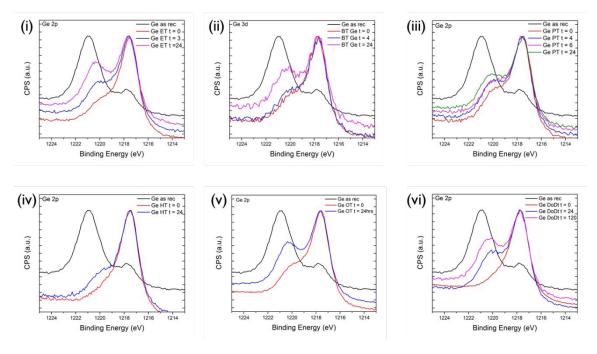


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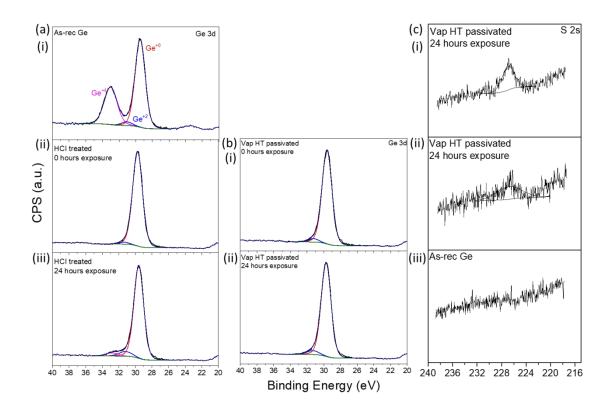
## **Supporting Information**

Vapor-phase passivation of chlorine-terminated Ge(100) using self-assembled monolayers of hexanethiol

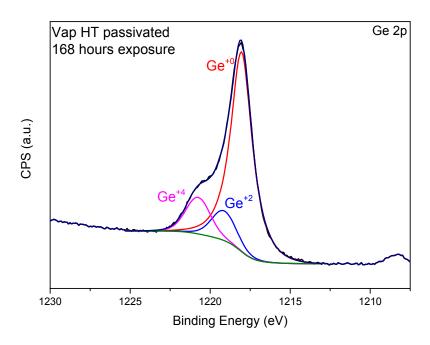


**Figure S1.** Ge 2p plots for Ge passivated by liquid-phase (i) ethanethiol (ii) butanethiol (iii) pentanethiol (iv) hexanethiol (v) octanethiol (vi) dodecanethiol showing progressive oxidation in time.

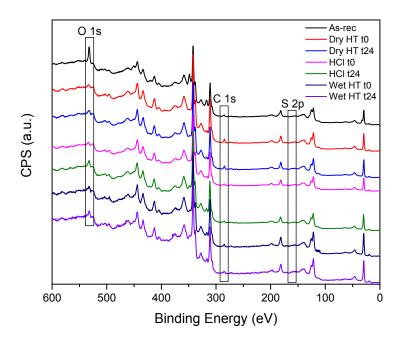
As discussed, a range of aliphatic thiol molecules with carbon backbones ranging in length from 2 to 12 carbons were investigated for their ability to passivate Ge and inhibit oxidation of the Ge in 24 hours. From inspection of Figure 1 (iv) in the supplementary section, it is clear that the hexanethiol passivated Ge experiences little oxidation upon exposure to the ambient for 24 hours. Hexanethiol outperformed the other thiols tested and so was chosen for trials using the vapor-phase approach that is detailed in this work.



**Figure S2.** Ge 3d and S 2s XPS measurements of (a,i) As-received Ge, (a,ii) HT vapor-phase passivated Ge with 0 hours exposure to ambient temperature and 40% RH (a,iii) 24 hours exposure to ambient temperature and 40% RH (b,i) Ge which has had the native oxide removed using HCl and 0 hours exposure to ambient temperature and 40% RH (b,ii) Ge which has had the native oxide removed using HCl and 24 hours exposure to ambient temperature and 40% RH (c,i) S 2p peak for samples (a,i-iii)



**Figure S3**. Ge 2p spectra for the hexanethiol vapor-phase passivated Ge after 168 hours exposure to the ambient. GeO<sub>2</sub> thickness is 0.25 nm. Suboxide thickness is 0.21 nm.



**Figure S4**. Survey spectra of as-received Ge (black), vapor-phase hexanethiol passivated Ge with 0 (red) and 24 hours (blue) exposure to 40% RH at 20°C, HCl treated Ge with 0 (pink) and 24 hours (green) exposure to 40% RH at 20°C and liquid-phase hexanethiol