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

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Keywords:

Germanium, Passivation, Self-Assembled Monolayers, Oxidation, X-ray Photoelectron Spectroscopy, Thiols.

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Abstract:

Continued scaling of electronic devices shows the need to incorporate high mobility alternatives to silicon, the cornerstone of the semiconductor industry, into modern field effect transistor (FET) devices. Germanium is well poised to serve as the channel material in FET devices as it boasts an electron and hole mobility more than twice and four times that of Si, respectively. However, its unstable native oxide makes its passivation a crucial step towards its potential integration into future FETs. The International Roadmap for Devices and Systems (IRDS™) predicts continued aggressive scaling not only of the device size but also of the pitch in nanowire arrays. The development of a vapor-phase chemical passivation technique will be required to prevent the collapse of these structures that can occur due to the surface tension and capillary forces that are experienced when tight pitched nanowire arrays are processed via liquid-phase chemistry. Reported here, is a vapor–phase process using hexanethiol for the passivation of planar Ge(100) substrates. Results benchmarking it against its well-established liquid-phase equivalent are also presented. X-ray photoelectron spectroscopy (XPS) was used to monitor the effectiveness of the developed vapor-phase protocol where the presence of oxide was monitored at 0 h, 24 h and 168 h. Water contact angle (WCA) measurements compliment these results by demonstrating an increase in hydrophobicity of the passivated substrates. Atomic force microscopy (AFM) monitored the surface topology before and after processing to ensure the process does not cause roughening of the surface, which is critical to demonstrate suitability for nanostructures. It is shown that the 200 minute vapor-phase passivation procedure generates stable, passivated surfaces with less roughness than the liquid-phase counterpart.

Introduction:

Silicon (Si) is an essential part of modern technology since it forms the basis of the integrated circuits that are found in electronic devices. It also plays a critical role in infrared sensors,[1] solar panels [2] and chemical sensors[3] and has been the semiconductor of choice for more than 60 years, owing to its relative abundance, mechanical strength and stable native oxide. However, as the need for faster, more efficient processors grows, other materials [4-7] and novel architectures [8] are being studied with the intention that they be incorporated in devices alongside Si.

As mentioned, germanium (Ge) is an attractive candidate as a channel material, however, the germanium's native oxide is a complex system with a range of oxidation states (+1, +2, +3, +4).[9] The bulk of this oxide, GeO_2, is problematic from a device perspective since it is unstable and the interface between it and the underlying Ge is characterized by defects which lead to charge trapping and poor overall device performance.[10] In FET devices, the interface between the dielectric and the underlying channel material is critical to the operation of the device. Ultimately, it is the nature of the native oxide that has hindered the practical use of Ge to date. GeO_2 can be removed by treating the Ge with a halide acid (most commonly HF or HCl) solution, however, the resulting H-terminated or Cl-terminated Ge surfaces have been shown to rapidly reoxidize upon exposure to the ambient.[11-13] It is for this reason that the oxide must be removed and replaced with a passivating layer which inhibits re-oxidation such that a more reliable dielectric can be deposited on the passivated Ge surface.

There have been a number of reports on the passivation of Ge using liquid-phase chemistry. Cullen *et al*. first reported the liquid-phase chemical functionalization of a Cl-terminated Ge surface using ethyl Grignard in 1962.[14] Choi and Buriak then demonstrated the hydrogermylation of H-terminated Ge which mirrored the hydrosilylation reactions which had been carried out on Si.[15] Hanrath *et al.* have subsequently shown that the hydrogermylation reaction is applicable to H-terminated Ge nanowires also.[16] Both the Grignard chemistry and the hydrogermylation reaction result in a Ge-C bond. Alkanethiol liquid-phase chemistry has also been developed for Ge which results in the formation of a Ge-S bond.[17] The vapor-phase passivation of Group IV semiconductors has also been explored and dates back to the early 1960's whereby Si and Ge were passivated by halides [14, 18-23], a range of organics [13, 24-29], nitrides and oxynitrides

[30-33]. For example, Degen *et al.* have reported the vapor-phase passivation of Si(100) and Si(111) using short-chain alkynes for NEMS and MEMS devices.[34] Kosuri *et al.* have described the adsorption kinetics of 1-decyene on H-terminated Si(100)[35] and Si(111)[36] and also the adsorption kinetics of 1-alkanethiols on Ge(111)[37] surfaces. Takenaka *et al.* have reacted Ge surfaces with vaporized tertiarybutylarsine (TBA) which is an arsenic source for Ge doping.[38, 39] In this report, a facile approach for the vapor-phase passivation of oxide-free, chlorine-terminated Ge(100) using a short-chain alkanethiol (1-hexanethiol) at ambient pressure and low temperature (140°C) is demonstrated.

The International Roadmap for Devices and Systems (IRDS™) predicts that the fin/nanowire diameter, channel length and fin/nanowire pitch of these devices will all decrease in size from one technology node to another.[40] The greatest predicted decrease in size is in the fin/nanowire pitch. Vapor-phase passivation routes offer the ability to passivate structures with small dimensions and pitches without causing the damage that liquid-phase alternatives can cause. An example of the impact of liquid-phase chemical processing on the structure of suspended nanostructures can be seen in **Figure 1**, where released Si nanowires have stuck together due to capillary forces, after dipping in an aqueous solution of hydrofluoric acid (HF). An example of a novel liquid-phase approach that has been shown to be effective at passivating nanostructures is to conduct the passivation reactions in a critical-point drier as demonstrated by Tao *et al*. for the alkylation and amination of Si.[41] Alternatively, vapor-phase alternatives such as the one documented here, can be implemented.

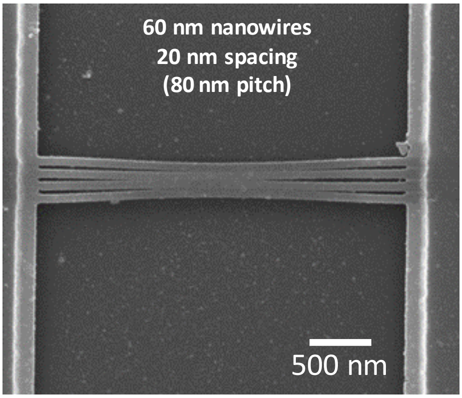
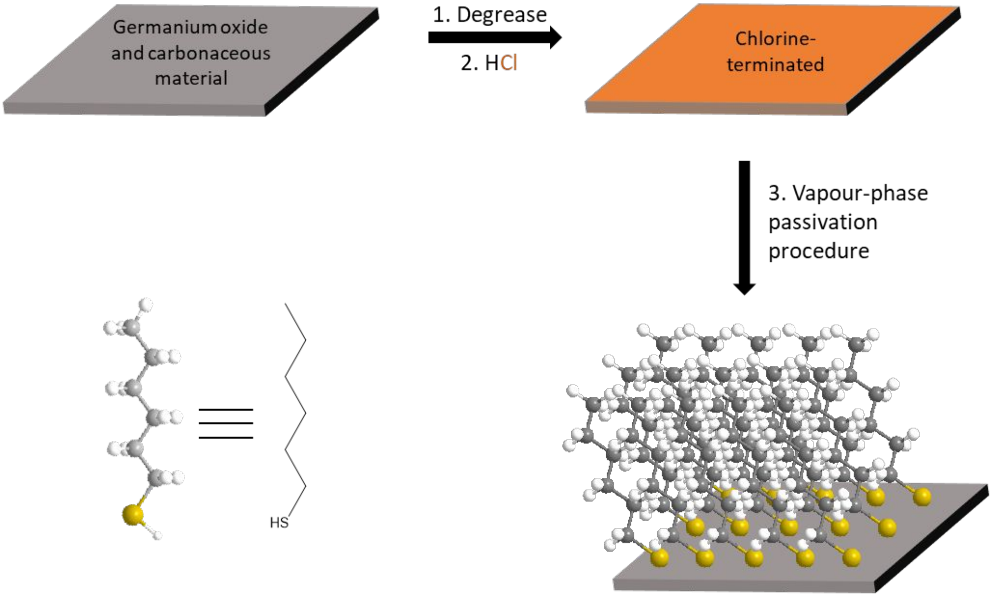


Figure 1. SEM image of 60 nm long Si nanowires with a 20 nm spacing after dipping in HF highlighting the effect of the capillary forces experienced during liquid-phase processing

To date, the bulk of the work carried out on self-assembled monolayers (SAMs) on Ge has focused on using dodecanethiol, which has 12 carbon atoms, to form SAMs on the Ge surface.[37, 42, 43] The preference for this work was to choose a thiol molecule with the highest vapor pressure possible (to enable effective vaporization) while still forming good quality monolayers. 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 underlying Ge in 24 hours (see **Figure S1**). Hexanethiol (HT) was ultimately chosen as the aliphatic thiol molecule to passivate Ge in this study due to its relatively high vapor pressure and effective passivation of Ge.



Scheme 1. Schematic of oxide removal and passivation procedure for Ge using hexanethiol

A SAM is formed when a single layer of molecules bonds to a surface in a self-limiting fashion to yield a surface that is chemically stable. Herein, HT molecules are reacted in the vapor-phase with a Cl-terminated Ge(100) surface. A mechanistic explanation for what occurs during the 1-alkanethiol passivation of Cl-terminated Ge(100) has been discussed by Bent *et al.*[13] They explore three possible routes for the passivation; namely a hydrohalogenic elimination pathway, an elimination and subsequent insertion pathway and a pathway which involves the cleavage of the dimer bond between Ge atoms at the surface. Their density functional theory calculations show that adsorption of 1-alkanethiols on halide-terminated Ge surface via hydrohalogenic acid elimination (**Figure 2**) is kinetically favorable at room temperature. Thus, the reaction of HT with Cl-terminated Ge(100) is likely to occur via this pathway and the Ge dimer bond is likely to remain unbroken.[13]

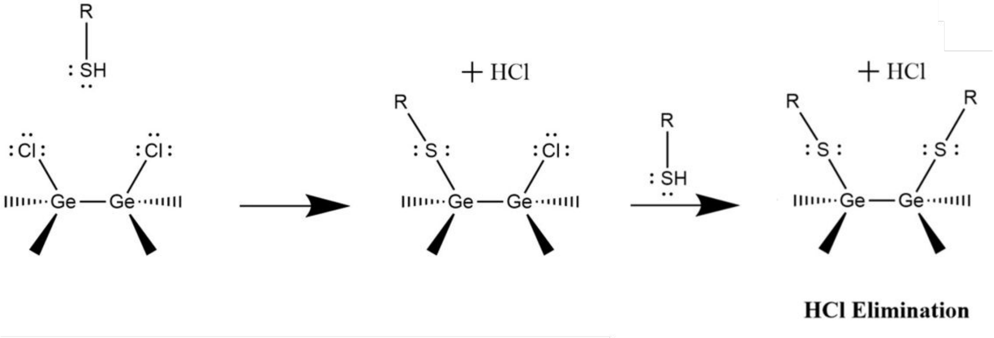


Figure 2: Proposed HCl elimination pathway for thiol reaction with Cl-terminated Ge

The reaction between the Cl-terminated Ge(111) surface and alkanethiol molecules was also observed by Bent et al. and although not calculated directly, they expect hydrohalogenic acid elimination reactions similar to those at halogenated Ge(100) to be kinetically favorable at halogenated Ge(111) surfaces. Bent et al. observed the same general thiolation trends for Ge(100) and Ge(111) surfaces however, there were some differences. After the thiolation reaction, higher levels of both sulfur and carbon were detected at the Ge(100) surface, which indicated higher conversion of surface halides to surface thiolates on Ge(100) than on Ge(111).[13] With that said, the thiolation of Cl-terminated Ge surfaces occurs for both Ge(100) and (111) surfaces. The literature on the thiolation of other facets of Cl-terminated Ge is sparse however it has been shown for H-terminated Ge(110) surfaces that thiol passivation is achieved.[44] Consideration of the passivation of various facets of Ge is important in the context of both Ge nanostructures and planar Ge surfaces. In relation to nanostructures, the top of the structure may be Ge(100), but crystal orientation of the sidewalls will vary depending on the selectivity of etch used in their fabrication. In relation to planar Ge, it is important to recognize that the Ge(100) surfaces used in this study are not atomically flat (**Figure 4 (i))** and that microfacets that locally resemble Ge(111) and higher index surfaces are invariably present. With that said, the studies, as described above, carried out on varied facets indicate that the reaction always proceeds, even if the coverage varies somewhat.

A common use for SAMs on Ge is to inhibit the growth of the unreliable oxide.[42, 43] In this study, the authors demonstrate a method to passivate oxide free, Cl-terminated Ge(100) using HT in the vapor-phase. This method is shown to be effective at preventing the regrowth of native Ge oxide for 24 hours.

Methods:

All chemicals were purchased from Sigma-Aldrich unless otherwise stated. P-type germanium wafers were purchased from Umicore. Ge wafers were cut into 1 cm^2 coupons and degreased by sonication in acetone for 3 minutes then rinsed in IPA and dried under a stream of N_2. GeO_2 was removed by dipping the coupons in 20% HCl for 10 minutes followed by drying under N_2. To achieve vapor-phase passivation, the coupons were loaded into a HiP MS series micro reactor (**Figure 3**) in a glovebox with an atmosphere of < 0.5ppm O_2 and H_2O. The reactor was assembled in the glovebox to ensure no water vapor was present which could have oxidized the chlorine-terminated, oxide-free Ge prior to the vapor-phase thiol reaction. The assembled reactor was then connected to HiP three way/two stem connection valves on both the inlet and exhaust. The reactor was then loaded into a furnace.

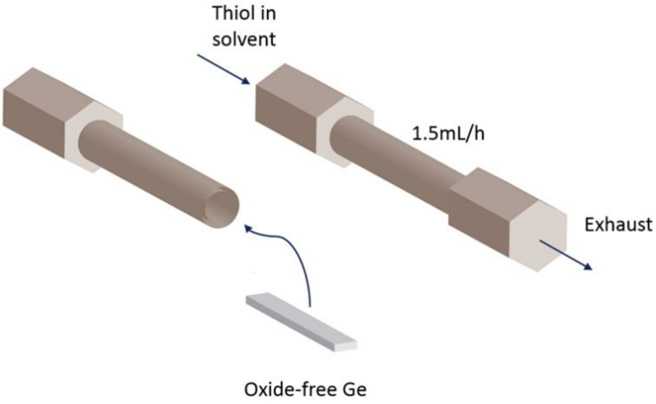


Figure 3. Schematic of HiP MS series micro reactor configuration

A 0.1M solution of thiol in toluene was degassed using the freeze-pump-thaw (FPT) method. This method involves freezing the thiol solution under

N_2 using liquid nitrogen and then allowing the solution thaw under vacuum (10^{-3} Torr) to remove undesirable gases present in the solvent. This method was repeated 3 times - until there was no more evolution of gas from the thiol solution. The degassed thiol solution was then syringed from the round-bottom flask using a 10 mL Luer-lock syringe which had been dried in a vacuum oven at 60°C overnight and then purged with N_2 prior to filling with the thiol solution. The Luer-lock syringe was used to pump the thiol solution at 1.5 mL/hr into the reactor at 140°C, carried by a constant flow of H_2 in Ar. After 200 minutes, the furnace was turned off and the injection of the thiol solution into the reactor was stopped. At this point, 5 mL of the thiol solution had been pumped through the reactor. The reactor was then allowed to cool for 30 minutes before the samples were removed. The samples were then sonicated in acetone for 5 minutes, rinsed with propanol and dried under a stream of N_2. For comparison, a liquid-phase chemical procedure for passivation of Ge was conducted also. In this case, a 0.1M solution of HT in toluene was degassed using the FPT method described previously. Oxide-free, Cl-terminated Ge samples were refluxed in the solution under an N_2

atmosphere using Schlenk line apparatus for 24 hours as is common in the literature to achieve thiol SAMs of high quality on Ge.[13, 29, 43] Samples were exposed to 40% relative humidity (RH) at 20°C in a Votsch temperature test chamber to emulate ambient conditions for 24 hours to track what affect the ambient had on the samples.

Atomic force microscopy was used to determine if the processing affected surface roughness. Water contact angle analysis was used to determine the hydrophobicity of the sample surface which gives an indication of the quality of the SAM and X-ray photoelectron spectroscopy was used to get elemental analysis of the Ge surface post reaction and after exposure to the ambient for 24 hours to determine if the passivated surface was resistant to oxidation. Passivated samples were transported under a positive pressure of N_2 in a SPI-DRY™ Sample Preserver to the characterization tools.

1. Atomic Force Microscopy (AFM)

All AFM measurements in this study were taken using tapping mode Veeco Multimode V at room temperature over a 3 x 3 μm^2 scanning area. Tapping mode is preferred to contact mode when working with SAMs since the SAM can be affected by the probe being in constant contact with the surface. Tapping mode bypasses this problem since the probe is not dragged along the surface.

2. Water Contact Angle (WCA)

An image of a 50 µL drop of deionized water on the Ge surface was obtained and the angle formed between the water, Ge surface and air was measured. The greater the angle, the more hydrophobic the sample. Here, the wettability of a Ge surface gives an indication as to whether the thiol molecule has reacted with that surface. Considering the tail of the HT molecule is non-polar in nature, an increase in hydrophobicity indicates that a thiol SAM is present on the Ge surface.

3. X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra were acquired on an Oxford Applied Research Escabase XPS System equipped with a CLASS VM 100 mm mean radius hemispherical electron energy analyzer with multichannel detectors in an analysis chamber with a base pressure of 5.0 × 10^{-9} mbar. A pass energy of 50 eV, a step size of 0.7 eV and a dwell of 0.3 s was used for survey spectra which were swept twice. All core level scans other than the S 2p and 2s were acquired with a step size of 0.1 eV, a dwell time of 0.1 s and a pass energy of 20 eV averaged over 10 scans. The S 2p and 2s scans were acquired with a step size of 0.1 eV, a dwell time of 0.1 eV and a pass energy of 50 eV averaged over 20 scans. This was done to maximize the intensity of the S 2p peaks so accurate peak fitting could be carried out. A non-monochromated Al-Kα X-ray source (1486.58 eV) at 100 W power (10 mA, 10kV) was used for all scans. All spectra were acquired at a take-off angle of 90° with respect to the analyzer axis and were charge corrected with respect to the C 1s photoelectric line at 284.8 eV. A Shirley type background was used for construction and peak fitting of synthetic peaks. Synthetic peaks were a mix of Gaussian-Lorenzian, the Ge 2p spectra were fit using Gaussian-Lorentzian peak shape GL(90) for the elemental Ge peak and Lorentzian peak shape LA(1.53,243) for all other peaks. The relative sensitivity factors used are from a CasaXPS library containing Scofield cross-sections.

Results & Discussion:

Atomic Force Microscopy & Water Contact Analysis:

An industry requirement for the passivation of Ge is that its surface remains oxide-free for a queue-time of 24 hours. This allows for maintenance or repair of instrumentation, which may result in the exposure of processed Ge to the ambient during device fabrication. Processed Ge wafers require a sufficiently robust passivation layer to avoid reoxidation of the substrates. Processes developed on planar Ge must be non-destructive such that they be transferrable to highly ordered, densely packed, high aspect-ratio Ge nanostructures. As a result, AFM was used to track the effect the processing had on the roughness of planar Ge surfaces. Since the surface to bulk ratio for nanostructures is high, it is imperative that any processing has a negligible impact on surface roughness. Results for the liquid-phase passivation of Ge using HT are included for comparison.

Prior to the vapor-phase passivation of the Ge surface, the native oxide was removed using a 20% solution of HCl. This step relies on wet chemical processing which would not be compatible with nanostructures, however in the context of an industrial setting a vapor phase alternative would be applied. The RMS value obtained for a clean Ge surface is 0.30 nm as seen in **Figure 4 (i)**. The inset in **Figure 4 (i)** highlights how the surface prior to any processing is hydrophilic, a shallow angle of less than 50° is obtained when a 50 uL drop of millipore deionized water is deposited onto the surface. This value is consistent for literature values of ultrasonic cleaned Ge surfaces.[48] The surface is hydrophilic since the water interacts favorably with the GeO_2 film present on the surface. After the HCl etch, a Cl-terminated Ge surface with an RMS value of 0.30 nm was obtained. Removing the oxide with HCl does not cause an increase in the surface roughness. The inset in **Figure 4 (ii)** illustrates how the chlorine-terminated Ge surface is also hydrophilic. A water contact angle of less than 50° is obtained since the water molecules interact favorably with the Cl-terminated Ge surface. This is consistent with the literature on Cl-terminated Ge whereby angles of 39-50° are observed.[48, 49] The AFM image in **Figure 4 (iii)**, illustrates how the vapor-phase HT passivation reaction does not cause an increase in Ge surface roughness and the degree of hydrophobicity of the Ge surface sharply increases to over 90°. Increasing contact angle measurements for alkanethiol SAMs have been shown to correlate with the length of the alkanethiol molecule.[46] On Ge(100), alkanethiol SAMs consisting of 1-dodecanethiol molecules have been shown to display WCA of > 100°,[42] while SAMs consisting of 1-octadecanethiol molecules (C18) have been shown to display WCA of > 115°.[50] In this study, HT, having a shorter C backbone, was found to form a SAM on Ge that yield a surface with a WCA of 90°. The sharp increase in the hydrophobicity of the Ge surface is a clear indication that the vapor-phase reaction occurred between the Cl-terminated Ge surface and the HT molecules. For comparison, the AFM and WCA data for a Ge surface which has been passivated using the liquid-phase chemistry approach have been included also. It is clear from the AFM image in **Figure 4 (iv)** that the surface roughness of the Ge is affected by the liquid-phase passivation procedure where an RMS value of 0.61 nm is observed along with a WCA of 85°. The increased WCA indicates that a HT SAM is present on the surface.

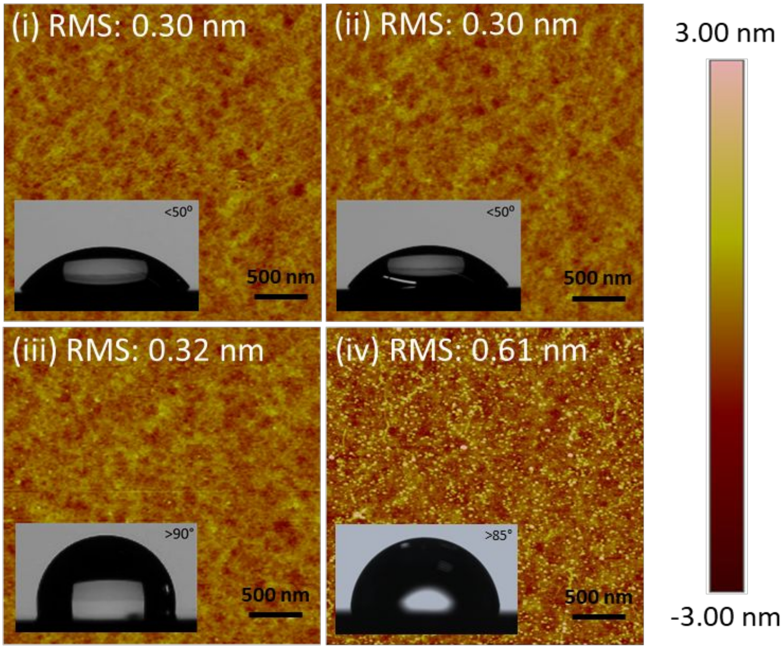


Figure 4. AFM images with water contact angle insets of (i) as-rec Ge (ii) HCl treated Ge (iii) HT vapor-phase passivated Ge with 0 hours exposure to the ambient (iv) HT liquid-phase passivated Ge with 0 hours exposure to the ambient

X-ray Photoelectron Spectroscopy characterization:

In the literature, when discussing the oxidation of Ge, it is common to discuss the Ge 3d peak primarily; however, the 3d transition comes from electrons with high kinetic energy and therefore from a greater sampling depth when compared to the electrons from the 2p transition which have lower kinetic energy and so are more surface sensitive. Thus, in an attempt to highlight what is occurring at the surface of the Ge, the Ge 2p peak will be presented in this study. When fitting the oxide peaks, the suboxide peak position was fixed at 1.1 eV greater than the elemental Ge peak. GeO_2 peak position was not fixed since a trend was observed whereby the peak position shifted to higher binding energy upon oxidation. Oxide thickness was calculated using the method outlined by Murakami *et al.*[51]

$$d_{GeO_2} = \lambda_{GeO_2} sin\theta \, ln\left(\frac{I_{Ge}^{\infty} \; I_{GeO_2}}{I_{GeO_2}^{\infty} \; I_{Ge}} + 1\right)$$

Where λ_{GeO_2}, the inelastic mean free path for the Ge 2p transition is 0.9 nm; the photoemission angle θ is 90°; $I_{Ge}^{\infty}/I_{GeO_2}^{\infty}$ is the ratio of the Ge 2p signal from infinitely thick Ge to infinitely thick GeO_2 and is determined as 1.73; I_{GeO_2} is the intensity of the of native oxide (GeO_2) peak from curve fitting the Ge 2p transition; I_{Ge} is the intensity of the metallic Ge peak from curve fitting the Ge 2p transition. This calculation was repeated to determine the thickness of the suboxide (GeO_x) component for each sample also. In this case, I_{GeO_x}, the fraction of suboxide (GeO_x) from curve fitting the Ge 2p was used in place of I_{GeO_2}.

Figure 5 (i) depicts the Ge 2p spectrum for an as-received Ge sample that has undergone no processing. As expected, there is a large peak at 1221.14 eV that corresponds to Ge^{+4} from GeO_2. There is also a peak evident at 1218.89 eV which is attributed to the suboxide, GeO. The thickness of the GeO_2 on as-rec Ge is 2.12 nm which is in agreement with literature values for as-rec Ge(100).[52] The thickness of the suboxide component was 0.56 nm. The suboxide component of Ge likely has contributions from Ge in +1, +2 and +3 states however these cannot be accurate resolved with the instrumentation available. Treatment of the as-received Ge with HCl removed both the native oxide and the suboxide component leaving a Cl-terminated surface which oxidized upon exposure to the ambient. This is evident in **Figure 5 (ii, iii)** where the Ge 2p peaks corresponding to the native oxide and suboxide are no longer present after the HCl dip but return after 24 hours of exposure to the ambient. A GeO_2 film, 0.34 nm thick grows in 24 hours of exposure to the ambient indicating that Cl-termination does not sufficiently prevent reoxidation of the Ge surface.

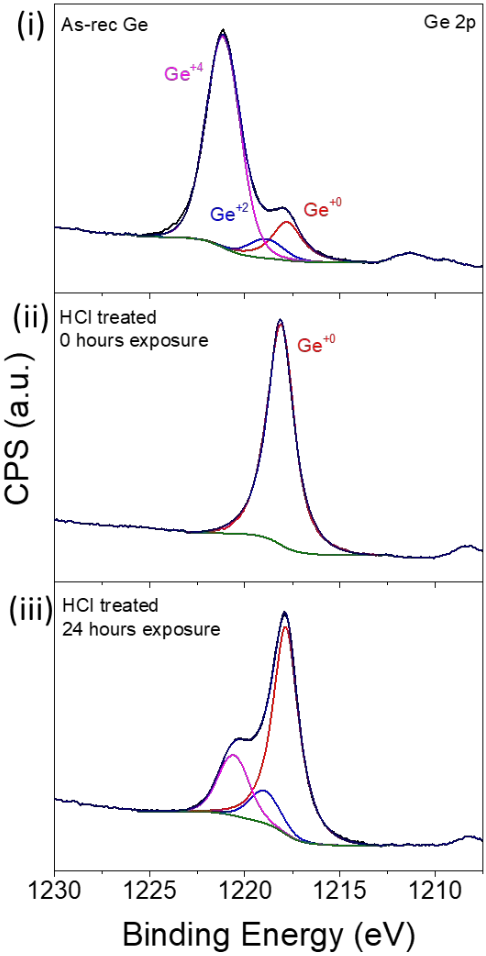


Figure 5. Ge 2p plots for (i) as-rec Ge (ii) and (iii) Cl-terminated Ge after 0 and 24 hours exposure to the ambient respectively

Figure 6 (i) depicts the Ge 2p spectra for a Ge sample that has had the native oxide removed by a HCl etch followed by passivation using HT in the vapor-phase. No GeO_2 is detected after the passivation reaction however, there is a component at 1219.2 eV which is likely attributable to Ge^{+2} from a mixture of Ge-O and Ge-S after the passivation reaction. An XPS tool with higher resolution would be needed to attempt to resolve these components. The calculated thickness of these components is 0.16 nm. After 24 hours of exposure to the ambient, the GeO_2 film thickness was 0.08 nm. The growth of oxide is minimal and as such can be used as a proxy for quality of SAM on the Ge surface. The more stable and uniform the SAM, the slower the growth of oxide. In this case, the vapor-phase passivated Ge exhibits inhibition of oxide growth and thus one can infer that a stable SAM is present. The peak at 1219.2 eV is still present after the passivation reaction is unchanged with a calculated thickness of 0.16 nm. After 168 hours of exposure to the ambient, GeO_2 thickness was calculated to be 0.25 nm with the thickness of the component at 1219.2 eV calculated to be 0.20 nm indicating that continued oxidation does occur albeit slowly. The thickness of the oxide film on the HT vapor-phase passivated sample after 168 hours exposure to the ambient is less than that of the Cl-terminated sample after only 24 hours of exposure (0.25 nm vs. 0.34 nm). The 168 hour Ge 2p spectrum is presented in **Supporting Information** section (**Figure S3)**.

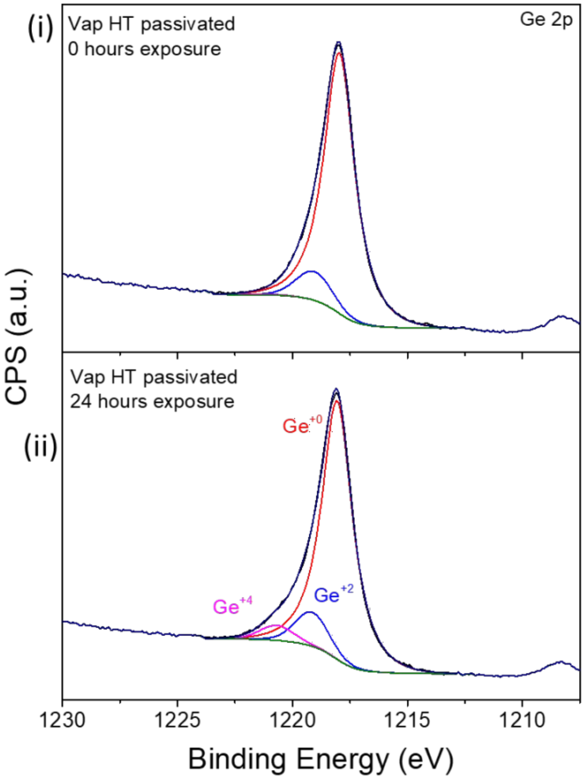


Figure 6. (i) and (ii) Ge 2p plots for HT vapor-phase passivated Ge with 0 and 24 hours exposure to the ambient respectively

An inspection of the O 1s peaks for the vapor-phase passivated Ge directly after the passivation reaction and after 24 and 168 hours of exposure to the ambient is illustrated in **Figure 7**. There is little growth in the intensity of the O 1s peak after 24 hours however after 168 hours some growth is observed indicating that the HT SAM passivation is effective at inhibiting oxidation of the Ge over 24 hours but that in the following 144 hours, a small amount of GeO_2 growth occurs (0.17 nm growth in the 144 hours proceeding the first 24 hours).

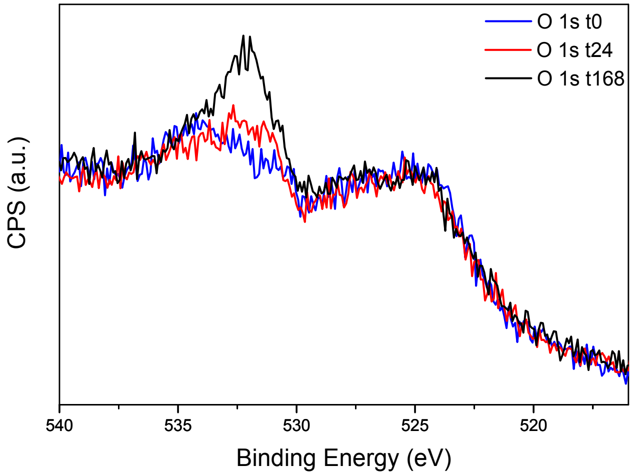
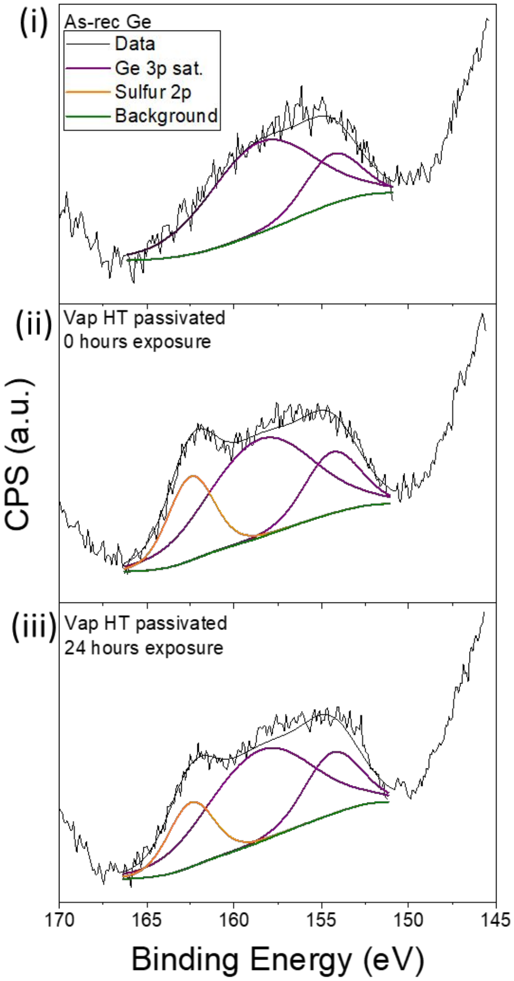


Figure 7. O 1s spectra of Ge passivated by HT in the vapor-phase after 0 (blue), 24 (red) and 168 (black) hours exposure to the ambient

The S 2p peak occurs at 162.3 eV which overlaps with a Ge 3p satellite feature, however through peak fitting, the S 2p peak can be clearly differentiated from the Ge 3p sat. There is no S 2p peak present in the as-rec Ge sample (**Figure 8 (i)**), as expected. However, a clear S 2p peak is observed at 162.3 eV in **Figure 8 (ii)** for the HT passivated sample. That peak is still evident after 24 hours of exposure to the ambient (**Figure 8 (iii)**), albeit with slight lower intensity, which indicates that the thiol SAM is stable on the surface for 24 hours. A possible explanation as to why the intensity of the S 2p peak diminishes slightly in 24 hours is that the growth of a small amount of oxide on the surface in 24 hours displaces the thiol molecules, resulting in a slightly less intense S 2p peak. The XPS measurements showing the presence of sulfur on the vapor-phase HT treated surface is clear indication that the vaporized HT reacted with the Cl-terminated Ge surface. The presence of the S 2p peak after 24 hours and the minimal growth of oxide observed in **Figure 6** indicates that the HT SAM on the Ge surface is stable and more effective than chlorine at preventing oxidation from the ambient for 24 hours.


(i)
As-rec Ge
Data
Ge 3p sat.
Sulfur 2p
Background
(ii)
Vap HT passivated
0 hours exposure
(iii)
Vap HT passivated
24 hours exposure
CPS (a.u.)
170
165
160
155
150
145
Binding Energy (eV)

397

Figure 8. (i) as-rec Ge showing no S peak (ii) HT vapor-phase passivated Ge with 0 hours exposure to the ambient (iii) HT vapor-phase passivated Ge with 24 hours exposure to the ambient

For comparison with the vapor-phase passivation approach, **Figure 9** elucidates the liquid-phase passivation of Ge, where some native oxide is present directly after the passivation reaction and the oxide thickness is 0.21 nm. The presence of this oxide indicates that the during the 24-hour processing, a small amount of Ge oxidation occurs. This is not the case with the shorter (200 minute) vapor-phase reaction where there is no detectable GeO_2 directly after the passivation reaction. Shorter processing times are desirable since they decrease the likelihood that oxidation can occur. The thickness of the oxide for the liquid-phase passivated sample increases to 0.34 nm after 24 hours of exposure to ambient conditions (a growth of 0.13 nm).

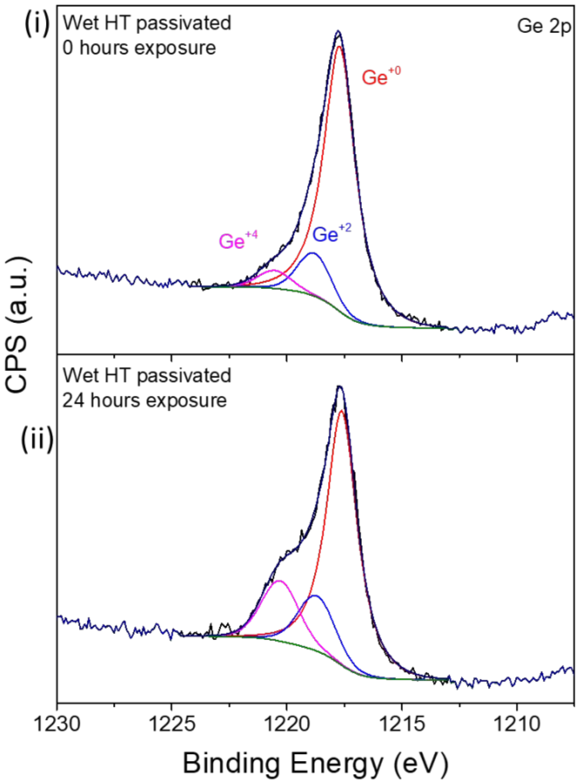


Figure 9. (i) and (ii) Ge 2p spectra for the liquid-phase passivation of Ge illustrating the presence of native oxide after 0 and 24 hours exposure to the ambient respectively

This XPS data, coupled with the WCA data from **Figure 4** indicate that the liquid-phase passivation reaction yields a SAM of which does not inhibit oxidation of the Ge as effectively as the vapor-phase passivated sample. The vapor-phase passivation method results eclipse those of the liquid-phase chemical passivation in relation to oxidation inhibition over 24 hours of exposure to the ambient. A summary of the oxide thicknesses is tabulated in **Table 1.**

	GeO_2 thickness (nm)	
Sample	0 hrs exposure	24 hrs exposure
As-Rec	2.12	2.12
HCl treated Ge	0	0.38
Vap. HT Passivated Ge	0	0.08
Liq. HT Passivated Ge	0.21	0.34

Table 1. Oxide thicknesses for as-rec, HCl-treated, vapor-phase passivated and liquid-phase passivated Ge(100) samples

Estimation of Overlayer Thickness:

XPS thickness measurement of the SAM overlayer for the vapor-phase passivated Ge was performed following the methodology originally defined by Cumpson *et al. [53]*

$$\ln\left(\frac{I_O S_O}{I_S S_S}\right) - \left(\frac{\lambda_O}{\lambda_S}\right)\frac{1}{\lambda_O \cos\theta} - \ln 2 = \ln \sin h\left(\frac{t}{2\lambda_O \cos\theta}\right)$$

where I_o and I_s represent the respective measured peak intensities of the overlayer (HT molecules) and the substrate peaks, S_o and S_s refer to the relative sensitivity factors for the overlayer and the substrate respectively. λ_o and λ_s are the attenuation lengths of electrons in the overlayer and the substrate. θ is the emission angle with respect to the surface normal. The peak intensity of the overlayer peak, I_o, and the peak intensity of the substrate peak, I_s, were determined using CasaXPS software after a transmission correction. The relative sensitivity factors for the substrate peak S_s and the overlayer peak S_o were also obtained from the CasaXPS library and manually inputted into the data processing software to remove instrumental factors which may affect quantification. The practical electron attenuation length (EAL) in the overlayer, l_o, was estimated, using the NIST Electron Effective Attenuation Length database, to be 2.58 ± 0.2 nm for the Ge 3d component. Using this method, the thickness of the SAM overlayer was estimated to be approximately 1 nm which is in accordance with the length of one HT molecule – the expected thickness of the monolayer.

Conclusion:

In this study, it has been shown that a facile and mild 200 minute vapor-phase passivation reaction of Ge(100) using HT yields a Ge surface that resists oxidation for 24 hours. The procedure does not cause an increase in surface roughness. The significance of this is apparent when considering Ge nanostructures especially. This passivation procedure could be implemented on structures that would otherwise be damaged by liquid-phase chemical processing – an important step on the road to realizing Ge's potential as a channel material in modern devices.

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Author Contributions

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Abbreviations

Ge, germanium; Si, silicon; SAM, self-assembled monolayer; XPS, x-ray photoelectron spectroscopy; WCA, water contact angle; AFM, atomic force microscopy; HT, hexanethiol; DoDT, dodecanethiol; HCl, hydrochloric acid; HF, hydrofluoric acid.

Supporting Information

Ge 2p XPS spectra for a liquid-phase passivation of Ge by ethanethiol, butanethiol, pentanethiol, hexanethiol, octanethiol and dodecanethiol. Ge 3d and S 2s XPS spectra for vapor-phase passivation of Ge by hexanethiol. Ge 2p XPS spectra for vapor-phase hexanethiol passivated Ge after 168 hours exposure to the ambient. XPS survey spectra.

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