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Authors	Collins, Gillian;Aureau, Damien;Holmes, Justin D.;Etcheberry, Arnaud;O'Dwyer, Colm
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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 Spectrocopie, Institut Lavoisier Versailles, Université de Versailles Saint Quentin-en-Yvelines, 78035 Versailles Cedex, France*

Abstract

Many applications of germanium (Ge) are underpinned by effective oxide removal and surface passivation. This important surface treatment step often requires H-X (X = Cl, Br, I), or HF etchants. Here, we show that aqueous citric acid solutions are effective for the removal of GeOx. The stability of citric acid treated Ge(100) is compared with HF and HCl and analyzed by X-ray photoelectron spectroscopy. Further Ge surface passivation was investigated by thiolation using alkane mono and dithiols. The organic passivation layers show good stability with no oxide regrowth observed after 3 days of ambient exposure.

Introduction

Surface modification is central to many applications of planar and nanostructured germanium (Ge). Due to intrinsic fluorescence and biocompatibility, functionalized Ge nanoparticles have applications for bioimaging and drug delivery[1, 2]. The broad spectral window (1000-4000 cm^{-1}) of Ge has been utilized for functionalized FTIR-biosensors.[3] Ge has long been of interest for high-speed electronic and optoelectronic applications due to its superior carrier mobility, smaller band gap and greater absorption coefficient compared to Si.[4] The unstable, non-uniform oxide gives rise to a poor Ge/GeO_x interface characterized by a high density of surface states[5] and surface passivation was found to be somewhat

effective is lowering recombination velocities in Ge devices.[6] Passivation is particularly important in nanoscale applications due to high surface area to volume ratio. Surface modification increases the performance of Ge nanowires in lithium ion battery anodes[7], field effect transistors[8] and photodetectors.[9] The oxidation behaviour of Ge is complex[10] and dependant on the oxidative environment such humidity,[11, 12] crystal orientation[13] and dopant type[14]. While GeO_2 is water soluble, GeO is insoluble and Ge^{1+} and Ge^{2+} oxide species remain on the surface after water treatment. GeOx is typically removed by hydrohalogenic acids, with HF yielding a H-terminated surface, and HCl, HBr and HI resulting in Cl-, Br- and I-terminated surfaces, respectively.[11, 15, 16] HF increases surface roughness compared to HCl treatment for planer Ge[16] while HI treatment was found to cause roughening of Ge nanowire surfaces.[15] A further drawback of mineral acids is the safety precautions required due to their corrosive nature and the toxicity associated with HF.

Here, we report a mild but highly effective procedure for Ge oxide removal using aqueous citric acid solutions. An important strategy for robust Ge passivation is through covalent attachment of alkyl, aryl and thiol monolayers [15, 17 18]. The ability to use citrate-treated Ge surfaces for further passivation was investigated by reaction with alkane thiols. The passivation layers are analysed by XPS and show excellent oxidation resistance.

Experimental Details

Experimental details for the citric acid etching, and thiolation procedures of the citric acid functionalized Ge surfaces and details of the XPS and attenuated total reflectance infrared (ATR-IR) spectroscopy characterization are outlined in the Supporting Information.

Results and Discussion

Figure 1(a) shows the Ge 3d core level spectra for oxidized Ge(100) with the elemental Ge peaks located at binding energies of 29.8 and 30.4 eV corresponding to the Ge $3d_{5/2}$ and Ge $3d_{3/2}$ hyperfine split doublet, while oxide associated peaks are located at higher binding energies. After immersion into aqueous citric acid for 60 s, the Ge 3d core-level, shown in Figure 1 (a) and Ge 2p (Supporting Information Figure S1) show the surface to be oxide free (at least to the detection limits of

XPS), with successful removal of both GeO_2 and GeO. The O 1s spectra of the as-received and citric acid treated Ge (Ge-CA) also confirms oxide removal.

The effect of citric acid concentration on the efficacy of oxide removal was investigated using citrate solutions with concentrations of 2.4 M, 1.2 M, 0.48 M and 0.24 M for 60 s. The Ge 3d core level spectra, shown in figure 2 (a) revealed effective oxide removal from the surface when treated with all concentrations of citric acid solutions. Analysis of the more surface sensitive Ge 2p spectra, shown in figure 2 (b) revealed that higher concentrations of citrate solutions (2.4 M and 1.2 M) were marginally more effective than lower critic concentrations using a 60 s immersion time. The magnified spectra shown in figure 2(b) inset shows a sub-monolayer degree of oxide present after treatment with 0.48 M and 0.24 M citric acid.

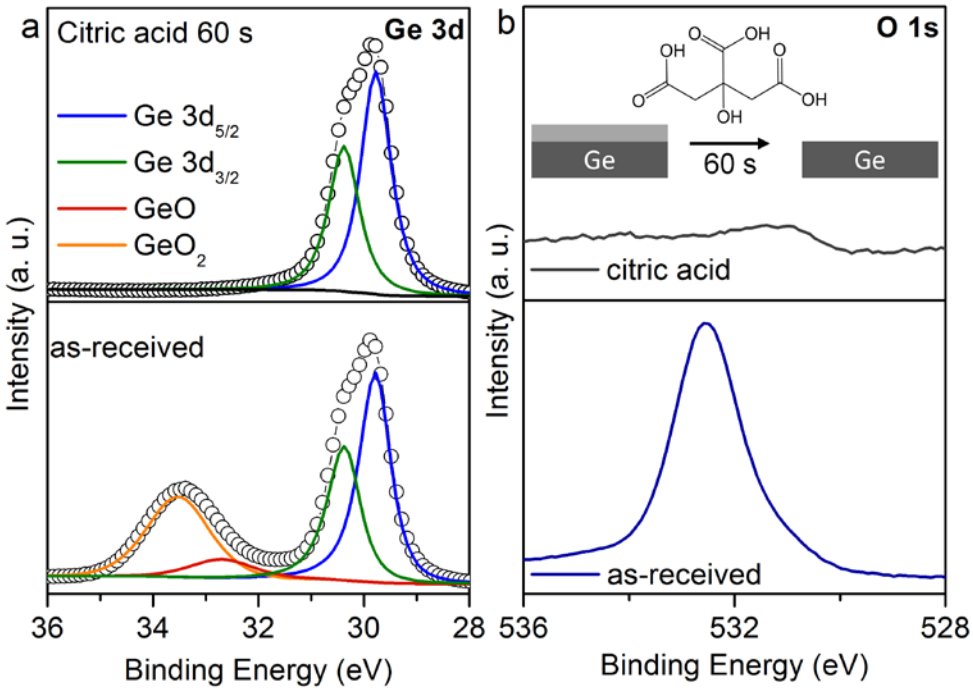


Figure 1. (a) Ge 3d and (b) core level XPS spectra of oxidized and citric acid treated Ge(100). Full experimental details are provided in the Supporting Information.

Figure 2(c) compares the Ge 3d core level spectra of citric acid treated Ge (Ge-CA) with freshly etched aq. HF and HCl solutions demonstrating that citric acid is as effective as HF and HCl for oxide removal. The relative stability of the Ge-CA was compared with Ge-H and Ge-Cl by exposing the samples to ambient conditions for 3 days after oxide removal. The Ge 2p spectra in figure 2(d) shows

that all samples undergo oxidation after 3 days and that the oxidation resistance of Ge-CA is similar to that of Ge-Cl.

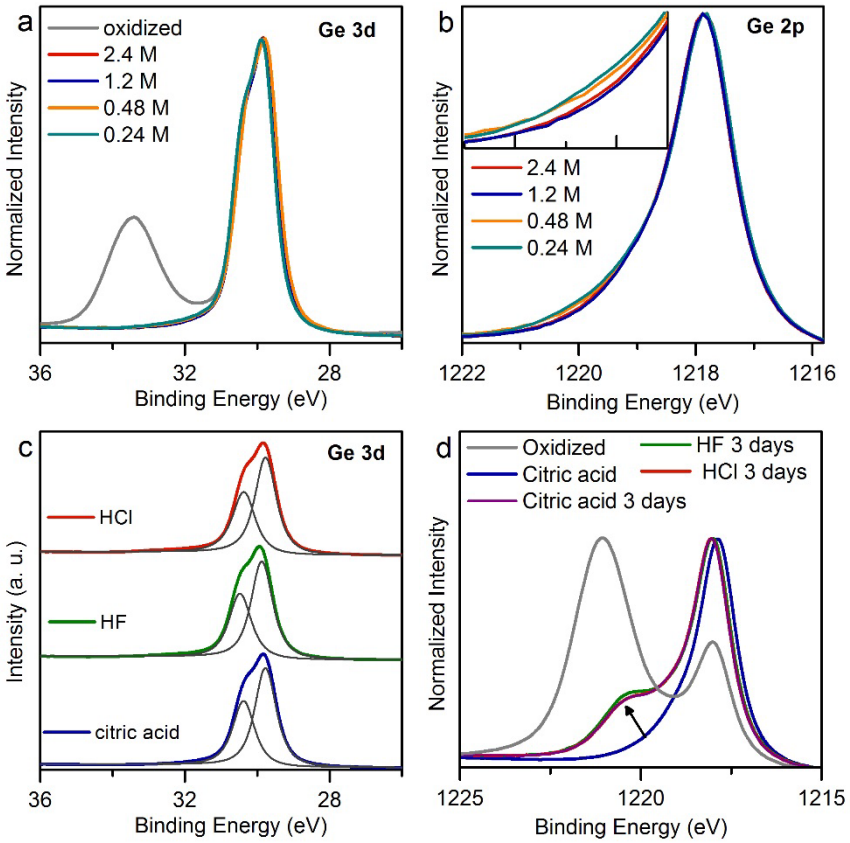


Figure 2. (a) Ge 3d and (b) Ge 2p core level spectra of Ge(100) treated with citric acid solution of varying concentration. (c) Ge 3d spectra of citric acid, HCl and HF treated Ge(100). (d) Ge 2p spectra of CA-, H- and Cl terminated Ge(100) after 24 h of ambient exposure. Spectra are overlapped for comparison, for full spectra see Supporting Information Figure S2 and S3.

The presence of citric acid species on the Ge surface is indicated by the FTIR spectra shown in Figure 4 comparing neat citric acid and Ge functionalized surface. The ν_a(C=O) stretch is clearly observed in the functionalized Ge spectra at 1720 cm^{-1}. A strong ν(C=O) vibration indicates that the surface molecules are predominately carboxylic acid (a 2.4 M aqueous solution of citric acid has a pH ~2 and is fully protonated). The low intensity peaks observed ~1550 cm^{-1} and 1390 cm^{-1} in the functionalized spectrum have been assigned to the asymmetric $\nu_a(COO^-)$ and symmetric $\nu_s(COO^-)$ stretch of the carboxylate anion, respectively.[19] Additional peaks located in the range of 1260-1150 cm^{-1} can be assigned to the coupled C-(OH) stretching and C-O-H bending modes.[20] An oxide free surface is indicated by the absence of the broad GeO_x absorption mode at 750-950 cm^{-1}.[21] A broad O-H

stretching absorption, indicative of H-bonding is also observed at 3100-3400 cm^{-1} originating from inter- and intramolecular hydrogen between the many protic groups on citric acid or possibly involve coordination with water molecules from the solution or rinsing step. It is should be noted that the IR experiments were not collected under inert atmosphere and interference of water adsorption from the air may also contribute to the spectra. Although, the binding mode of citric acid to the Ge surface was not investigated in detail, the absence of a Ge-O peak in the Ge 3d spectra and IR spectra suggests the citric acid is not attached by an alkoxy linkage (Ge-O-C) through the carboxylate group. Citric acid ligands may be physisorbed to the surface with strong intra- and intermolecular hydrogen bonding giving stability to the passivation layer. Chabal *et al.*[22] showed H-bonding added rigidity and excellent stability to phosphonic acid adsorbates on Si surfaces. Figure 3 (a) shows the C 1s spectra of the citric acid treated Ge surface with the C-C peak located a binding energy of 284.8 eV and two chemically shifted peaks at +1.6 eV (C-O) and +3.9 eV (C=O), which are in excellent agreement with the literature values for the carboxylate group.[23]

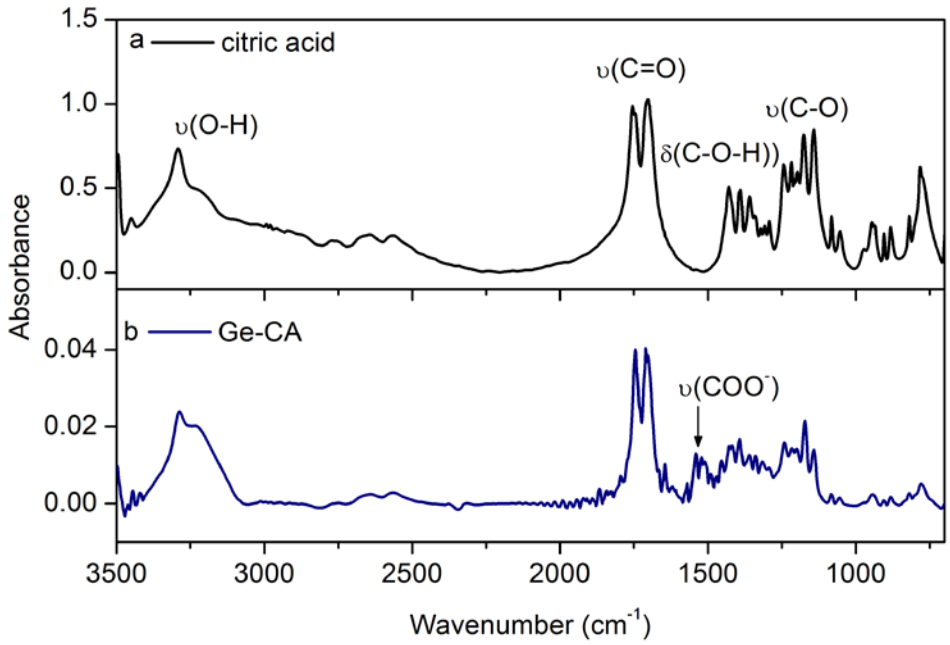


Figure 3. (a) FTIR spectrum of neat citric acid and (b) ATR-IR spectrum of citric acid functionalized Ge(100).

The ability to use Ge-CA surfaces for further passivation was investigated by reaction with alkanethiols. Figure 4 shows the C 1s core-level spectra after functionalization with dodecanethiol

(C12-SH), hexanedithiol (C6-dSH) and butanedithiol (C4-dSH). Surface functionalization results in an increase in the C-C peak intensity compared to Ge-CA for after thiolation. The intensity of the C-C peak increases from C4-dSH < (C6-dSH) < C12-SH, consistent with the longer chain length of the thiols. The relative intensity of the C-C is 1:1.3:2.2 which is in reasonable agreement with the theoretical ratio of 1:1.5:3 (Supporting Information Figure S4). C12-SH Ge is characterized by a peak at 284.4 eV, associated with the aliphatic carbon chain and a small peak located at a binding energy of 286 eV, attributed to the C-S.[24] No peaks associated with the citric acid ligands are observed, indicating their effective displacement by the thiol groups. In contrast to the alkanethiol, the C 1s spectra of the dithiols is best fit to four peaks at binding energies of 284.8 eV (C-C), 285.9 eV (C-S), 287 eV (C-O) and 289 eV (C=O). The presence of C=O peaks are observed for the dithiol functionalized surfaces, which may be due to the presence of citrate species.

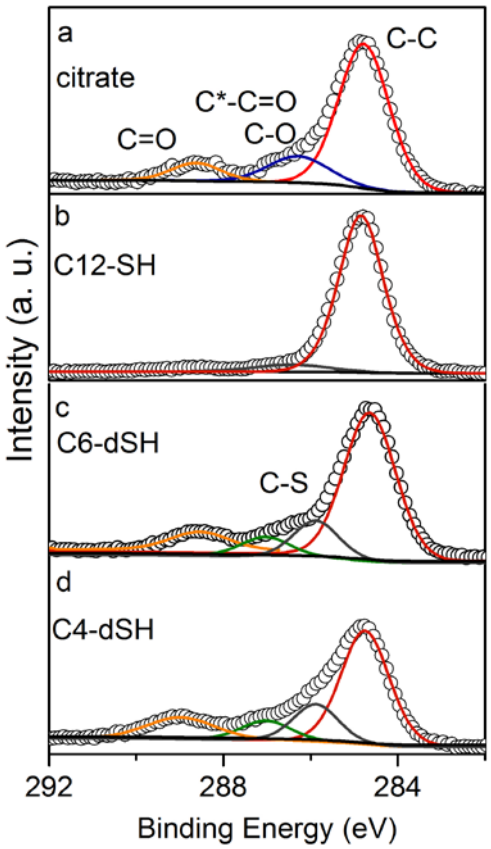


Figure 4. C 1s XPS of Ge (100) passivated with (a) citric acid (b) C12-SH (c) C6-dSH and (d) C4-SH.

Analysis of the S 2p core level, shown in figure 5 was conducted to further evaluate the thiol passivation. The S 2p components were fit to a doublet with a branching ratio of 0.5 and spin-orbit splitting of 1.2 eV. The presence of surface bound thiolates (Ge-S) are also confirmed by the S 2p core level spectra. The first component for all three thiols is located at a binding energy of 162.7 eV, assigned to bound thiolate group.[25] A second S 2p component located at a binding energy of 163.9 eV, can be assigned to free or unbound thiol.[26] Based in on the integral intensities of the S 2p spectrum, Ge functionalized with C12-SH contains ~29% physisorbed thiols, which is consistent with previous reports of alkanethiols on Ge.[27] For the dithiols the presence of unbound thiols is also associated with the terminal S-H group. The S 2p spectra for both dithiols show a greater degree of thiolate species compared to free thiol suggesting that a portion of the dithiols are bound to the Ge surface through both thiol groups of a single dithiol in a looped configuration. Comparing the S 2p integral intensities of free and bound thiols it is estimated that the Ge surface passivated with C6-dSH has 74% of the dithiols bound through one thiol group. The surface thiols of Ge functionalized by C4-dSH contain 60% of the dithiols bound by a single thiol.[28] The greater amount of doubly bound thiols on C4-dSH (40%) compared to C6-dSH (26%) may be associated with the shorter chain length of C4-dSH, bringing the terminal thiol group closer to the surface. Theoretical calculations of C4-dSH on Au determined a lying down configuration to be the most energetically favourable conformation.[29]

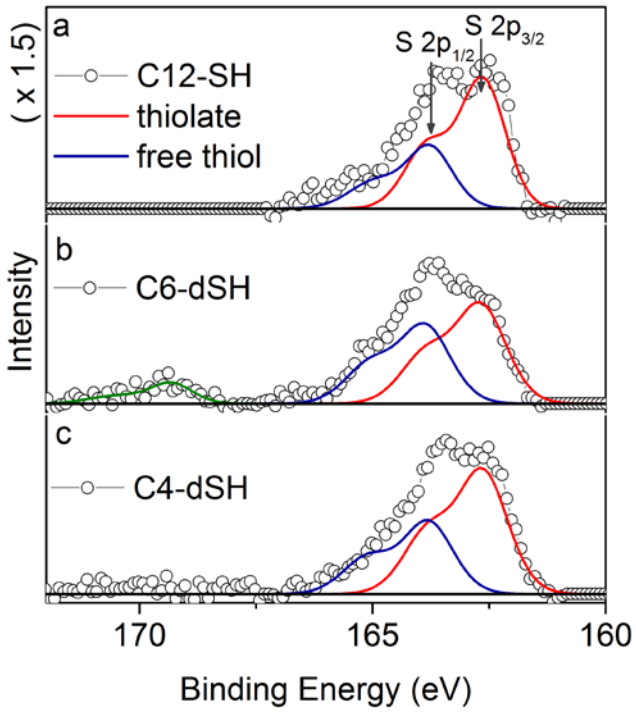


Figure 5. Background subtracted S 2p core-level spectra of Ge(100) functionalized with (a) C12-SH (b) C6-dSH and (c) C4-dSH.

The most notable difference in the S 2p spectra of the dithiol functionalized surfaces is the presence of the peak at 169 eV for C6-dSH which is absent for C4-dSH functionalized Ge. The peak comprises only 9% of the total S 2p intensity and S species at this binding energy are generally assigned to oxidized S species such as the sulphate or sulphinate group. Analysis of the C6-dSH surface after 3 days of the ambient exposure showed negligible changes in the S 2p spectra (Supporting Information Figure S6), confirming that the surface bound thiols do not under further oxidation. The formation of oxidized species may have formed during the functionalization or by a side reaction with citric acid.

Importantly, an oxide-free surface was maintained during the functionalization as shown by comparison of the Ge 3d spectra for C12-SH, C6-dSH and C4-dSH in figure 6. The stability of the thiolated surfaces was assessed after ambient exposure for 3 days. The Ge 3d spectra in figure 6 further show the thiolated surfaces have superior stability to citric acid passivated surfaces and remain oxide-free after 3 days, having greater oxidation resistance than thiol passivation from Ge-H, which are stable up to 12 h.[30]

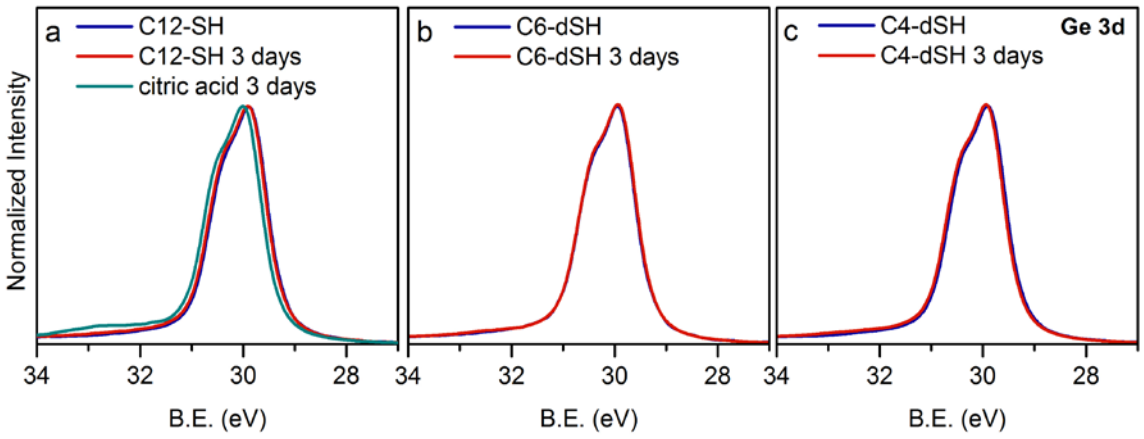


Figure 6. Ge 3d spectra of freshly passivated and air exposed for 3 days (a) C12-SH, (b) C6-dSH and (c) C4-dSH surfaces. The spectra of air exposed citric acid Ge is only shown in (a) for clarity.

Outlook

Aqueous citric acid solutions allow a simple method for Ge oxide removal, providing oxidation resistance similar to that of Ge-Cl. The Ge-CA surfaces can undergo thiolation reactions with mono and dithiols giving passivation layers that show no re-oxidation after 3 days of ambient exposure. This work represents an alternative to using hydrohalogenic acids which may be beneficial to applications where the use of mineral acids is not desirable e.g.in the presence of metal contacts or nanoscale Ge structures. The resulting oxide-free surfaces are highly hydrophilic which may be beneficial for the adhesion of polymer resists and coatings. Additional investigation to understand the specific interaction between the Ge surface and citric acid species and expanding functionalization strategies will be conducted.

Acknowledgements

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Supporting Information

The Ge 2p spectra of citric acid treated Ge, ambient exposed CA, HF and HCl treated surfaces, C1 and S 2p spectra of fresh and ambient exposed Ge are provided. This information is available free of charge via the Internet at http://pubs.acs.org/.

Author Information

To whom correspondence should be addressed email: g.collins@ucc.ie, c.odwyer@ucc.ie; Tel: +353 (0)21 4902732; Fax: +353 (0)21 4274097

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