

Atomic imaging and modeling of H₂O₂(g) surface passivation, functionalization, and atomic layer deposition nucleation on the Ge(100) surface

Tobin Kaufman-Osborn, Evgueni A. Chagarov, and Andrew C. Kummel

Citation: *The Journal of Chemical Physics* **140**, 204708 (2014); doi: 10.1063/1.4878496

View online: <http://dx.doi.org/10.1063/1.4878496>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/140/20?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Dual passivation of GaAs (110) surfaces using O₂/H₂O and trimethylaluminum

J. Chem. Phys. **139**, 244706 (2013); 10.1063/1.4852155

Soft x-ray photoemission study of the thermal stability of the Al₂O₃/Ge (100) interface as a function of surface preparation

J. Appl. Phys. **114**, 084312 (2013); 10.1063/1.4819214

InAs MOS devices passivated with molecular beam epitaxy-grown Gd₂O₃ dielectrics

J. Vac. Sci. Technol. B **30**, 02B118 (2012); 10.1116/1.3678206

Atomic imaging of nucleation of trimethylaluminum on clean and H₂O functionalized Ge(100) surfaces

J. Chem. Phys. **135**, 054705 (2011); 10.1063/1.3621672

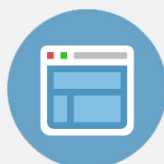
Atomic imaging of the monolayer nucleation and unpinning of a compound semiconductor surface during atomic layer deposition

J. Chem. Phys. **133**, 154704 (2010); 10.1063/1.3487737



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



Atomic imaging and modeling of $\text{H}_2\text{O}_2(\text{g})$ surface passivation, functionalization, and atomic layer deposition nucleation on the $\text{Ge}(100)$ surface

Tobin Kaufman-Osborn,¹ Evgueni A. Chagarov,² and Andrew C. Kummel^{1,2,a)}

¹*Materials Science and Engineering Program, University of California, San Diego, La Jolla, California 92093, USA*

²*Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093, USA*

(Received 23 January 2014; accepted 29 April 2014; published online 28 May 2014)

Passivation, functionalization, and atomic layer deposition nucleation via $\text{H}_2\text{O}_2(\text{g})$ and trimethylaluminum (TMA) dosing was studied on the clean $\text{Ge}(100)$ surface at the atomic level using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Chemical analysis of the surface was performed using x-ray photoelectron spectroscopy, while the bonding of the precursors to the substrate was modeled with density functional theory (DFT). At room temperature, a saturation dose of $\text{H}_2\text{O}_2(\text{g})$ produces a monolayer of a mixture of $-\text{OH}$ or $-\text{O}$ species bonded to the surface. STS confirms that $\text{H}_2\text{O}_2(\text{g})$ dosing eliminates half-filled dangling bonds on the clean $\text{Ge}(100)$ surface. Saturation of the $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Ge}(100)$ surface with TMA followed by a 200°C anneal produces an ordered monolayer of thermally stable $\text{Ge}-\text{O}-\text{Al}$ bonds. DFT models and STM simulations provide a consistent model of the bonding configuration of the $\text{H}_2\text{O}_2(\text{g})$ and TMA dosed surfaces. STS verifies the TMA/ $\text{H}_2\text{O}_2/\text{Ge}$ surface has an unpinned Fermi level with no states in the bandgap demonstrating the ability of a $\text{Ge}-\text{O}-\text{Al}$ monolayer to serve as an ideal template for further high- k deposition. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4878496>]

INTRODUCTION

To scale complementary metal-oxide-semiconductor (CMOS) devices, new materials with high carrier mobility have been investigated as potential replacements of the conventional silicon channel. Germanium has drawn significant interest due to its high electron and hole mobilities. However, Ge native oxide has very poor electronic properties due to a high interface trap density between Ge and Ge native oxide. This has caused challenges during MOSFET fabrication because most Ge based devices, even devices incorporating high- k gate oxide materials, have a GeO_x interfacial layer which can negatively affect device performance and/or increase equivalent oxide thickness (EOT).^{1,2}

In order to minimize the defect density that occurs at the interface between Ge and the gate oxide, a proper passivation method is required prior to gate oxide growth. Many different passivation methods have been studied on Ge including oxidation,^{3–7} sulfurization,^{8,9} nitridation,^{10–13} halogenation,^{14–16} and epitaxial growth of Si.^{17,18} These passivation methods must eliminate the dangling bonds on the Ge surface while remaining of angstrom thickness to minimize the EOT in a MOSFET. Not only should the passivation method satisfy the bonding requirements of atoms on the semiconductor surface, but it should also serve to functionalize the surface for subsequent atomic layer deposition (ALD) precursor deposition. ALD, in recent years, has gained significant attention as a superior method of depositing films of

uniform thickness while maintaining excellent compositional control.^{19–21} As this work describes, ALD gate oxide growth has the potential to bond to the Ge surface leaving an electrically passive and ideal interface which should not inhibit electrical performance of the full device. Recent work has shown promising results using $\text{H}_2\text{O}(\text{g})$ as a passivation and functionalization method to grow Al_2O_3 via ALD.²² However, $\text{H}_2\text{O}(\text{g})$ has some limitation in this application. A Ge surface dosed with a saturation dose of $\text{H}_2\text{O}(\text{g})$ leaves a large density of dangling bonds which act as interface traps, and $\text{H}_2\text{O}(\text{g})$ lacks thermal stability on Ge surfaces due to recombinative desorption at temperatures above 100°C .¹³

This study aims to improve on the water passivation mechanism by substituting $\text{H}_2\text{O}_2(\text{g})$. By selecting an oxidant with weak internal bonds, saturation of the Ge surface with reactive $-\text{OH}$ chemisorption species becomes much more effective. When a Ge surface is exposed to a saturation dose of $\text{H}_2\text{O}_2(\text{g})$, greater than 97% of surface Ge atoms become terminated with hydroxyl species which are more thermally stable than the chemisorptions species, $-\text{H}$ and $-\text{OH}$, on a $\text{H}_2\text{O}(\text{g})$ dosed Ge surface. By increasing the hydroxyl saturation coverage, trimethylaluminum (TMA) is able to nucleate in nearly every unit cell on the Ge surface, thereby resulting in a very low density of dangling bonds or interface trap states and a nearly ideal monolayer passivation and ALD nucleation layer. This study demonstrates for the first time the ability to electrically passivate all the dangling bonds on the Ge surface by combining an oxidant and reductant precursor while maintaining an electrically unpinned Fermi level thereby creating an ideal semiconductor-oxide interface.

^{a)} Author to whom correspondence should be addressed. Electronic mail: akummel@ucsd.edu

A very thin interfacial Al_2O_3 layer is known to improve device performance demonstrating the need for an high density and electrically passive monolayer of Al_2O_3 .^{23,24} In this study, the reaction of $\text{H}_2\text{O}_2(\text{g})$ only and $\text{H}_2\text{O}_2(\text{g}) + \text{TMA}$ on the $\text{Ge}(100)$ surface was studied at the atomic level using UHV experimental techniques. The thermal behavior of these surfaces was studied by annealing in UHV conditions, while the surface was analyzed between each step using *in situ* x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Atomic models of the reaction of $\text{H}_2\text{O}_2(\text{g})$ on a clean Ge surface and TMA on a $\text{H}_2\text{O}_2(\text{g})$ functionalized Ge surface were developed based on density functional theory (DFT). Both experimental and theoretical results are consistent with $\text{H}_2\text{O}_2(\text{g})$ and TMA ALD on the Ge surface producing an electrically passive ideal interface that serves as an excellent template for further high-k deposition.

EXPERIMENTAL DETAILS

Sb-doped n-type Ge wafers ($0.005\text{--}0.020\ \Omega\text{ cm}$, Wafer World Inc.) were diced into rectangular pieces ($12 \times 4.5\text{ mm}$) and degreased via ultrasonication with acetone, methanol, and deionized water then dried with N_2 gas. All samples were loaded into a UHV chamber with a base pressure of 2×10^{-10} Torr. The samples were cleaned via repeated sputter and anneal processes. The sputtering was performed using a $1\text{--}1.5\text{ keV}$ of Ar^+ ion beam (Model 1403 ion gun, Nonsequitur Technologies) with a beam current of $0.6\text{--}0.9\ \mu\text{A}$ and at an incident angle of 45° for 30 min, while the sample temperature was maintained at 500°C via direct heating to avoid the adsorption of trace oxygen on the Ge sample. Following each sputter process, the samples were annealed at 700°C for 20 min. The samples were STM imaged with atomic resolution to confirm a contaminant free surface thereby verifying surface cleanliness before proceeding with each experiment.

The samples were transferred into a separate “dosing” chamber with a base pressure of 2×10^{-8} Torr to react precursors with the Ge surfaces. $\text{H}_2\text{O}_2(\text{g})$ and TMA were dosed by back filling the dosing chamber with the precursor vapors without carrier gas. Both $\text{H}_2\text{O}_2(\text{g})$ and TMA exposures were controlled by throttling valves on the $\text{H}_2\text{O}_2(\text{g})$ and TMA. The reaction pressures were measured using a convectron gauge, and the exposure was estimated in Langmuirs ($1\text{ Langmuir (L)} = 1 \times 10^{-6}\text{ Torr} \cdot \text{s}$). All dosing was performed at RT. A 30% solution of $\text{H}_2\text{O}_2(\text{aq})$ was employed which is known to produce a vapor containing 2.67% $\text{H}_2\text{O}_2(\text{g})$ at 25°C .²⁵ Although glass and Teflon tubing was employed, some of the $\text{H}_2\text{O}_2(\text{g})$ may have decomposed in the tubing or on the walls of the stainless steel dosing chamber. Therefore, the reported doses for $\text{H}_2\text{O}_2(\text{g})$ are the upper limits of the actual doses of $\text{H}_2\text{O}_2(\text{g})$ reacting with the surface. Since all results in this study employed saturation doses, knowledge of the exact dose is not material.

After $\text{H}_2\text{O}_2(\text{g})$ or TMA exposure, the samples were transferred to the main chamber for thermal annealing. The samples were heated via direct heating using a controlled heating ramp rate of 1°C/s , while the sample temperature was mon-

itored by a pyrometer. *In situ* analysis of the topography of the sample surfaces was performed using a STM (LT-STM, Omicron Nanotechnology). All STM and STS data were obtained at RT in a UHV chamber with a base pressure of 1×10^{-11} Torr following each surface treatment. STM images were acquired using constant-current mode STM ($I_{\text{sp}} = 0.2\text{ nA}$) with an applied sample bias between -1.8 and -2.0 V . The electronic structure of the surfaces of the samples was measured using STS operating in variable- z mode using a modulation signal (0.1 V , 650 Hz) supplied by an external lock-in amplifier, while sweeping the sample bias from -1 to $+1\text{ V}$ or -1.5 to $+1.5\text{ V}$.

An *in situ* monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology) was employed to examine the surface elements and their relative intensities. The XPS was operated in constant analyzer energy mode with a pass energy of 50 eV and the line width of 0.1 eV using an $\text{Al K}\alpha$ source (1486.7 eV). The takeoff angle was 30° from the sample surface with an acceptance angle of $\pm 7^\circ$. Data and peak shape analysis was performed using CASA XPS v.2.3 using a Shirley background subtraction method. The relative XPS intensity of each core-level spectra ($\text{C } 1s$, $\text{Al } 2p$, and $\text{O } 1s$) was quantified by calculating the peak area divided by the XPS sensitivity factor.

COMPUTATIONAL DETAILS

All presented DFT simulations were performed with the Vienna *ab initio* simulation code (VASP) using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and projector augmented-wave (PAW) pseudopotentials (PPs).^{26–31} The choice of PBE functional and PAW PP was confirmed by parametrization calculations indicating good reproducibility of experimental lattice constants, bulk moduli, and cohesive energies for bulk crystalline Ge. The STM simulations were performed using the Tersoff–Hamann approach.^{32,33} The Ge slabs were built as $2 \times 2 \times 3$ supercell (96 atoms) using PBE-optimized Ge unitcell lattice constants. The three bottom Ge layers were permanently fixed in bulk-like positions, and bottom Ge atoms were passivated by two relaxed hydrogen atoms each to simulate continuous bulk. The Ge slabs with or without passivation layer were relaxed using conjugate-gradient algorithm at $5 \times 5 \times 1$ Gamma-centered K-point grid below force tolerance level of 0.05 eV/\AA .

RESULTS AND DISCUSSION

$\text{H}_2\text{O}_2(\text{g})$ passivation/functionalization of $\text{Ge}(100)$

An atomically flat, sputter, and anneal cleaned $\text{Ge}(100)$ sample is shown in Fig. 1(a) showing the two surface reconstructions that occur at RT on the clean $\text{Ge}(100)$ surface. The clean surface was dosed at RT with $2.25 \times 10^5\text{ L}$ of $\text{H}_2\text{O}_2(\text{g})$, a near saturation dose. In STM of Ge, reaction with $-\text{H}$, $-\text{OH}$, or $-\text{O}$ produces dark sites, and the residual unreacted dangling bonds appear bright.^{13,34} The $\text{H}_2\text{O}_2(\text{g})$ reacts with the $\text{Ge}(100)$ surface giving a coverage greater than 0.97 ML of dark sites as shown in Fig. 1(b).

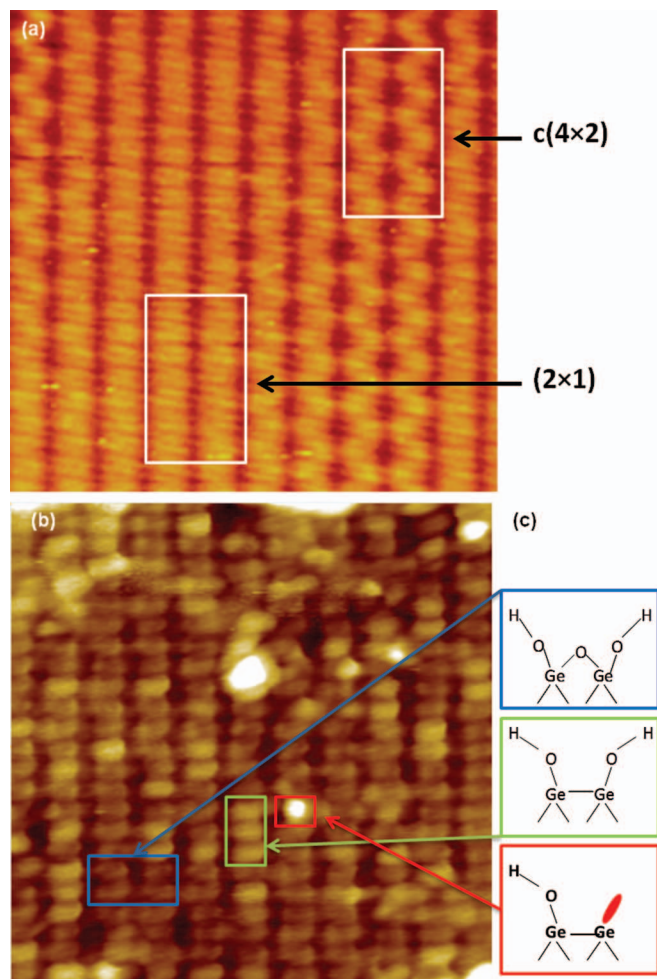


FIG. 1. STM image of clean and 2.25×10^5 L $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100). (a) Filled state STM image ($10 \times 10 \text{ nm}^2$, $V_s = -1.8 \text{ V}$, $I_t = 0.2 \text{ nA}$) of a clean Ge(100) surface showing both (2×1) and $c(4 \times 2)$ reconstructions. (b) Filled state STM image ($10 \times 10 \text{ nm}^2$, $V_s = -1.8 \text{ V}$, $I_t = 0.2 \text{ nA}$) of a 2.25×10^5 L $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100). The 2.25×10^5 L $\text{H}_2\text{O}_2(\text{g})$ dose at RT produces 0.97 ML of $\text{H}_2\text{O}_2(\text{g})$ dark chemisorption sites (blue and green boxes) on a Ge(100) surface. Bright spots (red box) are unreacted sites with $\frac{1}{2}$ filled dangling bonds. (c) Schematic diagrams of surface bonding configurations that correspond to the blue, green, and red boxes in the STM image.

During $\text{H}_2\text{O}_2(\text{g})$ dosing, dissociative chemisorption of $\text{H}_2\text{O}_2(\text{g})$ terminates the dangling bonds on Ge dimers with $-\text{OH}$ or $-\text{O}$ species resulting in a variety of surface chemisorbates bonding configurations shown in Fig. 1(c). These various surface bonding configurations change the electronic structure and, therefore, the STM tunneling current, resulting in a difference of brightness in constant current STM imaging. The two different surface bonding configurations are highlighted inside the green and blue boxes. Simple bonding models were developed based on bond enthalpies and confirmed below by DFT calculations. The green box highlights the bonding configuration where $\text{H}_2\text{O}_2(\text{g})$ has dissociated on a Ge dimer leaving each Ge atom terminated with an $-\text{OH}$ species. The blue box highlights the bonding configuration where $\text{H}_2\text{O}_2(\text{g})$ has dissociated on a Ge dimer terminating each Ge atom with an $-\text{OH}$ species and an additional $-\text{O}$ atom has inserted into the Ge dimer bond. The mechanism of this $-\text{O}$ insertion is discussed below and is a variant of the $-\text{O}$ in-

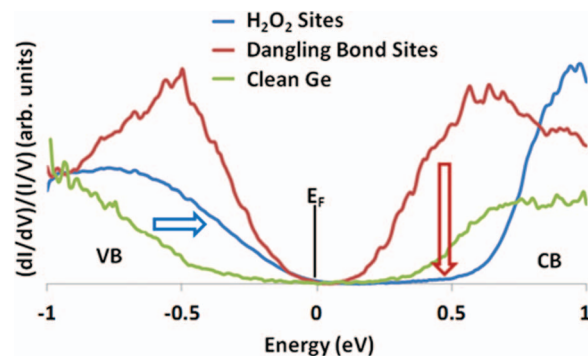


FIG. 2. STS of Clean and $\text{H}_2\text{O}_2/\text{Ge}(001)$. STS of a $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100) surface at RT. STS measured on H_2O_2 sites (blue curve) shows reduction of dangling bond states (red arrow) compared with dangling bond sites (red curve). Blue arrow highlights the Fermi level shift and pinning near the valence band.

section mechanism of Mui *et al.*³⁵ There are a few percent of unreacted Ge dangling bond sites which have a high tunneling current and are imaged as very bright spots on the surface; one dangling bond site is highlighted in the red box. During $\text{H}_2\text{O}_2(\text{g})$ dosing, background $\text{H}_2\text{O}(\text{g})$ is present. It is hypothesized that this did not affect the reaction of $\text{H}_2\text{O}_2(\text{g})$ with the Ge(100) surface due to the increased reactivity of $\text{H}_2\text{O}_2(\text{g})$ compared to $\text{H}_2\text{O}(\text{g})$.³⁶ However, if $\text{H}_2\text{O}(\text{g})$ dissociatively chemisorbed to the surface, the resulting Ge-H bond would be quickly replaced with a Ge-OH bond due to the difference in bond strength of Ge-O (659 kJ/mol) vs Ge-H (327 kJ/mol)³⁷ causing the following reaction: $\text{Ge-H} + \text{H}_2\text{O}_2(\text{g}) \rightarrow \text{Ge-OH} + \text{H}_2\text{O}(\text{g})$.

STS measurements yield $(dI/dV)/(I/V)$ curves which effectively plot the local density of states on the surface.^{32,38,39} STS measurements were conducted to further probe the electronic states of the $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100) surface. Only n-type samples were studied because pinning of the Fermi level on the Ge(100) surface results in the Fermi level being at the valence band edge, therefore, if p-type samples were used, it would be impossible to determine whether the Fermi level is pinned or not.^{13,40} On the clean n-type surface, Ge(100) has a Fermi level position (0 V in STS) just above midgap. This is attributed to the $\frac{1}{2}$ filled dangling bonds on surface Ge atoms even on a perfectly ordered clean Ge(100) surface.⁴¹ Fig. 2 compares the STS curves acquired from the dangling bond sites on unreacted sites of the $\text{H}_2\text{O}_2/\text{Ge}$ surface (Fig. 1 red box) with the $\text{H}_2\text{O}_2(\text{g})$ chemisorption sites (i.e., Ge-OH or Ge-O, Fig. 1 blue or green boxes) on Ge(100).

While the clean n-type Ge(100) surface shows a Fermi level slightly above the middle of the bandgap, the $\text{H}_2\text{O}_2(\text{g})$ dose pins the Fermi level near the valence band most likely due to the large surface dipole caused by the oxygen containing adsorbates on the surface (blue arrow).⁴⁰ The dangling bond sites have states near +0.4 eV consistent with the presence of conduction band edge dangling bonds. Conversely, on the $\text{H}_2\text{O}_2(\text{g})$ chemisorption sites, the states near +0.4 eV are completely eliminated demonstrating that the $-\text{OH}$ chemisorbed species passivate the dangling bond states (red arrow).

XPS data shown in Fig. 3(a) compares the oxygen coverage on Ge(100) surfaces dosed with equivalent doses

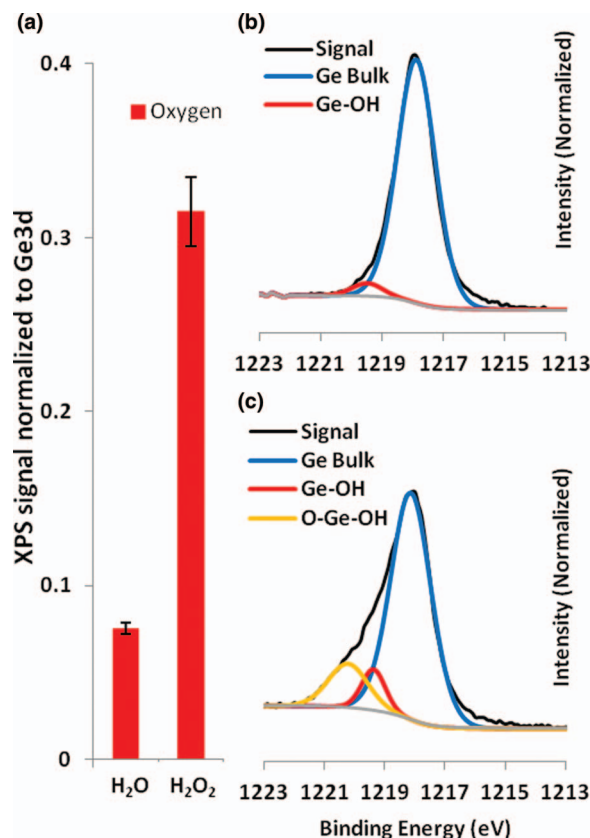


FIG. 3. XPS Comparison of 9×10^5 L H₂O(g) vs H₂O₂(g) Dosing at 25 °C on Ge(100). (a) XPS data showing peak area ratios of oxygen 1s to germanium 3d after relative sensitivity factor adjustment comparing oxygen coverage for equivalent 25 °C room temperature doses of H₂O(g) and H₂O₂(g) on a sputter cleaned Ge(100) surface. (b) XPS peak shape analysis of the Ge 2p peak after dosing H₂O(g) on a clean Ge(100) surface. A Ge-OH feature appears with a peak shift of 1.3 eV. (c) XPS peak shape analysis of the Ge 2p peak after dosing H₂O₂(g) on a clean Ge(100) surface. Two Ge-O_xH_y features appear with peak shifts of 1.3 eV and 2.1 eV.

(9×10^5 Langmuir) of H₂O(g) or H₂O₂(g) at 25 °C. Figs. 3(b) and 3(c) show the peak shape analysis of the Ge 2p signal and associated chemical shifts after a saturation dose of H₂O(g) or H₂O₂(g), respectively.

As seen in Fig. 3(a), more oxygen adsorbs to the surface when dosed with H₂O₂(g) compared to H₂O(g). H₂O(g) dosing at 25 °C results in less than half a monolayer of Ge-OH chemisorption sites and less than half a monolayer of Ge-H chemisorption sites.¹³ The H₂O₂(g) saturation coverage on Ge(100) results in at least two oxygen atoms per available Ge surface dimer from a combination of Ge-OH bonds and O-Ge-OH bonds, which is more than double the oxygen coverage compared to the H₂O(g) saturated Ge(100) surface.

The XPS spectra in Fig. 3(b) shows the H₂O(g) dose results in a 1.3 eV higher binding energy peak (red peak) than bulk Ge (blue peak) consistent with Ge-OH bonds. Fig. 3(c) shows the H₂O₂(g) dosing results in the formation of two new higher binding energy peaks consistent with two different surface Ge-O/Ge-OH bonding configurations. The H₂O₂(g) dose gives a large number of Ge-OH bonds which is 1.3 eV higher in binding energy compared to the bulk peak (red peak) as well as Ge surface atoms which are bonding to two -O/-OH species giving an even higher 2.1 eV binding energy shift

(yellow peak) consistent to what is seen in the STM images in Fig. 1(b) and DFT models below.

The differences in H₂O₂(g) vs H₂O(g) saturation coverage are not simply the result of H₂O(g) dissociation producing both Ge-OH and Ge-H sites. The 25 °C H₂O₂(g)/Ge(100) has a lower density of dangling bond sites and higher density of Ge-OH compared to 25 °C H₂O(g)/Ge(100). A previous report analyzed STM images of the H₂O(g) saturated Ge(100) surface and showed that a saturation dose of H₂O(g) at 25 °C provides 85% coverage on the Ge(100) surface and a dangling bond density of 15%,¹³ while, as seen in Fig. 1(b), a saturation dose of H₂O₂(g) at 25 °C provides a saturation coverage of >97% and a dangling bond density below 3%.

Fig. 4 presents a heuristic model of the H₂O(g) and H₂O₂(g) dissociation mechanism on Ge(100). It is hypothesized that H₂O(g) requires two neighboring empty sites to dissociatively chemisorb due to the high HO-H bond strength, while H₂O₂(g) does not require neighboring sites due to its weak internal bonds and ability to insert into Ge-Ge dimer bonds. This mechanism suggests when H₂O(g) dissociates across a pair of dimers, isolated empty sites are created which are unreactive to H₂O(g) thereby creating the high density of dangling bonds at 25 °C. It is hypothesized that H₂O₂(g) does not leave isolated unreactive sites due to a much weaker HO-OH bond. Therefore, a saturation dose of H₂O₂(g) on Ge(100) leaves Ge dimers terminated with either two or three oxygen species consistent with the STM image (Fig. 1) and DFT calculations below.

To investigate the thermal behavior of the H₂O₂(g) chemisorbed species on Ge(100), the 25 °C H₂O₂(g) dosed sample was annealed to 100 °C and 150 °C for 10 min. Fig. 5(a) shows a filled state STM image of the Ge(100) surface after a 2.25×10^5 L H₂O₂(g) dose and a subsequent 100 °C anneal. Fig. 5(b) shows STS measurements of the 100 °C annealed H₂O₂/Ge surface (blue curve) compared to the RT H₂O₂/Ge surface (red curve) and the clean Ge(100) surface (green curve).

For 100 °C annealing, Fig. 5(a), no additional dangling bond sites are formed, but there is a change in overall bonding configuration to a zig-zag symmetry consistent with either H₂ desorption from the surface or rearrangement of hydroxyl bonding configurations. XPS data (not shown) verify that the oxygen coverage on the 100 °C annealed surface is within 10% of the oxygen content on the un-annealed surface, while the Ge-OH peak shifts to a slightly lower binding energy by about 0.1 eV compared to the RT dosed surface. This is likely attributed to some of the hydroxyl groups inserting into the Ge dimer bonds consistent with the DFT model of the annealed surface proposed below. However, when the H₂O₂(g) saturated surface is annealed to temperatures above 150 °C, XPS shows the oxygen content decreases, and STM shows that the Ge dangling bonds are formed consistent with H₂O(g) desorption. This is in contrast to the H₂O(g) dosed Ge surface which exhibits recombinative desorption of H₂O(g) when annealed to only 100 °C.¹³

As seen in Fig. 5(b), the effect of a 10 min 100 °C anneal was studied to determine the effect of annealing on the electronic structure of H₂O₂/Ge(001). While the RT as-dosed surface shows a Fermi level very near the valence band

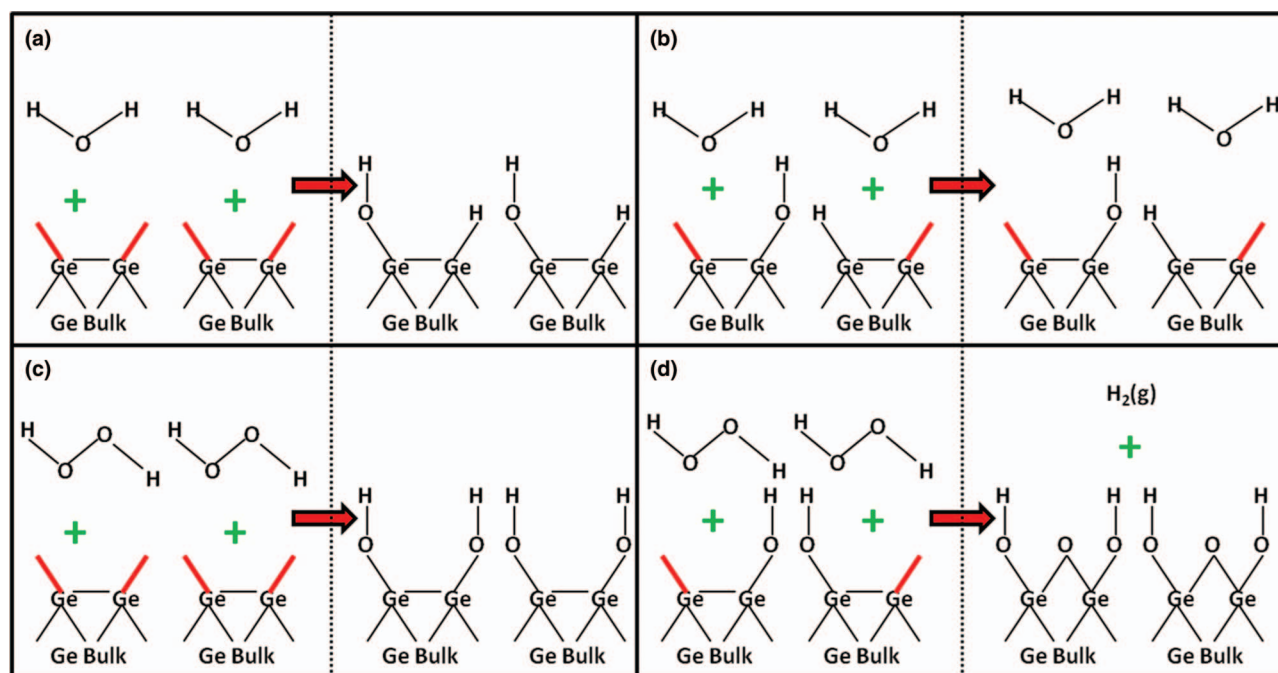


FIG. 4. Heuristic Model of $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2\text{O}_2(\text{g})$ Dissociation Mechanism on Ge(100). (a) Neighboring empty dimer sites available for dissociative chemisorption of $\text{H}_2\text{O}(\text{g})$. (b) Neighboring dimer sites with $\text{H}_2\text{O}(\text{g})$ dissociatively chemisorbed across the dimer row leaving two separated empty sites (red) which are unavailable for dissociative chemisorption of $\text{H}_2\text{O}(\text{g})$. (c) Neighboring empty dimer sites available for dissociative chemisorption of $\text{H}_2\text{O}_2(\text{g})$. (d) Neighboring dimer sites with $\text{H}_2\text{O}_2(\text{g})$ dissociatively chemisorbed across the dimer row leaving two separated empty sites. $\text{H}_2\text{O}_2(\text{g})$ is still able to dissociatively chemisorb on each single empty site and form a bridge bonded oxygen species in the dimer.

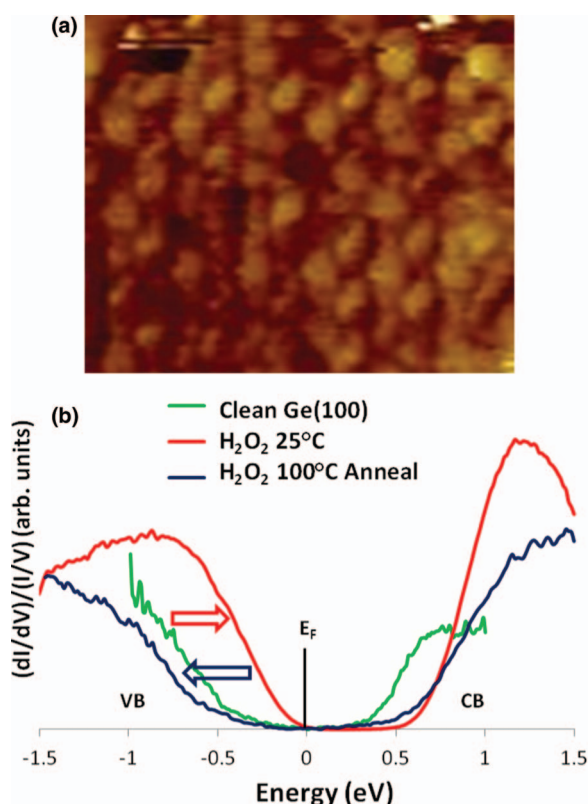


FIG. 5. STM of 100°C Annealed 2.25×10^5 L $\text{H}_2\text{O}_2(\text{g})$ Dose on Ge(100) & STS of Ge(100) and $\text{H}_2\text{O}_2/\text{Ge}(100)$ at RT and Annealed to 100°C . (a) Filled state STM image ($6 \times 5 \text{ nm}^2$, $V_s = -2.0 \text{ V}$, $I_t = 0.2 \text{ nA}$) of 2.25×10^5 L $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100) annealed for 10 min at 100°C . (b) STS measured on the 100°C annealed H_2O_2 sites (blue curve) shows a shift of Fermi level position towards the conduction band consistent with unpinning (blue arrow).

consistent with a large surface dipole (red arrow), annealing the surface to 100°C shifts the Fermi level towards the conduction band (blue arrow) likely due to the decrease of surface dipole caused by the change in surface bonding configuration.

ALD nucleation on the $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface via TMA dosing

To investigate the effect of using $\text{H}_2\text{O}_2(\text{g})$ in ALD nucleation, STM and XPS measurements were performed on a Ge(100) pre-dosed with $\text{H}_2\text{O}_2(\text{g})$ and subsequently dosed with TMA. Fig. 6(a) shows a STM image of the Ge(100) surface that was pre-dosed with 6×10^4 L of $\text{H}_2\text{O}_2(\text{g})$ at 25°C followed by 2.3×10^4 L of TMA at RT and subsequently annealed at 200°C for 5 min. Fig. 6(b) shows three line traces acquired on ordered vertical rows. Fig. 6(c) shows STS analysis of the n-type Ge(100) surface dosed with $\text{H}_2\text{O}_2(\text{g})$, annealed at 100°C , then dosed with TMA and subsequently annealed to 200°C . Note the data were collected with slightly less than full saturation of H_2O_2 and TMA doses allowing defect states to be observed.

The STM image in Fig. 6(a) shows ordered vertical rows (blue lines highlight row direction) along the Ge dimer row direction showing chemisorption of TMA onto the $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface. The line traces in Fig. 6(b) show uniform spacing ($\sim 8 \text{ \AA}$) that is consistent with the clean Ge(100) dimer row spacing. The STS in Fig. 6(c) shows the TMA/ H_2O_2 dosed Ge surface ordered rows (blue curve) have a slightly larger band gap compared to the clean Ge surface (green curve) consistent with O-Al-O bond formation. The

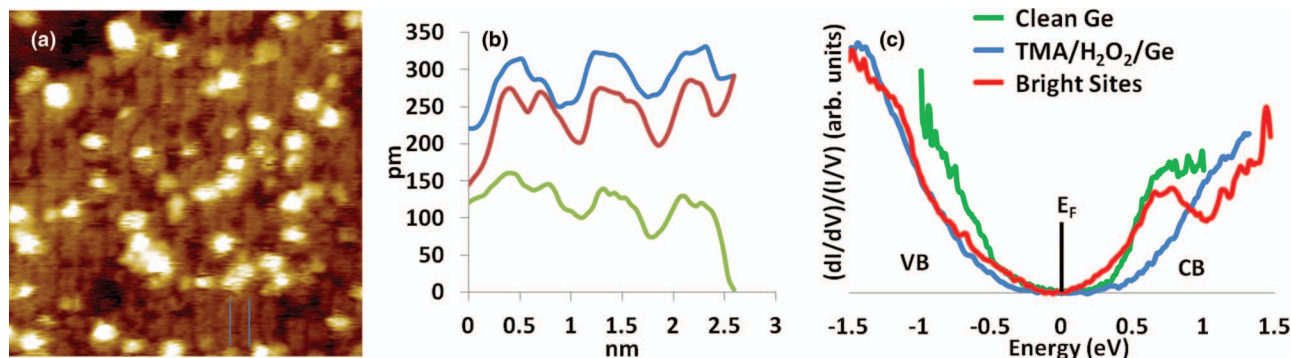


FIG. 6. STM Image and STS of 2.3×10^4 L TMA Dosed on a Ge(100) Surface Predosed with 6×10^4 L of $\text{H}_2\text{O}_2(\text{g})$ at 25°C and Subsequently Annealed at 200°C . (a) $15 \times 15 \text{ nm}^2$ STM image Ge(100) surface that was been pre-dosed with 6×10^4 L of $\text{H}_2\text{O}_2(\text{g})$ at 25°C followed by 2.3×10^4 L of TMA at RT and subsequently annealed at 200°C for 5 min. Vertical ordering in the same direction of the Ge dimer rows can be seen in the image (blue lines). Unreacted bright sites remain on the surface due to either incomplete saturation of the $\text{H}_2\text{O}_2(\text{g})$ dose or desorption of H_2O_2 chemisorption species that did not react with TMA and are volatile at annealing temperatures above 100°C . (b) Line trace analysis taken on three locations of the STM image showing uniform row spacing of 8.1 \AA with a standard error of 0.022. (c) STS measured on the clean Ge(100) surface (green curve), the TMA/ H_2O_2 /Ge surface (blue curve), and the bright sites on the TMA/ H_2O_2 /Ge surface (red curve). STS of the TMA/ H_2O_2 /Ge ordered rows on the surface shows no defect states in the bandgap and a Fermi level position slightly above midgap consistent with unpinning.

dosed surface has a Fermi level slightly above midgap which is consistent with unpinning as seen on the n-type clean Ge surface STS curve. Bright defect states (red curve) have a large number of conduction band edge states due to either incomplete saturation of the $\text{H}_2\text{O}_2(\text{g})$ dose or desorption of H_2O_2 chemisorption species that did not react with TMA and are volatile at annealing temperatures above 100°C .

Fig. 7 shows XPS analysis of a Ge(100) sample dosed with 9×10^5 L H_2O_2 at 25°C followed by 4×10^5 L TMA at 25°C . XPS shows that the as-dosed sample has a O:Al ratio of 1.3:1 and a C:Al ratio of 1.9:1. As the sample is heated to 220°C and 280°C , the carbon signal decreases to C:Al less than 0.8:1 consistent with methyl desorption. Annealing the sample may also slightly reduce the oxygen signal, while the aluminum remains constant consistent with Al–O–Ge bonds being stable on the surface up to 280°C . The 220°C and 280°C annealed surfaces have an O:Al ratio near 1:1 which is consistent with the DFT model of the bonding on the surface proposed below.

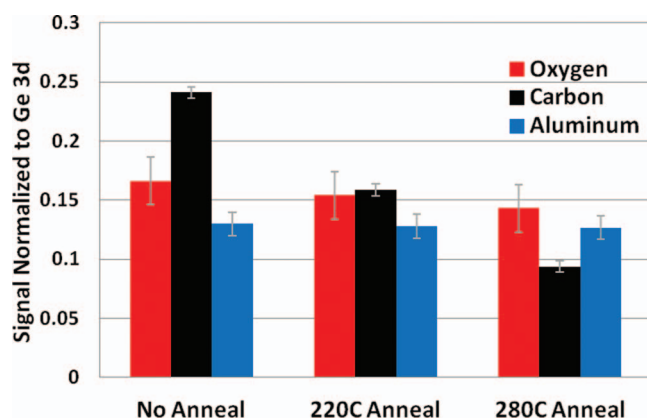


FIG. 7. XPS of 2×10^5 L of TMA Dosed on a Ge(100) Surface that was Predosed with 9×10^5 L of $\text{H}_2\text{O}_2(\text{g})$ vs Annealing Temperature. XPS showing elements on the Ge surface after a 25°C 9×10^5 L of $\text{H}_2\text{O}_2(\text{g})$ and 2×10^5 L of TMA as-dosed and after a 220°C and 280°C anneal. XPS sensitivity for core-level spectra was taken into account to compare intensities from different elements. All the data presented are derived from the ratios to the Ge3d peak feature intensity.

DENSITY FUNCTIONAL THEORY SIMULATIONS

DFT modeling and STM simulations were performed to verify proposed bonding configurations of the $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface (Fig. 1), 100°C annealed $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface (Fig. 5), and the TMA dosed and annealed $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface (Fig. 6). The DFT models were developed by placing –OH or –O groups from dissociated $\text{H}_2\text{O}_2(\text{g})$ onto the Ge(100) surface followed by a relaxation. A vacuum layer of around 15 \AA was added above the surfaces to eliminate spurious interaction through periodic-boundary conditions. The three bottom layers of the Ge slabs were permanently fixed in their bulk-like positions and the bottom most layer was passivated by H atoms to simulate continuous bulk. All simulated Ge slabs had 12 atomic layers (around 16 \AA tall) which, in combination with bulk-like fixation of the 3 bottom layers, was enough to emulate bulk-like behavior and avoid surface to surface interaction.

A variety of bonding configurations were modeled and only the lowest energy models are presented. Fig. 8(a) shows a side view of DFT models of the two lowest energy bonding configurations found on the $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100) surface. The STM simulations, shown above the DFT models, are consistent with the two bonding configurations shown in the STM image in Fig. 8(b). The STM simulations showing the HO–Ge–O–Ge–OH structure (blue box) are consistent with an oxygen insertion imaging as a dark spot in between the hydroxyl terminated Ge atoms. In STM, both these symmetric bright sites have the same brightness because the Ge–OH bond freely rotates at 25°C ; it is only an artifact of 0 K non-rotating Ge–OH bonds in the STM simulation causing the STM simulation to have asymmetric brightness. The dihydroxyl terminated Ge dimer (green box) is consistent with a brightness covering the entire Ge dimer due to the imaging of the hydroxyls and the Ge dimer bond. In both configurations, the chemisorbates align directly along the Ge dimer rows and cover nearly the full surface.

Fig. 9 shows the calculated density of states (DOS) of the clean Ge surface passivated with hydrogen atoms (red curve) representing a defect free surface compared to the Ge

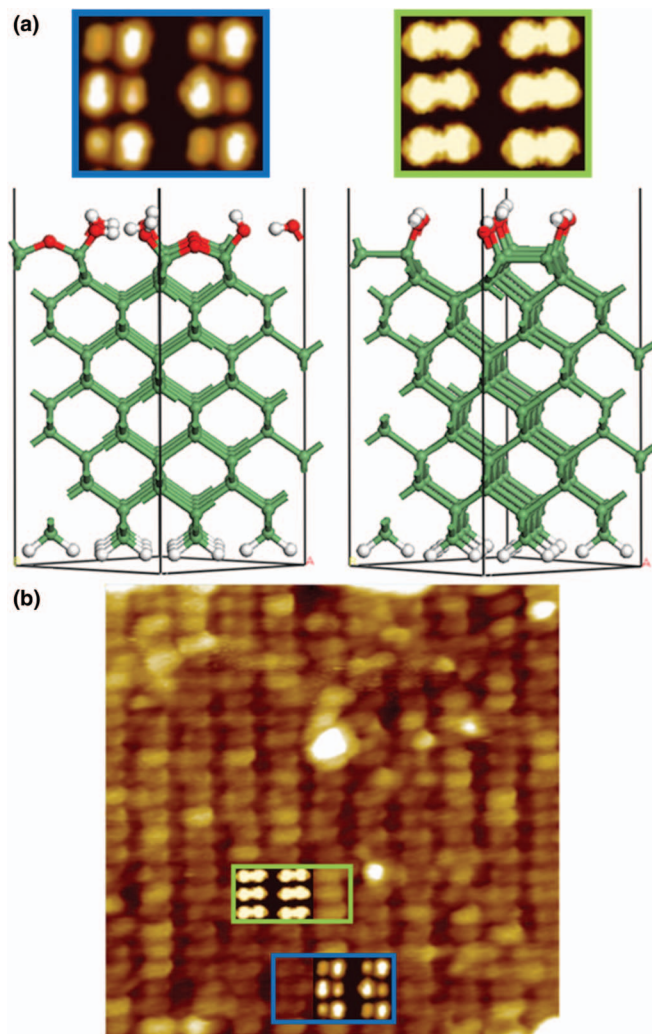


FIG. 8. DFT Models and Corresponding STM Image and Simulation of $\text{H}_2\text{O}_2/\text{Ge}(100)$. (a) DFT models and STM simulations showing two different bonding configurations of $\text{H}_2\text{O}_2(\text{g})$ dosed on the clean $\text{Ge}(100)$ surface at room temperature. Green circles correspond to germanium atoms, red circles correspond to oxygen atoms, and white circles correspond to hydrogen atoms. Green and blue outlines of STM simulations correspond with green and blue bonding configurations proposed in Fig. 1(b). (b) Filled state STM image (as seen in Fig. 1) of $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Ge}(100)$ with STM simulations overlaid on the surface.

surface dosed with $\text{H}_2\text{O}_2(\text{g})$ (black curve). The bandgap of the DFT calculated DOS is smaller than the actual bandgap of the system due to the standard PBE band gap underestimation. The H-passivated Ge surface, Fig. 9 red curve, shows an unpinned surface with the Fermi level near midgap as shown by the red curve in the enlarged inset in the top left corner of Fig. 9. After covering the surface with $-\text{O}$ and $-\text{OH}$ species via $\text{H}_2\text{O}_2(\text{g})$ dosing, the Fermi level is pinned p-type most likely due to the surface dipole as shown by the shift of the Fermi level into the valance band (black curve). This is consistent with the STS data shown in Fig. 2.

Fig. 10 shows a DFT model and STM simulation of the $\text{H}_2\text{O}_2(\text{g})$ dosed Ge surface annealed to 100°C . Annealing the $\text{H}_2\text{O}_2/\text{Ge}(100)$ surface to 100°C induces H_2 desorption and insertion of one oxygen species into the Ge dimer bond. Fig. 10(c) confirms the STM of the 100°C annealed

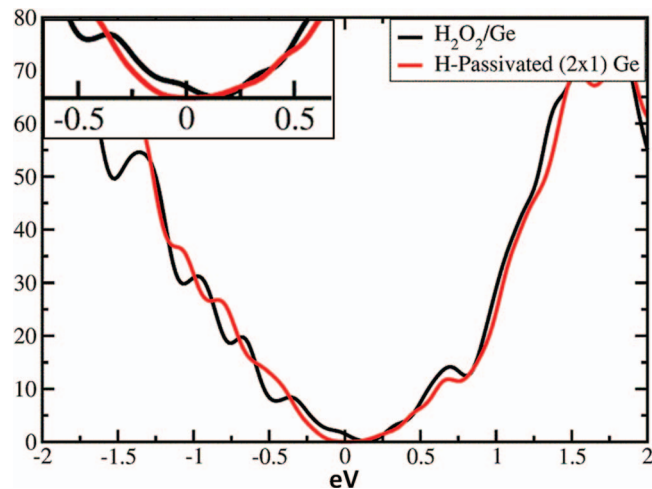


FIG. 9. DOS of H-passivated Ge surface and $\text{H}_2\text{O}_2/\text{Ge}$. Calculated DOS of H-passivated $\text{Ge}(100)$ surface (red curve) and $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Ge}(100)$ (black curve). DOS shows H-passivated surface is unpinned while $\text{H}_2\text{O}_2(\text{g})$ dosed surface is pinned p-type which was experimentally verified using STS as seen in Fig. 2.

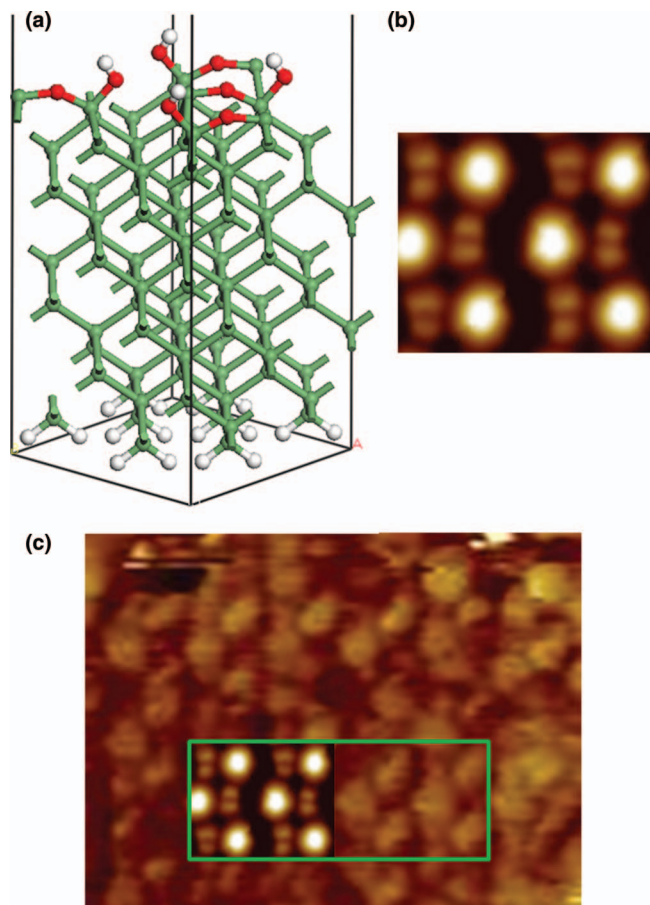


FIG. 10. DFT Model and Corresponding STM Image and Simulation of $\text{H}_2\text{O}_2/\text{Ge}(100)$ Annealed to 100°C . (a) DFT model of the $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Ge}(100)$ surface annealed to 100°C . Green circles correspond to germanium atoms, red circles correspond to oxygen atoms, and white circles correspond to hydrogen atoms. (b) STM simulation of the DFT model of the $\text{H}_2\text{O}_2(\text{g})$ dosed $\text{Ge}(100)$ surface annealed to 100°C . (c) Filled state STM image (as seen in Fig. 5) with STM simulation overlaid on surface.

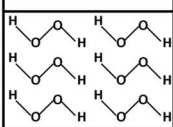

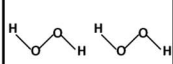
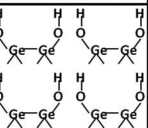

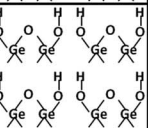
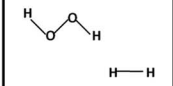
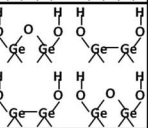
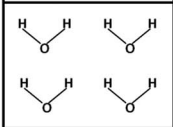
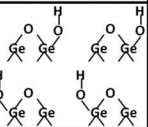
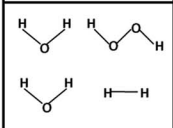
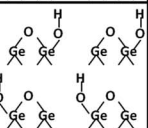
	Final Gas Phase Species	Gas Phase Energy (eV)	Final Surface Bonding Configuration	Surface Energy (eV)	ΔE Relative to Clean Ge Surface (eV)
(a)		-108.040		-473.317	0
(b)		-36.013		-564.191	-18.847
(c)		-13.452		-595.362	-27.457
(d)		-24.733		-579.781	-23.157
(e)		-57.061		-548.146	-23.85
(f)		-53.231		-548.146	-20.02

FIG. 11. Total energies of DFT unit cell models of clean Ge and $\text{H}_2\text{O}_2(\text{g})$ dosed Ge at 25°C and 100°C . (a) Clean Ge(100) surface unit cell total energy with six $\text{H}_2\text{O}_2(\text{g})$ molecules. (b) and (c) Two possible $\text{H}_2\text{O}_2(\text{g})$ dosed Ge room temperature bonding configurations unit cell total energies. (d) Mixed unit cell consisting of both (b) and (c) $\text{H}_2\text{O}_2(\text{g})/\text{Ge}$ bonding configurations unit cell total energy. (e) and (f) Mixed unit cell bonding configuration (d) annealed to 100°C total unit cell energy.

$\text{H}_2\text{O}_2/\text{Ge}(100)$ with the zig-zag structure formed via the anneal is consistent with STM simulation overlaid on the image.

Total energy calculations from the DFT models of each of the $\text{H}_2\text{O}_2/\text{Ge}$ bonding configurations were compared to de-

termine relative thermodynamic stability. In order to compare the total energy of each system relative to the initial clean surface, gas phase species were included in each total energy calculation to ensure all systems had the same number of atoms. Fig. 11 shows the total energies of each system, including gas phase reaction products and reacted surfaces. In Fig. 11, the fourth column shows the total surface energy, while the fifth column displays ΔE , the energy of each system relative to system A, which is the bonding configuration of the clean Ge surface with six gas phase $\text{H}_2\text{O}_2(\text{g})$ molecules. Systems B and C depict the two room temperature $\text{H}_2\text{O}_2(\text{g})$ dosed isolated Ge bonding configurations. System D depicts the mixed surface with half B and half C bonding configurations. Systems E and F depict the mixed surface D bonding configuration after 100°C anneal. Systems E and F show two different total energies due to the two different potential reactions that could occur which leave differing gas phase products. System E depicts the reaction where all gas phase species are formed due to water recombinative desorption off the Ge surface, while system F depicts the reaction that has partial water recombinative desorption and also remaining gas phase H_2O_2 and H_2 . As shown in Fig. 11, the surface becomes more stable (lower total energy) as more $\text{H}_2\text{O}_2(\text{g})$ chemisorbs to the surface via the mechanism proposed in Fig. 4, and the 100°C anneal transforms the mixed surface to a more thermodynamically stable configuration.

DFT simulations were performed to confirm the bonding structure and DOS of TMA dosed onto the $\text{H}_2\text{O}_2(\text{g})$ functionalized Ge surface and are shown in Fig. 12. This model was calculated by bonding monomethylaluminum (MMA) to the oxygen species on the HO-Ge-O-Ge-OH structure shown in the blue box of Fig. 8(a). Subsequently, the model was relaxed. During relaxation, the aluminum atoms pulled the oxygen that had previously inserted into the Ge dimer bond out of the dimer bond and instead bridge bonded between two aluminum atoms above the dimer. The relaxed structure has a ratio of Al, C, and O that is similar to what is seen in the XPS results in Fig. 7. The relaxed model is also consistent

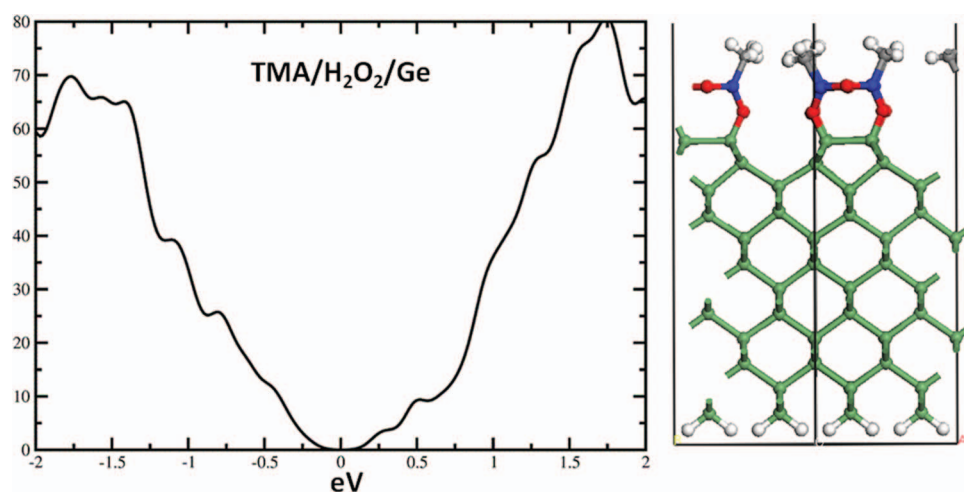


FIG. 12. DFT Model and DOS of TMA/ $\text{H}_2\text{O}_2/\text{Ge}(100)$. DFT model and DOS of the $\text{H}_2\text{O}_2(\text{g})$ dosed Ge(100) surface bonded to MMA species and relaxed to the lowest energy configuration. Green circles correspond to germanium atoms, red circles correspond to oxygen atoms, blue circles correspond to aluminum atoms, grey circles correspond to carbon atoms, and white circles correspond to hydrogen atoms. DOS shows no states in the band gap which was experimentally verified using STS as seen in Fig. 6(c).

with the STM image of the TMA/H₂O₂/Ge(100) (Fig. 6(a)) which has rows directly above the Ge dimer rows. As seen in the DOS of the H-passivated Ge defect free surface (Fig. 9), the DOS of this surface shows no states in the bandgap, consistent with the STS results in Fig. 6(c) demonstrating that the TMA/H₂O₂/Ge provides as good of an interface as the clean H-passivated Ge surface. The bandgap of the DFT calculated DOS is smaller than the actual bandgap of the system due to the PBE simulation method.

CONCLUSION

Functionalization and passivation of the Ge(100) surface was demonstrated using H₂O₂(g). 25 °C dosing of H₂O₂(g) leaves surface Ge dimers terminated with either two or three oxygen species while passivating the dangling bonds on the surface. Compared to conventional H₂O(g) functionalization of the Ge(100) surface for ALD, H₂O₂(g) more than doubles the oxygen concentration on the surface and provides a higher saturation coverage which thereby decreases the density of dangling bond defects during ALD of Al₂O₃. H₂O₂(g) also gives increased thermal stability compared to the H₂O(g) dosed Ge(100) which is important for potential applications as an ALD precursor. TMA was dosed on the H₂O₂(g) saturated Ge(100) surface and it formed a high density electrically passive monolayer of thermally stable Al–O bonds. DFT modeling and STM simulations verified all of the bonding configurations on the surface and were consistent with STM results. Using H₂O₂(g) as an oxidant precursor allows for a smaller amount of oxidant pre-pulsing, a more complete passivation of surface dangling bonds, an increased number of reactive ALD nucleation sites, and an increased thermal budget during ALD.

ACKNOWLEDGMENTS

This work was supported by Applied Materials, Global Foundries, and the Semiconductor Research Corporation (2451.001, 2181.001, 2051.001).

¹Y. Kamata, *Mater. Today* **11**, 30 (2008).

²M. Caymax, M. Houssa, G. Pourtois, F. Bellenger, K. Martens, A. Delabie, and S. Van Elshocht, *Appl. Surf. Sci.* **254**, 6094 (2008).

³A. Delabie, F. Bellenger, M. Houssa, T. Conard, S. Van Elshocht, M. Caymax, M. Heyns, and M. Meuris, *Appl. Phys. Lett.* **91**, 082904 (2007).

⁴F. Bellenger, M. Houssa, A. Delabie, V. Afanasiev, T. Conard, M. Caymax, M. Meuris, K. De Meyer, and M. Heyns, *J. Electrochem. Soc.* **155**, G33 (2008).

⁵D. Kuzum *et al.*, *IEEE Elect. Device Lett.* **29**, 328 (2008).

⁶C. H. Lee, T. Tabata, T. Nishimura, K. Nagashio, K. Kita, and A. Toriumi, *ECS Trans.* **19**, 165 (2009).

⁷H. Matsubara, T. Sasada, M. Takenaka, and S. Takagi, *Appl. Phys. Lett.* **93**, 032104 (2008).

⁸T. Maeda, S. Takagi, T. Ohnishi, and M. Lippmaa, *Mater. Sci. Semiconduct. Process.* **9**, 706 (2006).

⁹R. Xie and C. Zhu, *IEEE Elect. Device Lett.* **28**, 976 (2007).

¹⁰H. Kim, P. C. McIntyre, C. O. Chui, K. C. Saraswat, and M.-H. Cho, *Appl. Phys. Lett.* **85**, 2902 (2004).

¹¹T. Maeda, T. Yasuda, M. Nishizawa, N. Miyata, Y. Morita, and S. Takagi, *J. Appl. Phys.* **100**, 014101 (2006).

¹²T. Sugawara, R. Sreenivasan, and P. C. McIntyre, *J. Vacuum Sci. Technol. B* **24**, 2442 (2006).

¹³J. S. Lee, S. R. Bishop, T. Kaufman-Osborn, E. Chagarov, and A. C. Kummel, *ECS Trans.* **33**, 447 (2010).

¹⁴P. Ardalan, E. R. Pickett, J. S. Harris, A. F. Marshall, and S. F. Bent, *Appl. Phys. Lett.* **92**, 252902 (2008).

¹⁵S. Sun, Y. Sun, Z. Liu, D.-I. Lee, and P. Pianetta, *Appl. Phys. Lett.* **89**, 231925 (2006).

¹⁶R. Xie, M. Yu, M. Y. Lai, L. Chan, and C. Zhu, *Appl. Phys. Lett.* **92**, 163505 (2008).

¹⁷N. Taoka, M. Harada, Y. Yamashita, T. Yamamoto, N. Sugiyama, and S.-I. Takagi, *Appl. Phys. Lett.* **92**, 113511 (2008).

¹⁸B. De Jaeger *et al.*, *Microelectron. Eng.* **80**, 26 (2005).

¹⁹H. S. Nalwa, *Handbook of Thin Film Materials* (Academic Press, 2002).

²⁰M. Ritala, K. Kukli, A. Rahtu, P. I. Räisänen, M. Leskelä, T. Sajavaara, and J. Keinonen, *Science* **288**, 319 (2000).

²¹J. Aarik, A. Aidla, H. Mändar, V. Sammelselg, and T. Uustare, *J. Cryst. Growth* **220**, 105 (2000).

²²J. S. Lee, T. Kaufman-Osborn, W. Melitz, S. Lee, A. Delabie, S. Sioncke, M. Caymax, G. Pourtois, and A. C. Kummel, *J. Chem. Phys.* **135**, 054705 (2011).

²³S. Swaminathan, M. Shandalov, Y. Oshima, and P. C. McIntyre, *Appl. Phys. Lett.* **96**, 082904 (2010).

²⁴H.-B. Wang, D.-Y. Ma, F. Ma, and K.-W. Xu, *J. Vacuum Sci. Technol. B* **30**, 040601 (2012).

²⁵S. L. Manatt and M. R. Manatt, *Chem.-A Eur. J.* **10**, 6540 (2004).

²⁶G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).

²⁷G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

²⁸G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).

²⁹P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).

³⁰J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **78**, 1396 (1997).

³¹J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

³²J. Tersoff and D. Hamann, *Phys. Rev. B* **31**, 805 (1985).

³³J. Tersoff and D. Hamann, *Phys. Rev. Lett.* **50**, 1998 (1983).

³⁴T. Fukuda and T. Ogino, *Phys. Rev. B* **56**, 13190 (1997).

³⁵C. Mui, J. P. Senosiain, and C. B. Musgrave, *Langmuir* **20**, 7604 (2004).

³⁶L. Papagno, D. Frankel, Y. Chen, L. Caputi, J. Anderson, and G. Lapeyre, *Surf. Sci.* **248**, 343 (1991).

³⁷J. Kerr and D. Lide, *CRC Handbook of Chemistry and Physics*, 81st ed. (CRC Press, Boca Raton, FL, 2000).

³⁸R. M. Feenstra, J. A. Stroscio, and A. Fein, *Surf. Sci.* **181**, 295 (1987).

³⁹N. Lang, *Phys. Rev. B* **34**, 5947 (1986).

⁴⁰T. J. Grassman, S. R. Bishop, and A. C. Kummel, *Surf. Sci.* **602**, 2373 (2008).

⁴¹O. Gurlu, H. J. Zandvliet, and B. Poelsema, *Phys. Rev. Lett.* **93**, 066101 (2004).