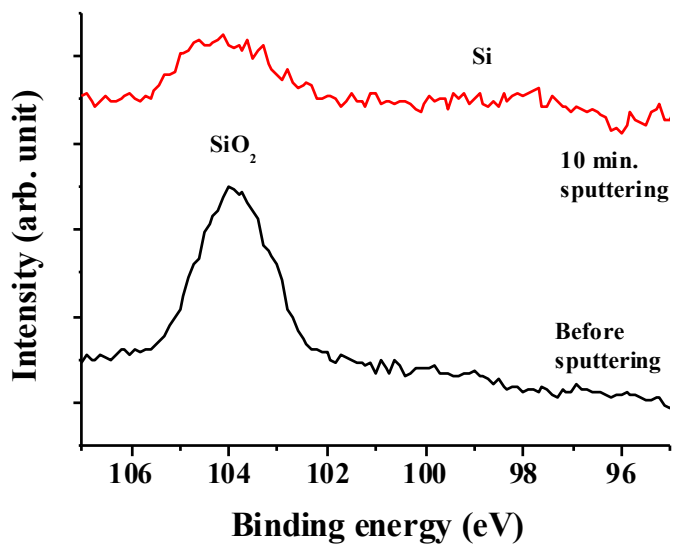


Figure S5. X-ray photoelectron spectrum of Si 2p of silicon deposit which was deposited on gold mesh (10 mA, 1500 s).

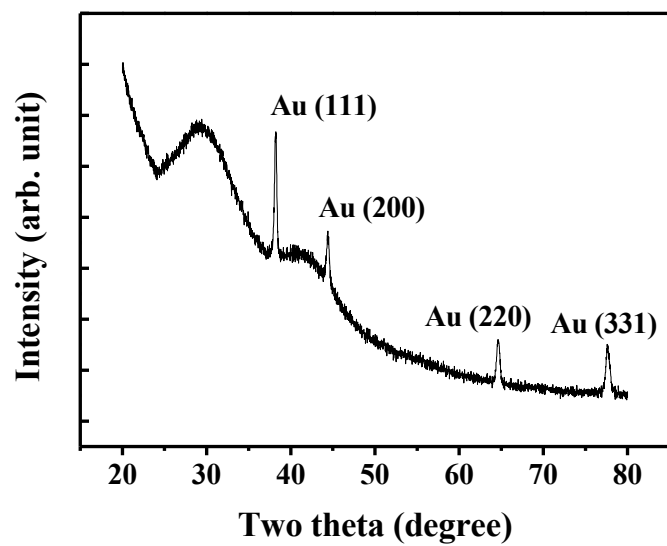


Figure S6. X-ray diffraction spectrum of germanium deposit on gold mesh.