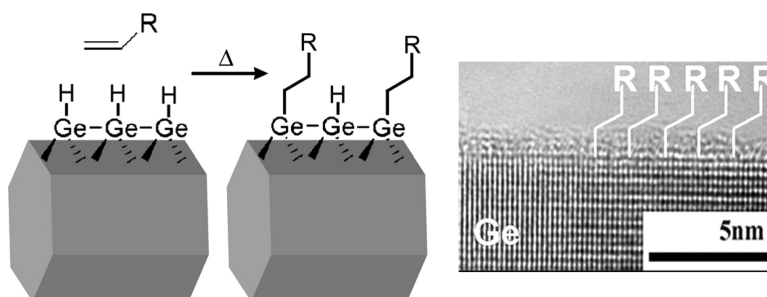


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Chemical Surface Passivation of Ge Nanowires

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Abstract: Surface oxidation and chemical passivation of single-crystal Ge nanowires with diameters ranging between 7 and 25 nm were studied. The surface chemistry differs significantly from that of well-studied monolithic atomically smooth single-crystal substrates. High-resolution Ge 3d XPS measurements reveal that Ge nanowires with chemically untreated surfaces exhibit greater susceptibility to oxidation than monolithic Ge substrates. Multiple solution-phase routes to Ge nanowire surface passivation were studied, including sulfidation, hydride and chloride termination, and organic monolayer passivation. Etching in HCl results in chloride-terminated surfaces, whereas HF etching leads to hydride termination with limited stability. Exposure to aqueous ammonium sulfide solutions leads to a thick glassy germanium sulfide layer. Thermally initiated hydrogermylation reactions with alkenes produce chemically stable, covalently bonded organic monolayer coatings that enable ohmic electrical contacts to be made to the nanowires.

Introduction

One-dimensional (1D) nanomaterials, such as nanotubes and nanowires, have been proposed for use in numerous applications due to their unique optical, mechanical, and electrical properties.^{1–4} In the context of both the processing and properties of nanowires, a detailed understanding of their surface chemistry is required to meet these technological expectations. For example, the chemical and electronic stability of nanowire surfaces is particularly important for applications such as nanowire-based computing and logic elements and chemical and biological sensors, which require direct interfacing with their surrounding environment.^{5–8} Nanowire dispersibility in a variety of solvents is also critical for the processing of these materials and their implementation as “building blocks” in device structures assembled using various approaches such as directed deposition from solution, spin-coating, inkjet printing, imprint lithography and stamping, as well as mechanical manipulation. While there has been significant effort focused on covalent chemical modifications of carbon nanotube surfaces^{9–12} there

have been very few reports on the chemical modification of semiconductor nanowire surfaces.^{13–15}

Germanium (Ge) nanowires produced by gold nanocrystal-seeded SFLS (supercritical fluid–liquid–solid) synthesis^{16,17} provide a powerful model experimental system for studying the surface passivation chemistry of nanostructures. The nanowires are crystalline with few dislocation defects, and their surfaces are relatively smooth with well-defined interfaces. They can be characterized using surface science techniques, such as X-ray photoelectron spectroscopy (XPS), and it is straightforward to perform high-resolution electron microscopy imaging of the semiconductor interface—a difficult and time-consuming task for monolithic substrates and porous semiconductors.

The surface chemistry of germanium’s congener, silicon (Si), is very well studied—perhaps more than any other element in the periodic table—because of its critical importance in the microelectronics industry. Silicon forms a very stable oxide and can be chemically passivated with a variety of organic species. The reaction mechanisms have been extensively investigated for solution-phase and vapor-phase oxidation, metallization, nitridation, and organic monolayer passivation of both the well-characterized Si surfaces of monolithic single-crystal substrates and the poorly characterized surfaces of porous Si.¹⁸ The situation for Ge is quite different. While many similarities exist between the surface properties of these two materials, there are some profound differences, specifically with respect to their oxide interfaces. Unlike the chemically and electronically stable Si/SiO₂ interface, the Ge/GeO_x interface is troubled with

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unfavorable electrical properties and poor chemical stability: for example, GeO_x dissolves in water to form $\text{Ge}(\text{OH})_4$ and does not provide the effective electrical tunnel barrier needed for transistor applications.^{19,20}

In this paper we report a comprehensive investigation of the surface chemistry of Ge nanowires. The inherent chemical stability of “bare” nanowires and oxidized nanowires in the presence of ambient atmosphere and water is determined using XPS. Various pathways for chemical passivation are then developed and explored, including sulfide-, chloride-, and hydride-terminated surfaces. Finally, methods for surface passivation by the formation of covalently bonded organic monolayers are developed.

Experimental Details

All chemicals were used as received from Aldrich, except for diphenyl germane (DPG), which was purchased from Gelest. DPG, hexane, 1-hexene, 1-pentyne, 1,3-cyclobutadiene, 2-methyl-1,3-butadiene, 1-octene, 1-dodecene, 1-dodecyne, methyl-MgBr, and octyl-MgBr were purchased anhydrous, packaged under nitrogen, and stored under nitrogen until use.

Ge Nanowire Synthesis. The Ge nanowires used in this study were synthesized by a gold (Au) nanocrystal-seeded process in supercritical hexane using the organogermane precursor, DPG, as the Ge source, as described in detail elsewhere.^{16,17} Dodecanethiol-coated Au nanocrystals are synthesized using room-temperature two-phase arrested precipitation. The Au nanocrystals are then injected along with DPG into a high-temperature, high-pressure continuous flow reactor at 385 °C and 8 MPa. The resulting nanowires are single crystals with few crystallographic defects. They exhibit a predominant $\langle 110 \rangle$ growth direction with diameters ranging from 7 to 25 nm.

Surface Passivation. Different strategies for chemically modifying the nanowire surfaces were explored that required reactions both outside and inside the reactor. For nanowire surface chemistry modifications outside of the supercritical fluid reactor, nanowire samples were deposited onto inert Teflon or Au-coated Si substrates. Wet and dry oxidation was investigated by submersion in deionized water or exposure to a dry air atmosphere. Sulfidation experiments were carried out using nanowires etched in 2% HF for 5 min. The nanowires were submersed in a 4 vol % $(\text{NH}_4)_2\text{S}$ aqueous solution at 60 °C for 20 min, followed by a methanol rinse. Chloride- and hydride-terminated nanowires were produced by immersion in aqueous 5% HCl or 5% HF for 5 min, respectively. Organic monolayer passivation was achieved by exposure to alkene, alkyne, or diene species at elevated temperature in the supercritical fluid reactor. In these reactions, the nanowires were first synthesized, and then the reactor was flushed with excess anhydrous supercritical hexane ($T = 385$ °C and $P = 8$ MPa) to remove carbonaceous contamination and reaction byproducts. After flushing with supercritical hexane, the reactor was cooled to 220 °C before injecting the alkene, alkyne, or diene species. For in situ thiol passivation, the reactor was cooled to 80 °C before injecting 1-octanethiol. The surface treatment was allowed to proceed for ~ 2 h before flushing the system once more with hexane. Prior to characterization, the nanowires were rinsed with excess hexane, chloroform, and 2-propanol to remove physisorbed organic species. All samples were stored under an inert nitrogen atmosphere (< 1 ppm O_2).

Characterization. The nanowires were characterized by high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (HRSEM, LEO1530), Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). HRTEM images were acquired from nanowires deposited over a

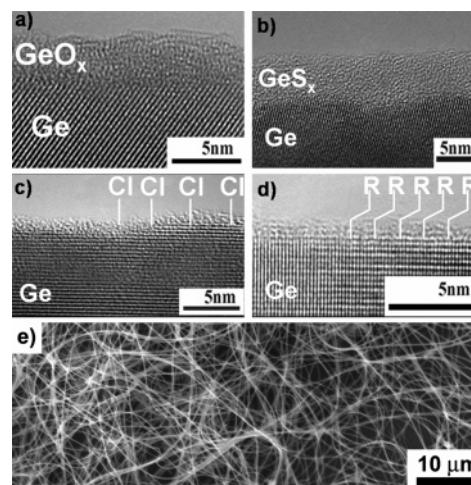


Figure 1. High-resolution TEM images of (a) untreated Ge nanowire surface showing the nonuniform oxide and carbonaceous contamination coating and Ge nanowires with (b) sulfide coating, (c) chloride termination, and (d) covalently bonded hexyl monolayer termination. (e) High-resolution SEM image of Ge nanowires.

vacuum background on lacey carbon TEM grids using a JEOL 2010F field-emission TEM operating at 200 kV. Spatially resolved elemental characterization was obtained using energy-dispersive X-ray spectroscopy (EDS, Oxford INCA) and electron energy-loss spectroscopy (EELS, Gatan Enfina DigiPEELS) on TEM samples. HRSEM imaging was performed using a LEO 1530 field-emission gun SEM. XPS data were acquired using a Physical Electronics XPS 5700 equipped with a monochromatic Al X-ray source (Al $K\alpha$, 1.4866 keV). Extensive efforts were taken to avoid atmospheric exposure and unintentional oxidation of the ~ 0 h XPS sample, and exposure of those nanowires to the atmosphere was no greater than 10 min. FTIR spectra were obtained on a Thermo Mattson Infinity Gold FTIR. FTIR spectra of nanowires with hydrogermylated surfaces were acquired in transmission mode from nanowires deposited on Si substrates. FTIR spectra reported for HF-etched nanowires were acquired in reflectance mode (54°) from Ge nanowires on a Au-coated Si substrate. For the electrical measurements, Pt metal electrodes were deposited by electron-beam-assisted metal chemical vapor deposition (CVD) on a FEI Strata DB235 dual-beam SEM/FIB to contact individual nanowires drop cast from a toluene dispersion onto an oxidized Si wafer. The Pt contact lines were connected to gold contact pads patterned using electron-beam lithography. The electrical measurements were performed under nitrogen using a Karl Suss PM5 electrical probe station connected to an Agilent 4145B semiconductor parameter analyzer.

Results and Discussion

Ge Nanowire Surface Oxidation. The crude product isolated from the reactor consists of Ge nanowires with a thin oxide layer coated by a thicker layer of carbonaceous contamination.¹⁶ The thick carbonaceous layer is readily stripped from the surface by either flushing the reactor with supercritical hexane prior to isolating the product or rinsing the nanowires with organic solvents such as hexane or chloroform after removal from the reactor. The remaining “native” germanium suboxide (GeO_x) layer has a typical thickness of 3–4 nm, as shown in Figure 1a, with a residual thin hydrocarbon film detectable by EDS under the TEM. Due to the high GeO_x solubility in aqueous solutions, it can be removed by exposure to dilute HCl or HF acid solutions or even pure water.²⁰ However, acid treatment is much more effective at removing the oxide layer than submersion in pure water, as the water treatment leaves a residual oxide on the surface with nonuniform thickness, possibly as a result

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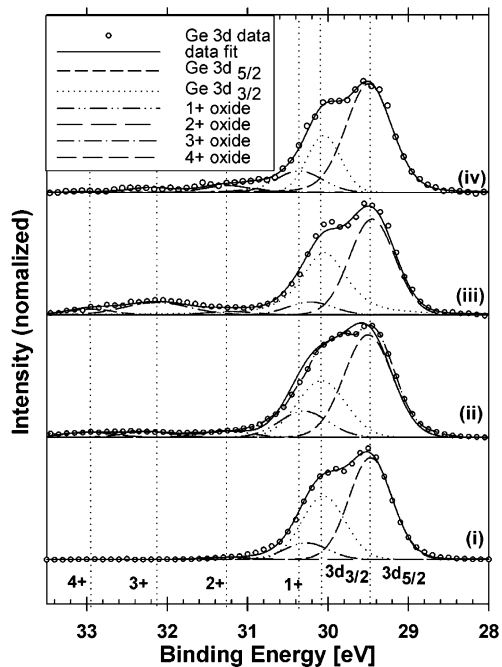


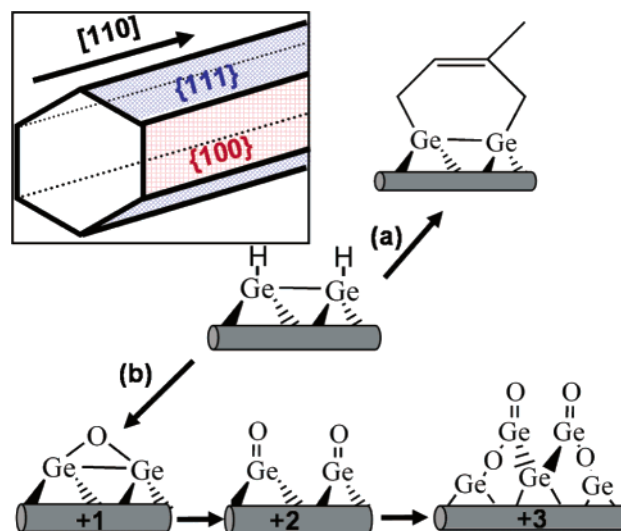
Figure 2. High-resolution Ge 3d XPS of Ge nanowires: (i) immediately after removal from reactor; (ii) after exposure to dry air for 168 h; (iii) after immersion in water for 30 min; (iv) after annealing in nitrogen at 300 °C after immersion in water. Spectral deconvolution was carried out as described in ref 22. (An expanded view of curve iv with a clearer view of the peak contributions from the four Ge oxidation states can be found in the Supporting Information).

of the residual thin carbonaceous layer that could shield the etching in some places or subtle variations in surface roughness that become exacerbated during the corrosion process.

From a device and applications standpoint, the germanium oxide that forms in the presence of water and air is not at all desirable. In addition to the poor chemical stability discussed below, the Ge/GeO_x interface is plagued by a high density of fast and slow surface states²¹ and poor electronic passivation that results in large gate leakage currents. However, the oxidation chemistry that occurs on Ge nanowire surfaces deserves attention. The oxidation of the Ge surfaces is relatively complex and has been found to depend on the oxidation environment and the crystallographic orientation of the Ge surface.²² Almost nothing is currently known about the corrosion processes that occur at the surface of single-crystal semiconductor nanowires. In the context of developing effective surface passivation strategies of semiconductor nanowires, the underlying oxidation processes must be understood in order to understand the effects of chemical treatments.

High-resolution Ge 3d photoelectron spectroscopy of Ge nanowires provides information about the oxidation states of the Ge surface after exposure to various chemical environments. Schmeisser et al.²² studied the Ge 3d photoemission spectra of oxidized Ge(100) and Ge(111) surfaces and isolated four surface oxidation states with a core level shift of 0.85 eV per Ge–O bond or per oxidation state (Ge is octahedrally coordinated in the +4 oxidation state with each O shared by two Ge atoms). Figure 2 shows Ge 3d photoemission spectra obtained from Ge nanowires exposed to various oxidative environments. The XPS

Scheme 1. Possible Surface Reactions on the Ge Nanowire Surface^a



^a (a) Thermally initiated hydrogermylation reaction of Ge–H-terminated surface with 2-methyl-1,3-butadiene. (b) Surface oxidation via either wet or dry processes resulting in 1+, 2+, and 3+ Ge oxidation states. (Inset) Expected {111} and {100} surface faceting for a single-crystal nanowire elongated in the $\langle 110 \rangle$ growth direction.

spectra were deconvoluted to determine the extent of oxidation and the Ge oxidation state. The Ge 3d peak exhibits a 3d_{3/2} and 3d_{5/2} spin–orbit splitting of 0.585 eV with an intensity ratio of 0.58. The Ge¹⁺ oxidation state exhibits a peak contribution shifted by 0.85 eV.²² The Ge nanowires with ~0 h of atmospheric oxygen exposure exhibit a measurable amount of oxide on the surface with Ge in the +1 oxidation state only. Limited exposure to oxygen (in a dry atmosphere) leads to surface oxidation. Prolonged exposure to oxygen increases the extent of oxidation with the appearance of Ge²⁺ and Ge³⁺ species along with an increase in the amount of Ge¹⁺ species (evident from the Ge¹⁺ peak intensity relative to the 3d_{3/2} and 3d_{5/2} peaks). In contrast to Si, Ge is known to form an oxide with a stable +2 oxidation state, which corresponds to either a Ge=O double bond geometry (see Scheme 1) or two bridge-bonded oxygen atoms.²² After approximately 1 week of exposure to a dry atmosphere environment, oxidation of the Ge nanowire surface becomes self-limiting as no noticeable changes in the oxidation states in the nanowire XPS profiles are observed with continued exposure to atmospheric oxygen. HRTEM images of nanowires subjected to dry atmosphere for 1 week or longer typically show oxide thicknesses ranging from 3 to 4 nm.

In contrast to Ge nanowires oxidized in a dry environment, nanowires immersed in deionized water show a large amount of Ge³⁺ species in the XPS spectra—in nearly equal proportion to the Ge¹⁺ peak. Ge²⁺ species also appear to be present on nanowire surfaces oxidized in a wet environment in nearly the same proportion as those oxidized under dry conditions; however, in HRTEM images of the interface, the overall oxide thickness of wet oxidized samples is thinner. Since GeO_x is soluble in water, one might anticipate that all of the Ge³⁺ species would be immediately etched from the surface after forming; however, this does not appear to be the case, and a residual GeO_x layer remains after removing the nanowires from water. The formation of the 3+ oxidation state requires that more Ge bonds break, meaning that the oxidation process must be more extensive (see Scheme 1). Oxidation of Ge nanowires to Ge³⁺

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occurs readily in water but not in dry atmosphere. Theoretical work by Johnson and Panas²³ showed that the reaction between water and the two possible Ge^{2+} chemical configurations of $\text{Ge}=\text{O}$ and double bridge-bonded $\text{Ge}-\text{O}-\text{Ge}$ is much more thermodynamically favorable for $\text{Ge}=\text{O}$ than $\text{Ge}-\text{O}-\text{Ge}$ species, which provides an indication that the Ge^{2+} species on the nanowires exposed to water are chemically in the form of $\text{Ge}=\text{O}$ (as depicted in Scheme 1).

Annealing oxidized bulk $\text{Ge}(111)$ and $\text{Ge}(100)$ with Ge^{3+} surface-exposed species at 300 °C for 15 min in ultrahigh vacuum (UHV) has been shown by Schmeisser et al.²² to eliminate the Ge^{3+} species, with a shift in oxidation state to favor the Ge^{2+} species. Thermal annealing of water-oxidized Ge nanowires at 300 °C on a hot plate in a nitrogen glovebox (<1 ppm O_2) nearly eliminates Ge^{3+} oxide species and leaves the Ge^{1+} species. A very small amount of Ge^{2+} species is also present in the spectra after annealing. The predominance of Ge^{1+} species sharply contrasts the observed enrichment in Ge^{2+} on Ge (111) and Ge (100) surfaces annealed in UHV under controlled O_2 environments.²² Furthermore, the oxidation states observed via wet and dry oxidation of the nanowires differ significantly from those observed on Ge (111) and (100) surfaces by Pabhakaran and Ogino.²⁴ This difference could be the result of nanowire surface curvature or surface roughness favoring the formation of single-bridge-bonded $\text{Ge}-\text{O}-\text{Ge}$ as shown in Scheme 1, as opposed to the Ge^{2+} (i.e., $\text{Ge}=\text{O}$) species predominantly observed on bulk single-crystal surfaces.

The native GeO_x with octahedral coordination does not provide suitable chemical or electronic passivation. In contrast, Gregory et al.²⁵ reported the formation of a tetrahedrally bonded Ge oxide, which they found to be stable in both water and HF. We attempted to form such a layer on the Ge nanowires; however, we found that the chemical processing steps were too severe—for example, using their 40% HF and 30% H_2O_2 etching solution diluted 100 times dissolved the nanowires nearly immediately.

Sulfidation. As an alternative to oxygen, higher chalcogens such as S or Te have been proposed as surface termination candidates for Ge.^{26,27} Under UHV conditions, LEED and XPS results have shown that S adsorbs to $\text{Ge}(100)$ in a $\text{S}/\text{Ge}(100)-(1 \times 1)$ bridge-bonded form that saturates all dangling bonds.²⁶ Some literature reports have suggested that S termination of Ge (100) under UHV conditions might also be extended to the aqueous sulfidation of Ge (100) surfaces.²⁸ Other results by Lyman et al.,²⁹ however, indicated that the aqueous treatment of Ge (001) surfaces results in a thin GeS_x layer. We explored sulfide passivation of Ge nanowires using similar reaction conditions as those reported in the literature.^{28,29}

Figure 1b shows the surface of a sulfide-treated Ge nanowire imaged by TEM. The nanowire exhibits a 5 nm thick amorphous GeS_x coating. XPS data obtained for the sulfide-treated Ge

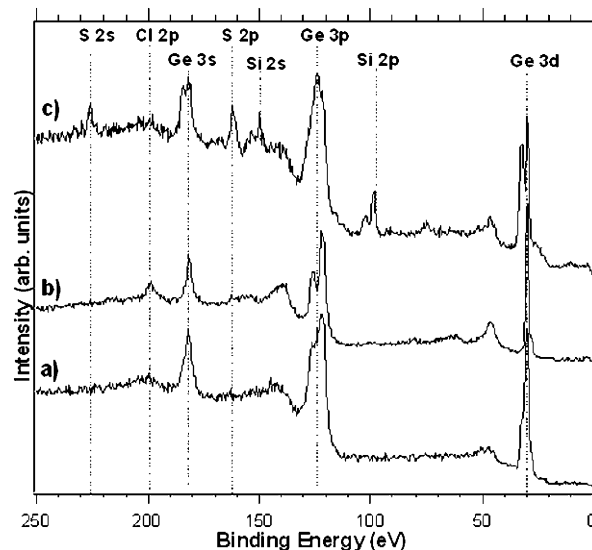


Figure 3. XPS of Ge nanowires: (a) before chemical surface modification, (b) after chlorination with HCl, and (c) after sulfidation with $(\text{NH}_4)_2\text{S}$.

nanowires (see Figure 3c) show the S 2s and S 2p peaks as well as a splitting of the Ge 3d peak indicative of the presence of $\text{Ge}-\text{S}$ bonds. The presence of S in the surface layer was confirmed by EDS, with the notable absence of O. In contrast to the sulfide monolayers²⁸ or the very thin glassy layers²⁹ observed to form on $\text{Ge}(100)$ surfaces, the GeS_x layer on the nanowires is relatively thick, which is unfavorable for electrical device applications. Lyman et al.²⁹ attributed the formation of the amorphous GeS_x surface layer in their experiments to a high step density or miscut Ge (100) substrates. The Ge nanowires obviously exhibit a different surface structure than the monolithic $\text{Ge}(100)$ substrates due to their severe surface curvature and faceting, which appears to make them more susceptible to sulfidation.

To provide better chemical stability using $\text{Ge}-\text{S}$ surface chemistry, Han and co-workers^{30,31} examined the formation of alkanethiol monolayers on H-terminated $\text{Ge}(111)$ surfaces. They formed self-assembled monolayers by exposing H-terminated Ge surfaces to alkanethiol solutions at room temperature. The monolayers were found to be stable up to 450 K. Our attempts to form alkanethiol monolayers on Ge nanowires by similar methods to those used by Han et al.³⁰ were not successful, presumably due to the poor chemical stability of H-terminated Ge nanowires relative to H-terminated Ge substrates (see discussion below). However, using an alternate approach—exposure to octanethiol at 80 °C directly in the reactor after synthesis—did successfully produce organic monolayers on the nanowires. Figure 4 shows an HRTEM image of the surface of a Ge nanowire that had been treated with octanethiol along with an FTIR spectrum of the nanowires, which shows the presence of the hydrocarbon layer on the nanowires. It appears that prevention of surface oxidation (i.e., exposure to water or oxygen) is critical to the formation of alkanethiol monolayers on the Ge nanowires.

Chlorination/Hydrogen Termination. The chlorination of $\text{Ge}(111)$ surfaces was first reported in 1962 by Cullen et al.,³²

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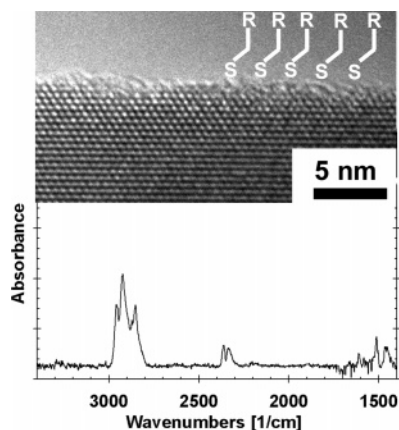


Figure 4. (Top) HRTEM image of a Ge nanowire treated with 1-octanethiol. Notice the absence of the surface oxide layer that is characteristic of untreated nanowires. (Bottom) FTIR spectra of octanethiol-exposed Ge nanowires. The absorbance peaks correspond to the asymmetric and symmetric methylene stretching modes— $\nu_a(\text{CH}_2) = 2928 \text{ cm}^{-1}$ and $\nu_s(\text{CH}_2) = 2855 \text{ cm}^{-1}$ —and to the asymmetric in-plane and symmetric stretching modes of the terminal methyl groups— $\nu_a(\text{CH}_3, \text{ip}) = 2954.5 \text{ cm}^{-1}$ and $\nu_s(\text{CH}_3, \text{-FR}) = 2871 \text{ cm}^{-1}$ —of the adsorbed hydrocarbon species. The peaks in the $2300\text{--}2400 \text{ cm}^{-1}$ range result from background CO_2 .

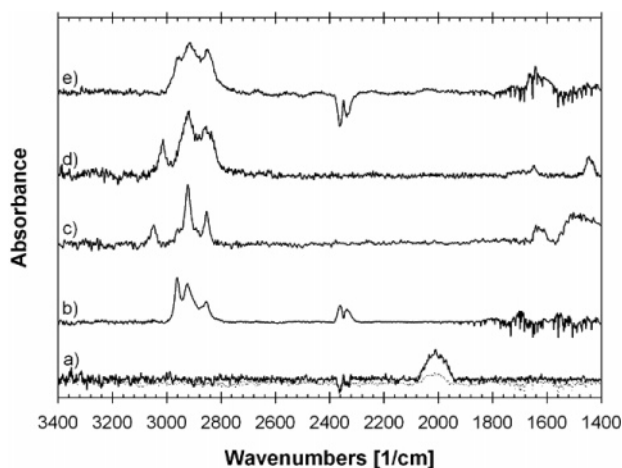


Figure 5. FTIR spectra of Ge nanowires (a) after immersion in 5% HF for 2 min (the dotted line shows the spectrum of the same sample after 20 min of atmospheric oxygen exposure) and after treatment in the reactor at $220 \text{ }^\circ\text{C}$ with (b) 1-hexene, (c) 1-pentyne, (d) 1,3-cyclobutadiene, and (e) 2-methyl-1,3-butadiene as discussed in the text.

who exposed an oxidized Ge(111) surface to HCl gas at $\sim 90 \text{ }^\circ\text{C}$. The HCl treatment results in the removal of $\sim 200 \text{ nm}$ of Ge in the form of GeCl_4 gas to leave a chlorinated Ge surface. Obviously this chlorination procedure is far too aggressive to be applied to $\sim 10 \text{ nm}$ diameter Ge nanowires. We applied a milder aqueous approach developed by Lu³³ that is more suitable for chlorinating Ge nanowires. The Ge nanowires are soaked in 5% HCl for 5 min at room temperature and dried under nitrogen. TEM images of chlorinated Ge nanowire surfaces, such as that shown in Figure 1c, reveal clean and abrupt Ge surfaces with near complete removal of the amorphous surface oxide layer. XPS data also verified the chloride termination, with the appearance of the Cl 2p signal (Figure 3b) and the absence of oxide signal in the high-resolution Ge 3d spectra. (see Figure 6a).

The nanowires can also be hydride-terminated by immersing Ge nanowires in 5% HF for 2 min. On the basis of thermody-

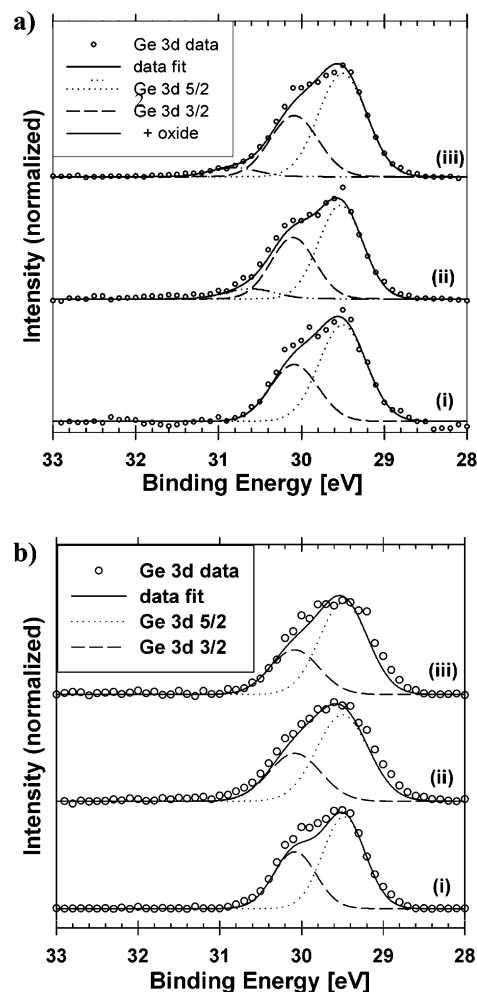


Figure 6. Ge 3d XPS of Ge nanowires. (a) Nanowires passivated with isoprene: (i) after HCl etching; exposed to isoprene (ii) before and (iii) after 10 h of immersion in deionized water. Note that the weak Ge^{2+} signal present in curve ii does not increase after water exposure (curve iii). (b) Nanowires passivated with octanethiol: (i) directly after thiol treatment, (ii) after 1 week of dry atmosphere exposure, and (iii) after 15 h of exposure to deionized water. Note the absence of oxide characteristic peaks.

namic considerations, exposure of a Ge surface to HF should result in F termination, since the Ge–F bond (485 kJ/mol) is stronger than the Ge–H bond (321 kJ/mol).²⁰ However, Choi and Buriak³⁴ demonstrated that kinetic factors dominate the formation of the surface species. FTIR spectra of HF-treated nanowires (Figure 5a) showed broad vibrations at 2010 cm^{-1} , characteristic of GeH_x . However, the stability of this hydride layer is limited to only a few minutes in the presence of oxygen, as evidenced by the absence of the $\nu(\text{GeH}_x)$ vibrational mode after 20 min of exposure to dry atmosphere. In contrast, hydride-terminated bulk Ge(100) surfaces are stable in air for up to 1 h.³⁴ The initial stages of wet and dry oxidation of H-terminated Si surfaces were investigated by Niwano et al.,³⁵ who suggested that the faster oxidation in water relative to dry air is due to substitution of surface hydrogen by –OH groups whereas the Si–H bond appeared more inert to oxygen exposure. Similar oxidation reactivities are expected for H-terminated Ge surfaces.

Alkylation via Hydrogermylation. Our first attempts at surface alkylation of the Ge nanowires utilized a two-step

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chlorination–alkylation approach. We expected that the surface-chlorinated Ge nanowires could provide a reactive template for organic monolayer passivation using a Grignard reaction with species such as octyl-MgBr, as demonstrated by Cullen et al.³² and more recently He et al.³⁶ for the alkylation of bulk Ge surfaces. While this two-step process was somewhat successful in producing monolayer passivation of the Ge nanowires, we found the direct thermally initiated hydrogermylation to be much more efficient and effective. Halogenation/alkylation³⁷ and hydrosilylation reactions^{38,39} on hydride-terminated Si surfaces have been well-studied for the formation of organic monolayers on Si surfaces. Buriak and co-workers³⁴ extended these methods to Ge, forming various organic monolayers on hydride-terminated Ge surfaces via either UV-initiated, Lewis-acid-mediated, or thermally initiated hydrogermylation reactions involving the insertion of unsaturated C=C bonds as the reactive species into Ge–H bonds at the surface forming Ge–C bonds as illustrated in Scheme 1. Among these three strategies, thermally initiated hydrogermylation is most easily integrated with the supercritical fluid nanowire synthesis, since the nanowire materials can easily be subjected to the passivation reaction without intermediate oxygen exposure or HF etching. The Ge nanowires used in this study predominantly exhibit the $\langle 110 \rangle$ growth direction and are characterized by $\{111\}$ and $\{100\}$ faceted surfaces, as recently experimentally verified by cross-sectional HRTEM imaging of Si⁴⁰ and Ge nanowire cross-sections.⁴¹ A recent STM study on Si nanowire surfaces by Lee and co-workers⁴² demonstrated that these facets undergo surface reconstruction, resulting in Si=Si dimer formation. Similarly, Ge=Ge dimers, which are also present in the surface reconstructions of bulk Ge $\{111\}$ and $\{100\}$ surfaces, may initially form on the Ge nanowire surface but presumably quickly convert to H-terminated surfaces in the supercritical fluid environment. Scheme 1 shows the example of the thermally initiated hydrogermylation reaction between 2-methyl-1,3-butadiene and the surface-bound Ge–H bonds.

The surface passivation was carried out in the reactor after completing the nanowire synthesis. The Ge nanowires settle on a native oxide-coated Si substrate placed inside the reactor. By first flushing with excess supercritical hexane, any surface contamination of reaction byproducts that coats the nanowires is removed. The reactor is cooled to ~ 220 °C before injecting the appropriate hydrocarbon species for the thermally initiated hydrogermylation reaction. Figure 1d shows a TEM image of the surface of 1-hexene-treated Ge nanowires. The nanowires exhibit clean abrupt surfaces—in sharp contrast to nanowires removed from the reactor without surface passivation. EDS and EELS (electron energy-loss spectroscopy) did not show the presence of oxygen; however, these techniques are not sensitive enough to detect very small amounts of O. High-resolution Ge 3d XPS spectra revealed a weak Ge¹⁺ signal, suggesting that

some oxidation still occurs either in the reactor or after removing the product from the reactor, perhaps as a result of incomplete surface termination. However, XPS (Figure 6a) revealed that further exposure to air *and even water* did not result in further oxidation.

Nanowires can be surface-treated with alkene, alkyne, and diene species. Figure 5b and c show the FTIR spectra of Ge nanowires coated with hexyl- and pentenyl-monolayers, respectively, formed by hydrogermylation reaction with hexene and pentene. The FTIR spectra of Ge nanowires with pentenyl-monolayer termination (Figure 5c) show the alkene C–H stretch at ~ 3050 cm⁻¹, whereas the hexyl-monolayer (Figure 5b) exhibits only the saturated $\nu(\text{CH}_2)$ stretches, indicating that the reaction of Ge nanowire surfaces with pentyne involves only one double bond in the organic molecule. The FTIR spectra of the Ge nanowires reacted with 1,3-cyclobutadiene and 2-methyl-1,3-butadiene in Figure 5d and e show monolayers with FTIR spectra similar to those obtained in UHV studies Diels–Alder reaction on single-crystal Ge surfaces.^{43,44} In UHV experiments the unsaturated bonds react with surface-bound Ge=Ge dimers via [2+2] or [4+2] cycloaddition reactions. The similarity of the FTIR spectra of reactions involving dienes in this work to the ones reported in UHV experiments^{43,44} suggests that the hydrogermylation reactions on Ge–H-terminated surfaces involve similar rearrangement of the double bonds of the surface-bound molecule.

The surface-coated Ge nanowires are much more chemically stable than the untreated nanowires. Figure 6a shows that exposure of the isoprene-passivated nanowires to oxidative conditions similar to those discussed above for the untreated nanowires did not lead to the formation GeO_x with higher oxidation states, although the presence of a small amount of Ge¹⁺ could not be excluded. In comparison to isoprene-passivated nanowires, octanethiol-treated nanowires exhibited even greater resistance to surface oxidation and the characteristic oxide peaks in XPS were absent after 15 h of direct submersion in water (see Figure 6b). Bodlaki et al.⁴⁵ recently reported on the ambient stability of chemically passivated bulk Ge(111) surfaces and noted significantly more robust surface passivation to reoxidation from alkyl-terminated surfaces compared to surfaces etched with HCl or HF. We directly compared the chemical stability of the organic monolayer-coated Ge nanowires treated with 2-methyl-1,3-butadiene with untreated surface-oxidized wires by submersing them side-by-side in deionized water, as shown in the photograph in Figure 7. The Ge nanowires were drop cast onto a gold-coated substrate (yellow background), making a brown film. The quality of the deposited nanowire film is much better for the hydrophobic surface-passivated nanowires because they are much more dispersible in the organic solvent used to cast the nanowires on the substrate. The substrates were fully submersed in deionized water, as shown in Figure 7a and c. The surface-oxidized Ge nanowires undergo rapid degradation in the aqueous environment, dissolving after only 120 min (Figure 7d). The oxidizing environment combined with the high solubility of GeO_x in water results in rapid nanowire corrosion. In sharp contrast, the organic

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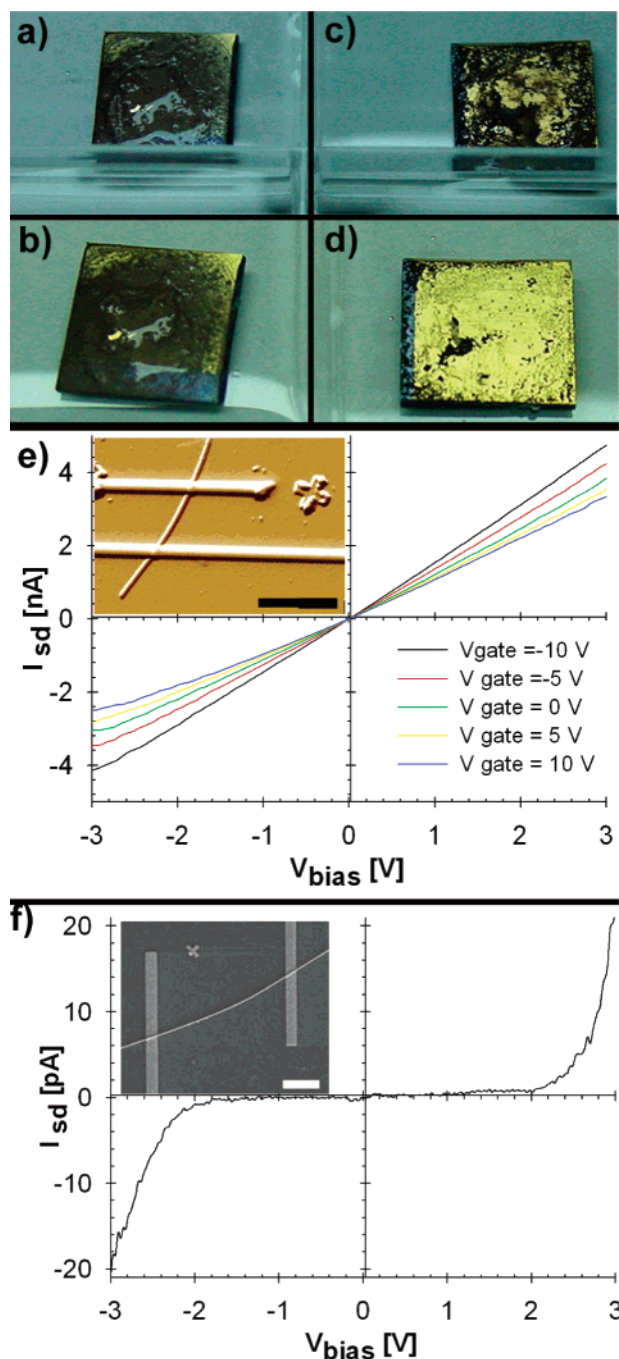


Figure 7. (a–d) Photographs of gold-coated substrates with a brown film of Ge nanowires. The nanowires were deposited on the substrate with a surface density of ~ 2 mg/cm² with either (c, d) untreated surfaces or surfaces treated with (a, b) 2-methyl-1,3-butadiene. The nanowires were immersed in deionized water. The images in a and c show the nanowires immediately after exposure to water. After 120 min under water, the Ge nanowires with untreated surfaces (d) have dissolved whereas the nanowires with organic monolayer passivation (b) are still present. (e, f) Room-temperature current–voltage measurements of (e) a freshly HCl-etched Ge nanowire and (f) an HCl-etched Ge nanowire after 24 h of exposure to dry air contacted with Pt electrodes deposited by e-beam assisted CVD. The fresh HCl-etched nanowires form ohmic Pt/nanowire contacts, whereas the oxidized nanowire exhibits significant rectification due to the Schottky barrier at each metal contact. (Insets in e and f) AFM and SEM images of the devices (with 2 μ m scale bars).

monolayer-coated Ge nanowires do not visibly decompose in the aqueous environment, as shown in Figure 7b, an image obtained after 10 h of water exposure. Most convincingly, high-resolution Ge 3d XPS data obtained from the isoprene-treated

samples after water immersion show amounts of minimal oxidation (see Figure 6a) with a complete absence of the Ge³⁺ oxidation state.

We also investigated the effect of the surface modification on the ability to form low-resistance electrical contacts to the Ge nanowires. Ge nanowires interfaced immediately after HCl etching with Pt contacts deposited by electron-beam-assisted metal CVD exhibit linear current–voltage transport with a p-type gate effect (see Figure 7e). In contrast, HCl-etched Ge nanowires exposed to the atmosphere for ~ 24 h prior to contacting with e-beam lithographically defined electrodes exhibit electrical transport behavior dominated by Schottky barriers at the contacts (see Figure 7f). Nanowires without chemical surface treatment obtained from the crude synthetic product exhibit *massive* contact resistance, and no measurable electrical current can be passed through the nanowire.

Conclusions

Although the Ge nanowires are highly sensitive to oxidation and corrosion when exposed to oxygen and water, organic monolayers can be chemisorbed to the surfaces of Ge nanowires for chemical passivation and stabilization. We found that the most effective surface treatment used in combination with the SFLS nanowire synthesis was the thermally initiated hydrogermylation approach. Alkenes, alkynes, and dienes are suitable monolayer precursors. Coating the Ge nanowires with these species left abrupt, clean nanowire interfaces. The nanowires are chemically robust and stable, even when immersed in water. Without surface passivation, the nanowires oxidize to form a suboxide, consisting mostly of Ge¹⁺ and some Ge²⁺ species when exposed to air and mostly Ge³⁺ and Ge¹⁺ when immersed in water. Passivation based on S through treatment with (NH₄)₂S did not yield robust well-characterized surface layers, with S penetrating into the Ge nanowires to form a thick GeS_x layer. Thiol passivation on HF-etched nanowires led to incomplete monolayer coverage, while direct postsynthesis thiol treatment in the reactor formed a well-defined monolayer-terminated surface. H- and Cl-terminated Ge nanowires also exhibited sharp, clean interfaces; however, they were found to be very sensitive to oxidation, making the use of these species for subsequent surface reactions (such as alkylation using Grignard reactions) impractical. Control of the surface chemistry is necessary to eliminate degradation and is also vital to the materials performance in future applications, particularly in the case of electronic applications, where good electrical contact between metal electrodes and nanowires is required. This study has shown that Ge nanowires can be chemically surface passivated using a few different routes to achieve stability under oxidative environments. Undoubtedly, rigorous control over organic monolayer chemistry on semiconductor nanowires will be a key requirement for future applications of these materials.

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Supporting Information Available: Magnified view of the XPS Ge 3d peak deconvolution for oxidized Ge nanowires. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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