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Supplementary Online Material

Termination of Ge Surfaces with Ultrathin GeS and GeS_2 Layers *via* Solid-State Sulfurization

Hui Chen,[1,2] Courtney Keiser,[3] Shixuan Du,[2] Hong-Jun Gao,[2] Peter Sutter,[1,*] and Eli Sutter[3,*]

[1]Department of Electrical & Computer Engineering, University of Nebraska-Lincoln, Lincoln NE 68588, USA

[2]Institute of Physics & University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, P.R. China

[3]Department of Mechanical & Materials Engineering, University of Nebraska-Lincoln, Lincoln NE 68588, USA

Supplementary Figures

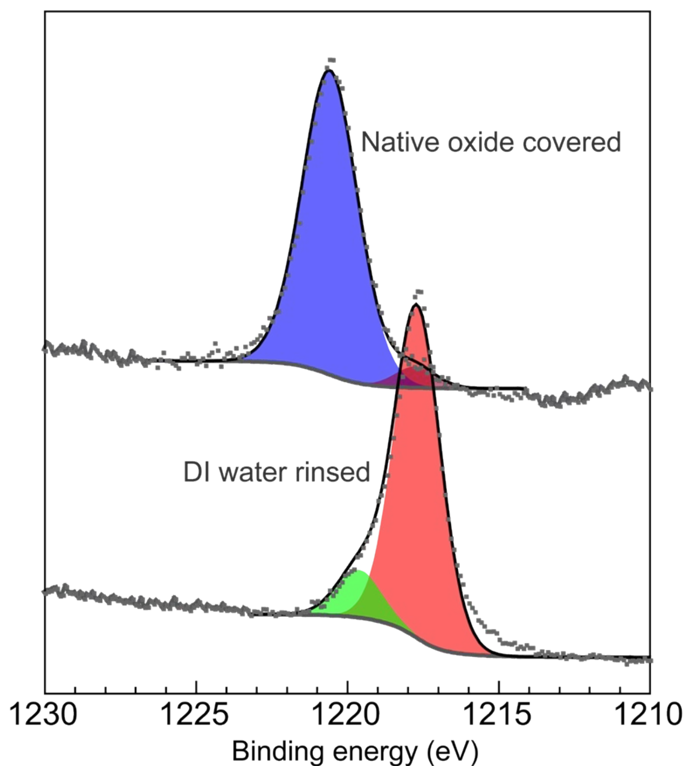

Figure S1: Ge(100) substrate preparation by DI water rinse. Comparison of surface sensitive Ge $2p_{3/2}$ XPS spectra of native oxide covered and DI water rinsed Ge(100). The predominant GeO_2 (Ge^{4+}) peak of the oxide covered Ge(100) is eliminated completely so that only Ge^0 and traces of Ge sub-oxides remain.

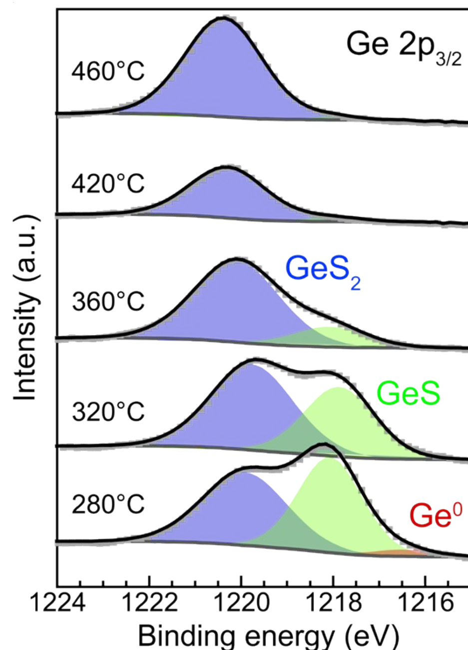

Figure S2: Evolution of surface sensitive Ge $2p_{3/2}$ XPS spectra with temperature of the sulfurization reaction. Comparison of surface sensitive Ge $2p_{3/2}$ XPS spectra of Ge(100) reacted with sulfur at temperatures between 280°C and 460°C. As expected, the Ge^0 component is at the detection limit already at the lowest temperature. The evolution of the peaks due to GeS and GeS_2 is consistent with the analysis of the Ge 3d XPS data presented in Figure 2.

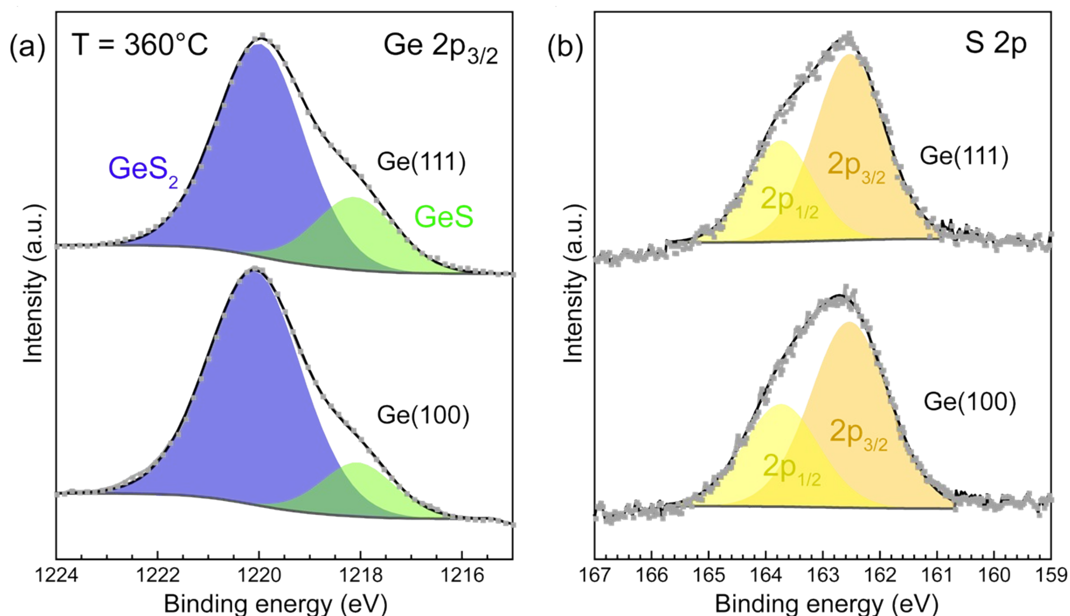

Figure S3: Effect of Ge surface orientation on sulfurization. (a) Comparison of surface sensitive Ge $2p_{3/2}$ XPS spectra of Ge(100) and Ge(111) reacted with sulfur at 360°C. **(b)** S 2p XPS spectra of the same samples.

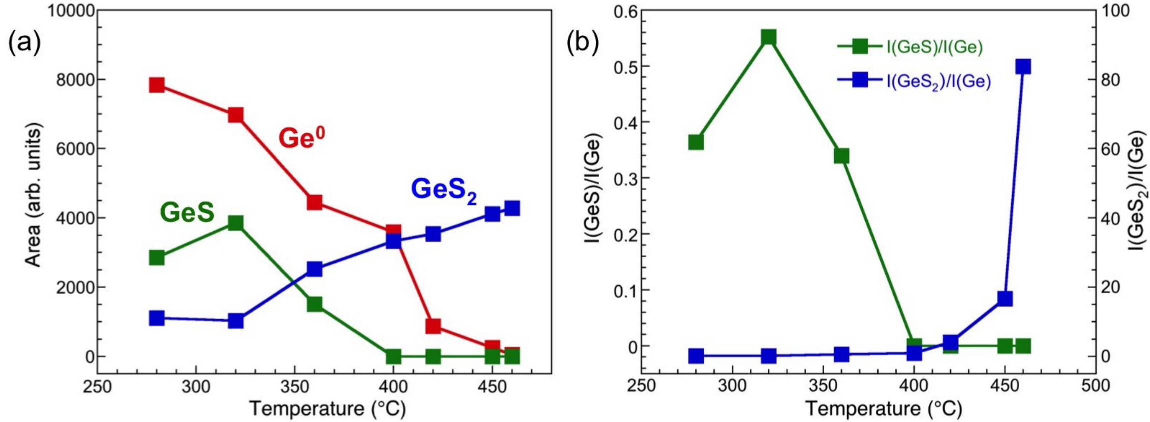

Figure S4: Ge 3d XPS data as a function of Ge(100) sulfurization temperature. (a) Fitted peak areas of the Ge^0, GeS, and GeS_2 components of the Ge 3d XPS spectra obtained on samples reacted with sulfur at different temperatures (corresponding to Fig. 1 (a) of the main text). **(b)** Intensity ratios I_{GeS}/I_{Ge} and I_{GeS_2}/I_{Ge} entering in equations (4) and (5) of the 3-layer model in the main text.

Supplementary Note: Error analysis for Figure 2(b)

The error bars shown in the Arrhenius plot of Fig. 2(b) of the paper were computed via an error propagation calculation based on equation (5) and using as input the estimated uncertainties in the fitted intensities of the Ge^0, GeS, and GeS_2 components of the Ge 3d XPS spectra shown in Fig. 1 (see also Fig. S4). The resulting estimated errors in the computed thickness of the growing GeS_2 film, $\Delta\left[t_{GeS_2}\right]$, were then used to derive the error bars in terms of the quantity shown in Fig. 2(b), namely $Ln\left(t_{GeS_2}\right)$. As expected, this procedure yields larger estimated errors for low and high reaction temperatures, where either the intensity of the GeS_2 component or the residual Ge^0 signal from the substrate are small. Smaller estimated errors are found in the intermediate temperature regime, where both GeS_2 and Ge^0 intensities are well above the detection limit.