Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Photoanodic pyramid texturization of n-Ge (100) in HCl solution: An unexpected anisotropy in the surface chemistry of etching

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SUPPLEMENTARY INFORMATION

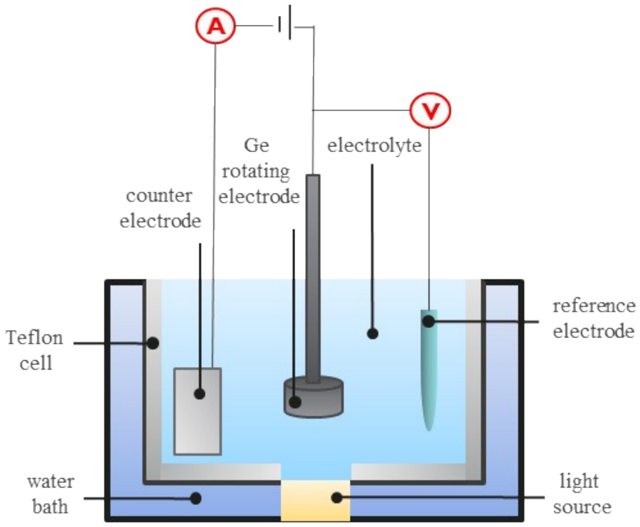


Fig. S1. Schematic diagram of a three-electrode electrochemical set-up.

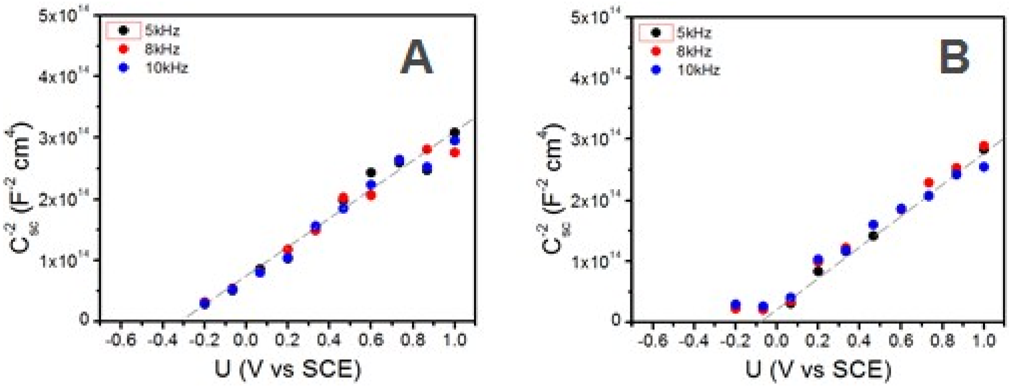
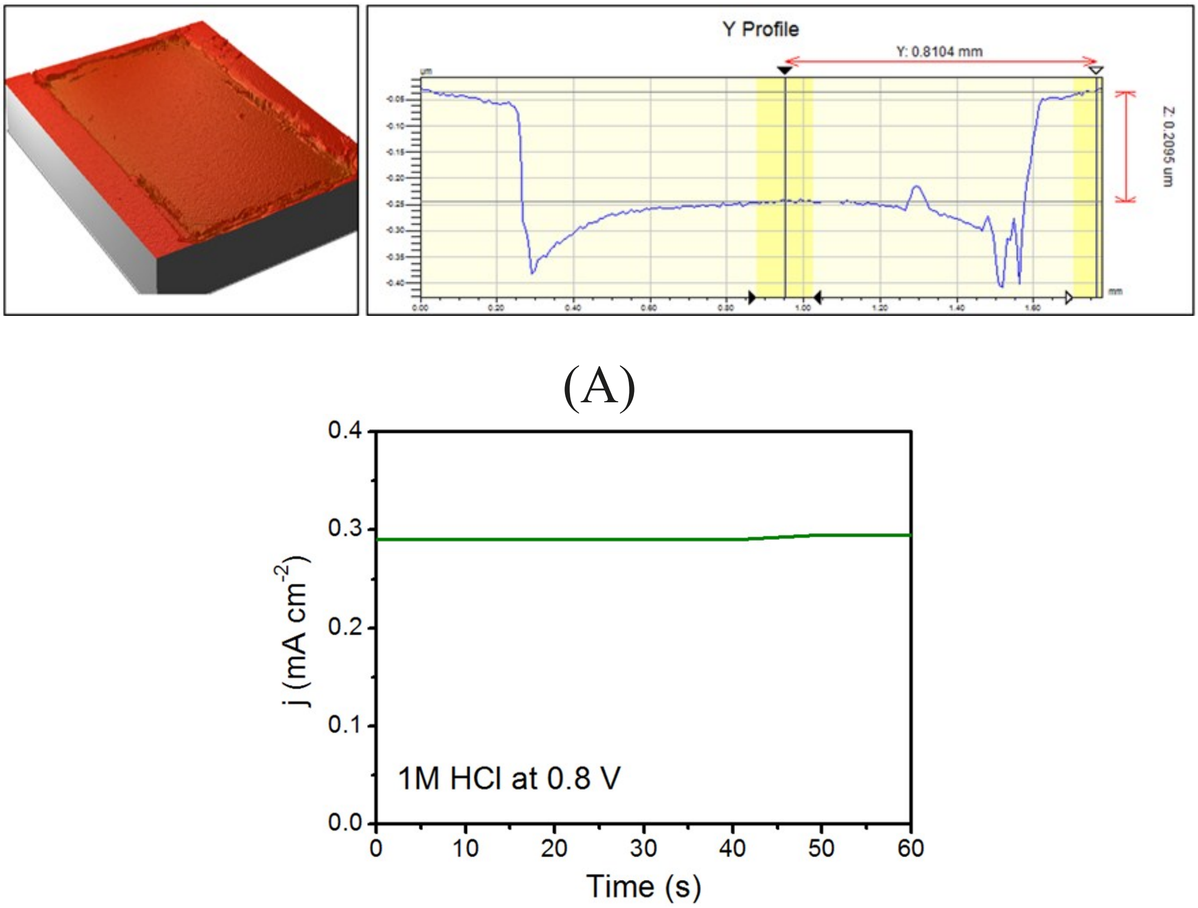


Fig. S2. Mott-Schottky plots (C_{sc}^{-2} vs V/SCE, f = 5, 8, and 10 kHz) of n-Ge (100) in 1M and 8M HCl (dark condition).

The Mott-Schottky characterization of n-type Ge (100) in 1M and 8M HCl solutions was performed by multiple frequency measurements (Fig S2A-B). Prior to each measurement, the Ge samples were anodically polarized. This produces a hydrophobic surface for the Ge electrode, which converts Ge-OH to Ge-Cl surface. The Mott-Schottky relationship (Eq. S1) is obtained, where C_{sc} is the capacitance of the space-charge layer (F m^{-2}), $\mathcal{E}$ is the relative permittivity ($\mathcal{E}_{Ge}$= 16.2), $\mathcal{E}_0$ is the vacuum permittivity (8.854 X 10^{-12} Fm^{-1}), q is the elementary electric charge (1.602 x 10^{-19} C), N the carrier density (m^{-3}), U is the applied potential (V), U_{fb} is the flat-band potential (V), $k_B$is the Boltzmann constant (1.380 x 10^{-23} J K^{-1}), and T is the absolute temperature (K).

$$\frac{1}{C_{sc}^2} = \frac{2}{q\mathcal{E}\mathcal{E}_0 N}\left(U - U_{fb} - \frac{k_B T}{q}\right) \qquad \text{(Equation S1)}$$

The capacitance (C) is plotted as C_{sc}^{-2} against the applied potential (V vs SCE) that generates a linear trend for both cases. Since the plots exhibit a linear relationship, this proves that the Ge electrode forms a Schottky junction. The flat-band potential, described as the potential where there is no net transfer of charge, can be determined from the intercept (U - U_{fb} - k_BT/q) of the plot and the carrier density, N, can be estimated from its slope. The net doping density obtained from the slope is 10^{16} cm^{-3}, which is in good agreement with the commercial value. As seen from the figure, the flat-band potentials of 1M HCl and 8M HCl are situated close to their corresponding onset anodic potentials, which attest the values to be acceptable. A shift of the flat-band potential (U_{fb}) to a more positive value is observed as the concentration of HCl is increased, which could be explained by surface charging of H^+.



(A)

(B)

Fig. S3. A) 2D and 3D picture of Ge surface etched in 1M HCl at 0.8V using profilometer. B) Chronoamperogram of Ge in 1M HCl at 0.8V in dark condition.

Fig. S3 contains data (A: volume/ Profilometry and B: current density/ Chronoamperommetry) that can be used to calculate the semiconductor valence dissolution as shown in Equation S2.

The table below presents the volume obtained from three (3) different experiments of electrochemical etching of Ge in 1M HCl at 0.8V for 1 minute. Extending the time even up to 1 hour obtain comparable values.

Table 1. Three different volumes measured from profilometry

Experiment #	Volume (cm^{-3})
1	6.70×10^{-7}
2	7.08×10^{-7}
3	4.83×10^{-7}

Sample calculation for experiment # 1 of Germanium (Ge) dissolution valence:

$\rho\ = density\ (g\ cm^{-3}) = 5.32\ cm^{-3}$

Molar mass = 72.64 $g\ mol^{-1}$

Volume of the pit measured from profilometer. (V= L x W x H)

$Volume = 0.000607\ mm^3$
$= 6.70\ \times 10^{-7}\ cm^3$

$$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right) \qquad \text{(Equation S2)}$$

$n = amount\ of\ Ge\ etched\ (mol)$
$I = Current\ (A)$
$t = time\ constant\ current\ was\ applied\ (s)$
$F = Faraday's\ Constant = 96485\ C\ mol^{-1}$
$z = valence\ of\ metal\ in\ solution$

$$\rho = \frac{m}{v} \qquad \text{(Equation S3)}$$

$\rho\ = density\ (g\ cm^{-3})$
$m\ = mass\ (g)$
$v\ = volume\ (cm^3)$

$m = \rho v$
$m = (6.70\ \times 10^{-7})(5.32)$
$m = 3.56\ x\ 10^{-6}\ g$

$$\frac{3.56\ x\ 10^{-6}}{72.64} = 4.90\ \times 10^{-8}\ mol$$

$n = \left(\frac{It}{F}\right)\left(\frac{1}{z}\right)$
$z = \left(\frac{It}{Fn}\right)$

$(I = 2.90\ \times 10^{-4}\ A)$
$(t = 60\ s)$

$$z = \left(\frac{(2.90\ \times 10^{-4})(60)}{(96485)(4.90 \times 10^{-8})}\right)$$

$$z = 3.68$$

Comparable values are obtained even under illumination.

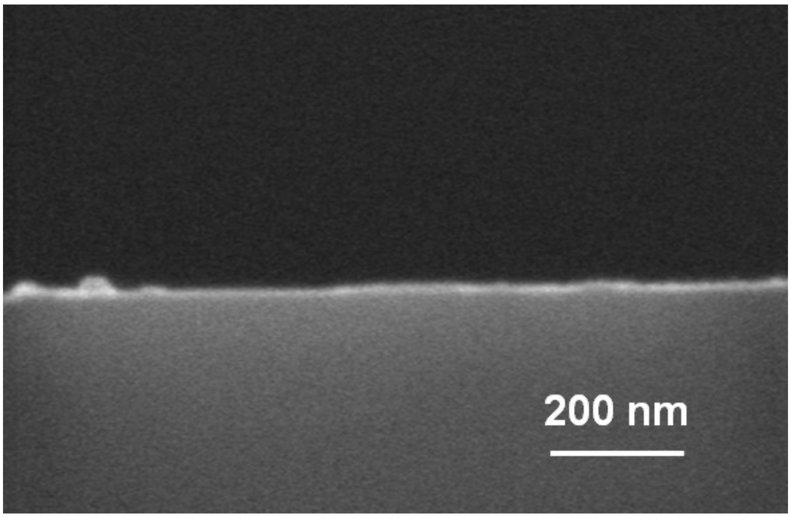


Fig. S4. Scanning electron microscopy (SEM) image of n-Ge (100) after 1 h electrochemical etching in 1M HCl.

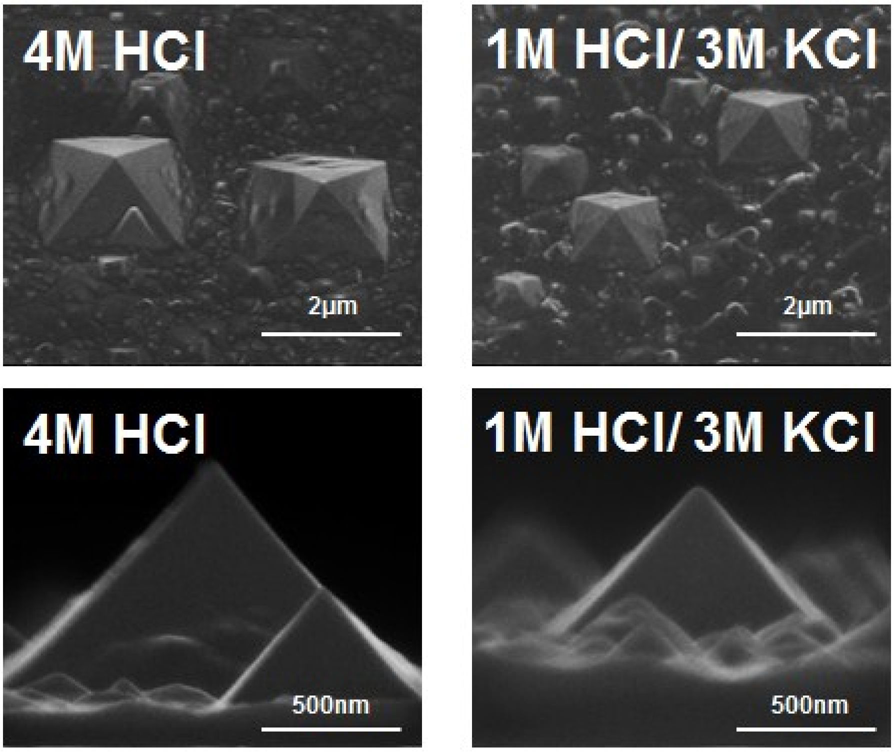


Fig. S5. Scanning electron microscopy (SEM) images of n-Ge (100) in 4 M HCl and 1 M HCl/3 M KCl.

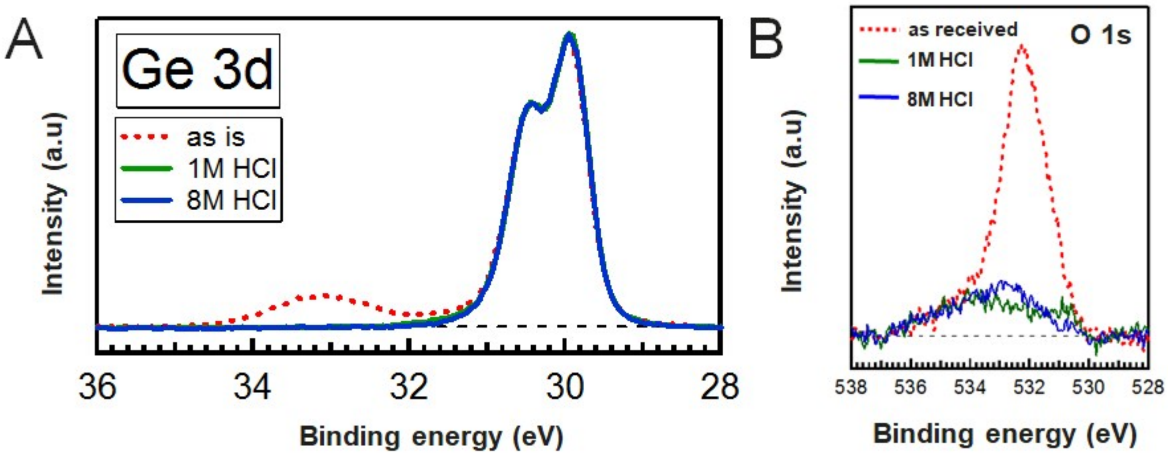


Fig. S6. Overlay XPS spectra of A) Ge3d and B) O1s.