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Authors	Collins, Gillian;Aureau, Damien;Holmes, Justin D.;Etcheberry, Arnaud;O'Dwyer, Colm
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Supporting Information

Germanium Oxide Removal by Citric Acid and Thiol Passivation from Citric Acid Terminated Ge(100)

Gillian Collins[†,ϕ]*, Damien Aureau[§], Justin D. Holmes[†,ϕ], Arnaud Etcheberry[§], and Colm O'Dwyer[†,ϕ]*

[†]*Department of Chemistry, University College Cork, Cork, Ireland.*

[ϕ]*Micro-nanoelectronics Center, Tyndall National Institute, Dyke Parade, Cork, Ireland.*

[§]*Centre de Spectroscopie, Institut Lavoisier de Versallies, Université de Versailles Saint Quentin-en-Yvelines, 78035 Versailles Cedex, France.*

Experimental Details

Oxide removal and functionalization: The Ge wafers were briefly rinsed with deionised (DI) water and immersed into citric acid solutions (0.24-2.4 M) for 60 s after which time they were removed, further rinsed with DI water and blown dry in a stream of N_2. H- and Cl terminated Ge surfaces were prepared by immersion into aqueous HF or HCl solution.[1] Thiol passivation of the Ge wafers was carried out by immersion into N_2 degassed toluene solutions of alkanethiols or dithiols, refluxed under N_2 for 18 h. After the reaction the wafers were immersed in toluene for 10 min followed by sonication for 10 min in fresh toluene and then chloroform. The wafers were dried in a stream of N_2.

X-Ray Photoemission Spectroscopy (XPS): XPS spectra were collected on a Thermo Electron K-Alpha spectrometer using a monochromatic Al Kα X-ray source (1486.6 eV). Spectra were referenced to the C 1s at 284.8 eV. The XPS spectra were processed using a Shirley background correction followed by peak fitting to Voigt profiles. The fwhm were allowed to

variety within reasonable value ranges in order to achieve best fit. The Ge 3d doublets were fit to Gaussian-Lorentzian profiles with an intensity ratio of 3:2 and a spin–orbit splitting of 0.585 eV. The S 2p components from 100 scans were fitted to a doublet with a branching ratio of 0.5 and spin-orbit splitting of 1.2 eV.

Attenuated total reflectance infrared spectroscopy (ATR-FTIR): Spectra were collected on a Nicolet 6700 Infrared Spectrometer equipped with a VariGATR (Harrick Scientific) and a liquid N_2 cooled MgCdTe (MCT) detector. The surface of the Ge ATR crystal was directly functionalized with citric acid using the procedure described about. Spectra were collected under p-polarization at a grazing angle of 60 °, using 1000 cumulative scans with a resolution of 2 cm^{-1}. The IR data was not collected under an inert atmosphere, thus some interference from adsorbed water cannot be ruled out.

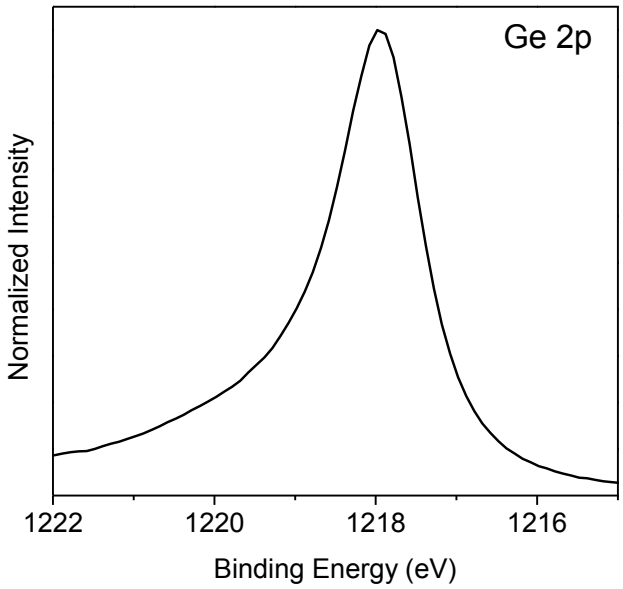


Figure S1: Ge 2p core level spectra after treatment with 2.4 M citric acid solution for 60 s.

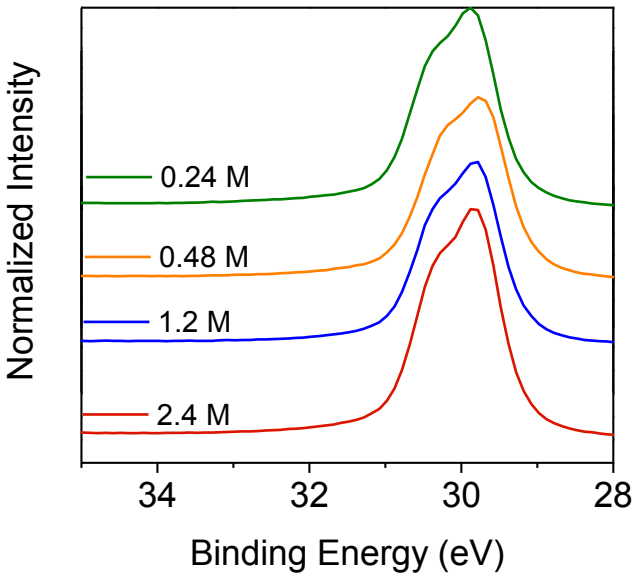


Figure S2: Ge 3d spectra after surface treatment with citric acid solutions of varying concentration.

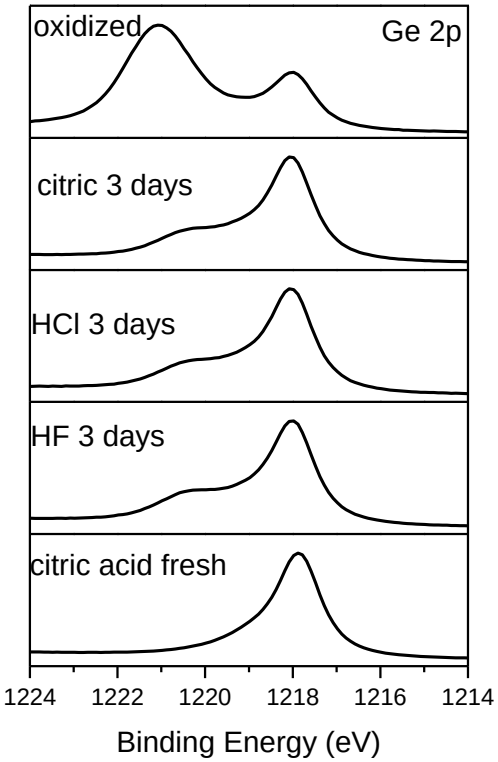


Figure S3. Ge 2p core level spectra comparing the re-oxidation citric acid terminated Ge with H- and Cl-terminated Ge(100).

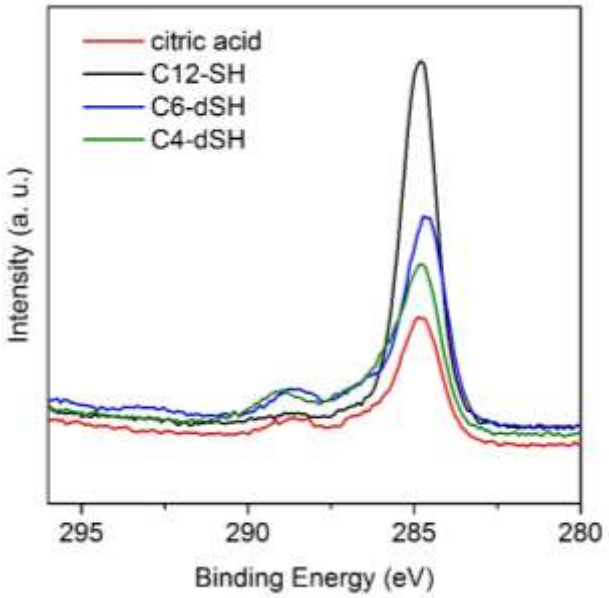


Figure S4: Comparison of C 1s spectra for citric acid and thiol functionalized Ge(100).

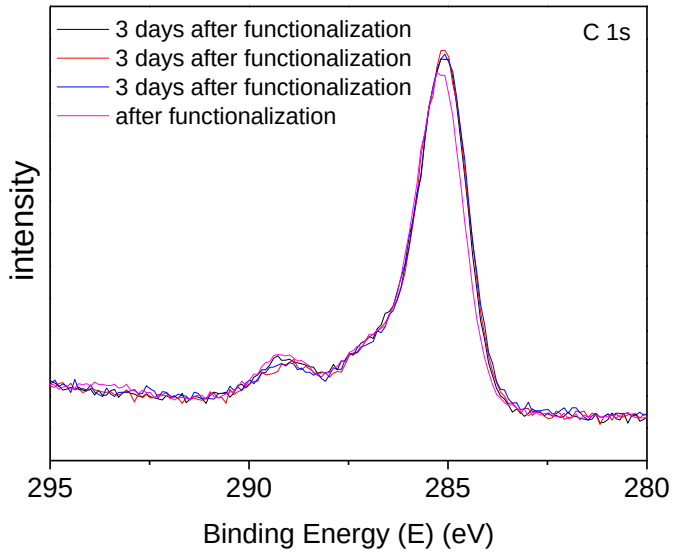


Figure S5: comparison of C 1s spectra of freshly prepared hexanedithiol passivated Ge(100) and after 3 days of exposure to air (3 data points for the air exposed sample are shown).

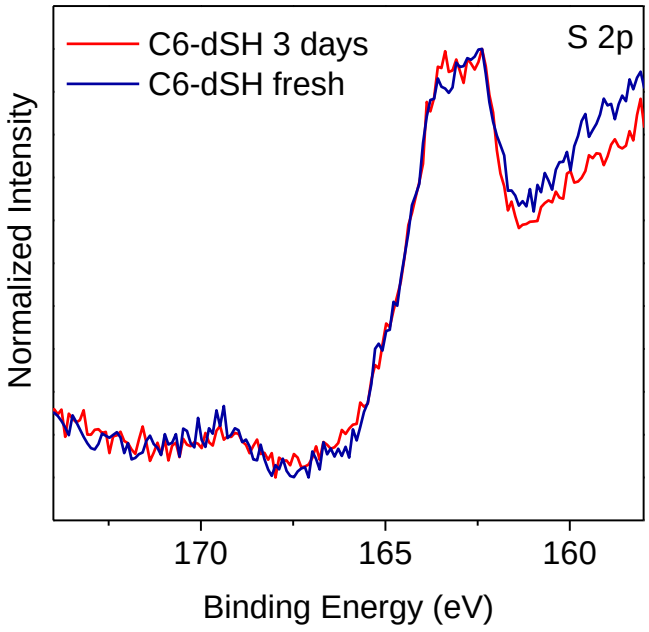


Figure S6: S 2p core level spectra of hexanedithiol functionalized Ge(100) immediately after passivation and after exposure to air for 3 days.

References

[1] Sun, Y.; Liu, Z. L., D.; Peterson, S.; Pianetta, P., Surface termination and roughness of Ge(100) cleaned by HF and HCl solutions. *Appl. Phys. Lett.* **2006,** *88*, 021903