Contents lists available at ScienceDirect

# Surface Science



journal homepage: www.elsevier.com/locate/susc

# Atomic imaging and modeling of passivation, functionalization, and atomic layer deposition nucleation of the SiGe(001) surface via $H_2O_2(g)$ and trimethylaluminum dosing



Tobin Kaufman-Osborn<sup>a</sup>, Evgueni A. Chagarov<sup>b</sup>, Sang Wook Park<sup>a</sup>, Bhagawan Sahu<sup>c</sup>, Shariq Siddiqui<sup>c</sup>, Andrew C. Kummel<sup>a,b,\*</sup>

<sup>a</sup> Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, USA

<sup>b</sup> Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, USA

<sup>c</sup> TD Research, GLOBALFOUNDRIES USA Inc., 257 Fuller Road, Albany, NY 12203, USA

# ARTICLE INFO

Article history: Received 2 June 2014 Accepted 23 August 2014 Available online 2 September 2014

Keywords: Silicon-germanium Hydrogen peroxide Scanning tunneling microscopy Scanning tunneling spectroscopy Atomic layer deposition X-ray photoelectron spectroscopy

# ABSTRACT

Passivation, functionalization, and atomic layer deposition (ALD) via  $H_2O_2(g)$  and trimethylaluminum (TMA) dosing were studied on the clean  $Si_{0.6}Ge_{0.4}(001)$  surface at the atomic level using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Chemical analysis of the surface was performed with in-situ X-ray photoelectron spectroscopy (XPS) while density functional theory (DFT) was employed to model the bonding of  $H_2O_2(g)$  chemisorbates to the substrate. A room temperature saturation dose of  $H_2O_2(g)$  covers the surface with a monolayer of – OH and – O chemisorbates. XPS and DFT demonstrate that the room temperature  $H_2O_2/SiGe$  surface is composed of only Ge–OH and Ge–O bonds while annealing induces an atomic layer exchange bringing Si to the surface to bond with – OH or – O while pushing Ge subsurface. The resulting Si–OH and Si–O surface is optimal because it can be used to nucleate high-k ALD and Si dangling bonds are readily passivated by forming gas. After  $H_2O_2(g)$  functionalization, TMA dosing, and a subsequent 230 °C anneal, ordering along the dimer row direction is observed on the surface. STS verifies that the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface has an unpinned Fermi level with no states in the band gap demonstrating the ability to serve as an ideal template for further high-k deposition.

© 2014 Elsevier B.V. All rights reserved.

# 1. Introduction

To further scale complementary metal–oxide semiconductor (CMOS) devices, materials with high carrier mobility have been studied. Much attention has been given to using SiGe as a channel material due to its high hole mobility and the facility to place Si channels or low Ge content SiGe under biaxial tensile strain for electron mobility enhancement in NMOS or to have a SiGe channel compressively strained by a higher Ge content SiGe or pure Ge to enhance hole mobility [1–3]. However, one of the main challenges in employing SiGe as a channel material is achieving a high quality interface between SiGe and a gate oxide [4]. As the oxide thickness is scaled down on the SiGe surface, a large drop in mobility is observed which is most likely caused by the poor quality Ge containing oxide which exists at the SiGe–oxide interface [5]. Therefore, a high quality and low defect density interlayer must be deposited between the semiconductor and the gate oxide.

\* Corresponding author. Tel.: +1 858 534 3368. *E-mail address:* akummel@ucsd.edu (A.C. Kummel). Several strategies have been studied to optimize the SiGe/oxide interface. On Ge(001), a good oxide/SiGe interface can be formed by growing a high quality GeO<sub>2</sub> layer using high temperature and high pressure oxidation[6–9]. However, oxidation of the SiGe surface to form an insulating layer is difficult because typical thermal oxidation preferentially oxidizes the Si leaving a Ge rich layer or Ge suboxide near the semiconductor–oxide interface which negatively effects the oxide properties [10]. Even if SiO<sub>2</sub> and GeO<sub>2</sub> could simultaneously be formed on SiGe, GeO<sub>2</sub> is problematic due to its water solubility and limited thermal stability. Another possible solution is to deposit an ultra-thin Si capping layer [11–15]. The Si capping layer can be very effective at reducing interface traps (D<sub>it</sub>) [14]. However, optimizing the Si cap thickness is crucial because too thin a cap can result in leakage current while too thick a Si cap can increase sub-threshold swing and lower hole mobility [15].

In an effort to improve performance on Si and SiGe devices, multilayered oxides (SiO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub>, ZrO<sub>2</sub>/HfO<sub>2</sub>, SiO<sub>2</sub>/ZrO<sub>2</sub>, etc.) have been studied with the goal of lowering EOT, reducing leakage current, increasing interfacial layer stability, suppressing dopant diffusion, and improving reliability. Many multilayered oxides include a low-k SiO<sub>2</sub>





**Fig. 1.** STM and STS of clean SiGe(001) (A) Filled state STM image ( $50 \times 50 \text{ nm}^2$ ,  $V_s = -1.8 \text{ V}$ ,  $I_t = 0.2 \text{ nA}$ ) of sputter and anneal cleaned SiGe(001). (B)  $10 \times 10 \text{ nm}^2$  inset of black square outline in (A) showing surface reconstruction (C) STS of clean (blue) and sputter damaged (green) SiGe(001) surface. The clean surface is unpinned with a Fermi level (0 V) slightly above midgap and the sputter damaged surface is pinned p-type consistent with large high density of valence band edge states. Dotted green line shows conduction band edge of sputter damaged surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

layer in an effort to optimize the semiconductor/oxide interface quality [16–21].

The goal of this study is to eliminate the need for the Si/SiO<sub>2</sub> capping layer by generating a Si–OH and Si–O terminated surface via  $H_2O_2(g)$  dosing and annealing which can directly nucleate high-k ALD and subsequently be treated with forming gas anneal process to passivate any persistent Si dangling bonds at the interface [22–25]. The effect of reacting  $H_2O_2(g)$  and TMA on the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface is analyzed because it has previously been shown on Ge, Si, and SiGe that a very thin interfacial  $Al_2O_3$  can improve device performance [26–28].

The present study reports upon the formation of a thermally stable passivation layer of monolayer thickness on  $Si_{0.6}Ge_{0.4}(001)$  which leaves the Fermi level unpinned while preventing low quality Ge suboxide formation eliminating the need for a low-k SiO<sub>2</sub> buffer layer. The surface bonding configurations and thermal behavior of the  $Si_{0.6}Ge_{0.4}(001)$  surface after  $H_2O_2(g)$  and TMA dosing were studied by annealing in ultrahigh vacuum conditions and analyzing the surface between each step using *in-situ* X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). Atomic models of the  $H_2O_2(g)$  passivated  $Si_{0.5}Ge_{0.5}(001)$  surface were developed using density functional theory (DFT) and were consistent with experimental results.  $H_2O_2(g) + TMA$  dosing on the SiGe surface was shown to produce an electrically passive interface which acts as an ideal template for additional high-k deposition; DFT modeling of the monolayer of aluminum oxide on SiGe(001) is consistent with an ordered electrically passive interface.

# 2. Experimental details

N-type  $Si_{0.6}Ge_{0.4}(001)$  wafers doped with  $4 \times 10^{19}$  cm<sup>-3</sup> P (Applied Materials) were diced into 12 mm  $\times$  5 mm pieces. Samples were degreased using acetone, methanol, and deionized water then dried with N<sub>2</sub> gas. Samples were loaded into a custom Omicron UHV chamber with a base pressure of  $2 \times 10^{-10}$  Torr then cleaned via repeated sputter



**Fig. 2.** STM image and STS of  $2 \times 10^4$  L H<sub>2</sub>O<sub>2</sub>(g) dosed SiGe(001) (A) Filled state STM image ( $15 \times 15$  nm<sup>2</sup>, V<sub>s</sub> = -1.8 V, I<sub>t</sub> = 0.2 nA) of  $2 \times 10^4$  L H<sub>2</sub>O<sub>2</sub>(g) dosed onto clean SiGe(001). The H<sub>2</sub>O<sub>2</sub>(g) dose at RT produces a nearly full monolayer of H<sub>2</sub>O<sub>2</sub>(g) dark chemisorptions sites (blue and green boxes) on a SiGe(001) surface. Bright spots (red box) are unreacted sites with half filled dangling bonds. (B) Schematic diagrams of surface bonding configurations that correspond to the blue, green, and red boxes in the STM image. (C) STS of H<sub>2</sub>O<sub>2</sub>(g) dosed SiGe(001) surface at RT (red curve) shows Fermi level shift toward the valence band (red arrow) compared to STS of clean surface (blue curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and anneal processes. The sputtering was performed using a 1–1.5 keV of Ar<sup>+</sup> ion beam (Model 1403 ion gun, Nonsequitur Technologies) with a beam current of 0.6–0.9  $\mu$ A for 30 min while the sample temperature was maintained at 500 °C via direct heating. Following each sputter process, the sample temperature was maintained at 500 °C for 20 min. Sample cleanliness was verified via STM before proceeding with each experiment.

SiGe surfaces were reacted with precursors in a separate "dosing" chamber with a base pressure of  $2 \times 10^{-8}$  Torr. Without carrier gas,  $H_2O_2(g)$  and TMA were dosed by back filling the dosing chamber with the precursor vapors. The doses of both  $H_2O_2(g)$  and TMA were controlled by throttling valves on the  $H_2O_2(g)$  and TMA. The reaction pressures were measured using a convectron gauge, and the exposures were estimated in Langmuirs (1 Langmuir (L) =  $1 \times 10^{-6}$  Torr 1 s). The SiGe(001) samples were maintained at 300 K during dosing. A 30% solution of  $H_2O_2(aq)$  was employed as the surface oxidant source. The  $H_2O_2(aq)$  solution is known to produce a vapor containing 2.7% H<sub>2</sub>O<sub>2</sub>(g) at 25 °C [29]. Glass and teflon tubing and teflon valves were employed to minimize the decomposition of the  $H_2O_2(g)$ ; however, some  $H_2O_2(g)$  may have reacted with the walls of the stainless steel dosing chamber. Therefore, the estimates of  $H_2O_2(g)$  exposures on the  $Si_{0.6}Ge_{0.4}(001)$  surfaces are the upper limits of the actual doses of  $H_2O_2(g)$ . However, knowledge of the exact dose is not material to the results because all results in this study employed saturation doses.

After dosing  $H_2O_2(g)$  or TMA, samples were transferred to the UHV chamber for thermal annealing. The sample temperature was monitored by a pyrometer during direct heating using a controlled heating ramp rate of 1 °C/s. The sample surface topography was analyzed using *in-situ* analysis via an STM (LT-STM, Omicron Nanotechnology). After each surface treatment, STM (scanning tunneling microscopy) and STS (scanning tunneling spectroscopy) data were obtained at RT in a UHV chamber with a base pressure of  $1 \times 10^{-11}$  Torr. STM images were acquired using constant-current mode STM ( $I_{sp} = 0.2$  nA) with an



**Fig. 3.** Ge 3d and Si 2p spectrum of  $H_2O_2/SiGe(001)$  (left) Ge 3d spectrum showing formation of a GeO<sub>x</sub>H<sub>y</sub> peak after a RT  $H_2O_2(g)$  dose and reduction of the GeO<sub>x</sub>H<sub>y</sub> peak as sample is annealed to 300 °C. (right) Si 2p spectrum showing absence of a SiO<sub>x</sub>H<sub>y</sub> peak after RT  $H_2O_2(g)$  dose and formation of a SiO<sub>x</sub>H<sub>y</sub> peak as sample is annealed to 300°C.

applied sample bias between -1.8 and -2.0 V. 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 V or -1.5 to +1.5 V, was implemented to measure the electronic structure of sample surfaces.

Chemical analysis was performed using an *in-situ* monochromatic XPS (XM 1000 MkII/SPHERA, Omicron Nanotechnology) to examine the surface elements and their relative intensities. XPS data was acquired in constant analyzer energy mode with a pass energy of 50 eV and a line width of 0.1 eV using an Al K $\alpha$  source (1486.7 eV). The takeoff angle was 30° from the sample surface (i.e. close to the surface parallel) with an acceptance angle of  $\pm$  7°. Peak shape and data analysis was performed using CASA XPS v.2.3 using a Shirley background subtraction method.

#### 3. Computational details

All presented first-principle simulations were performed with the Vienna Ab-Initio Simulation Package (VASP)[30, 31] applying projector augmented-wave (PAW) pseudopotentials (PP) [32, 33] and PBE (Perdew–Burke–Ernzerhof) exchange–correlation functional [34, 35]. The choice of PBE functional and PAW pseudopotentials was validated by parametrization runs demonstrating good reproducibility of experimental lattice constants and bulk moduli of crystalline bulk Si and Ge. The systems were relaxed by conjugate-gradient algorithm with force tolerance level of 0.02 eV/Å. The 3 bottom layers of the slabs were fixed in bulk-like positions and passivated by H atoms to simulate continuous bulk.

# 4. Results and discussion

Atomically flat and clean Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surfaces were prepared via multiple cycles of sputtering and annealing. Fig. 1(A&B) shows a typical filled-state STM image of a clean Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface. The surface of clean  $Si_{0.6}Ge_{0.4}(001)$  is known to be terminated with a high percentage of Ge atoms due to segregation of Ge to the surface [36-39]. This is consistent with the SiGe(001) surface being more thermodynamically stable when covered with under coordinated Ge atoms rather than under coordinated Si atoms. To determine the electronic structure of the clean  $Si_{0.6}Ge_{0.4}(001)$  surface, scanning tunneling spectroscopy (STS) measurements were performed. STS measurements generate (dI/dV)/(I/V) data which shows the local density of states on the surface [40-42]. Fig. 1(C) shows an average of 12 STS curves taken on the clean  $Si_{0.6}Ge_{0.4}(001)$  surface shown in Fig. 1(A) (blue curve). STS was only conducted on n-type samples because the Fermi level pins on the SiGe(001) surface near the valence band edge as shown by the average of STS curves acquired on a SiGe(001) sample which was damaged via sputtering without annealing. The sputter damaged surface (STS-Fig. 1(C) green curve, STM image not shown) shows the surface pins p-type consistent with a large density of valence band edge states. Therefore, if p-type samples were used, one would be unable to determine whether pinning had occurred. The clean n-type  $Si_{0.6}Ge_{0.4}(001)$ surface has an unpinned Fermi level position (0 V in STS) which is slightly above midgap. The Fermi level on clean n-type  $Si_{0.6}Ge_{0.4}(001)$ being slightly above midgap is identical to the Fermi level position on the clean Ge(001) surface. This is consistent with the presence of metallic states near the Fermi level caused by 1/2 filled dangling bonds on surface Ge dimers on the Ge-terminated ordered sputter cleaned Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface [43, 44].

In order to passivate and functionalize the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface, the surface was exposed to a near saturation dose of  $2 \times 10^4$  L of H<sub>2</sub>O<sub>2</sub>(g) at room temperature (RT). Fig. 2 shows an STM image of the H<sub>2</sub>O<sub>2</sub>(g) dosed Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface; the H<sub>2</sub>O<sub>2</sub>(g) induced dark site formation. DFT analysis shown later determined that H<sub>2</sub>O<sub>2</sub>(g) dosing of the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface results in – OH and – O adsorbates bonded to the surface. This is consistent with both STM imaging and STM



**Fig. 4.** STM and line trace of TMA/H<sub>2</sub>O<sub>2</sub>/SiGe(001) (A)  $16 \times 20 \text{ nm}^2$  STM image of SiGe(001) pre-dosed with  $4 \times 10^5 \text{ Lof H}_2O_2(g)$  at RT followed by  $5 \times 10^4 \text{ Lof TMA}$  at RT and subsequently annealed at 230 °C for 20 min. (B) Line trace analysis of four different areas of STM image. Vertical ordering is seen in the STM image and line trace analysis confirms uniform row spacing of 8.3 Å with a standard error of 0.023 Å.

simulations of -OH and -O adsorbates on the  $H_2O_2(g)$  dosed Ge(001) surface which also image as dark sites [45]. Models of the -OH or -Ospecies are shown in Fig. 2(B). Unreacted sites (Fig. 2, red box) are imaged as very bright (white color in Fig. 2A) due to their dangling bonds while reacted sites have an altered electronic structure resulting in a difference of brightness when imaged in constant current mode STM. This allows differentiation between the two different bonding configurations which are highlighted inside the blue and green boxes in Fig. 2. The green box in the STM image shows two H-O-Ge-Ge-O-H dimer sites aligned vertically (medium brightness) while the blue box in the STM image shows three H-O-Ge-O-Ge-O-H dimer sites aligned vertically (darkest sites). The proposed models were developed using bond enthalpy calculations and are confirmed below using DFT calculations. As previously shown on the pure Ge(001) surface, the bonding configuration shown in the green box occurs when H<sub>2</sub>O<sub>2</sub>(g) dissociates on a Ge dimer terminating each Ge atom with an – OH species [45]. The blue box shows the bonding configuration where an -0 atom has inserted into the Ge dimer bond which is already terminated by two -OH species. The OH-Ge-O-Ge-OH site appearing darker in filled state imaging than the OH-Ge-Ge-OH site is consistent with the bridging O atoms causing the valence electrons to be more tightly



**Fig. 5.** STS of clean SiGe(001) surface (blue curve) and TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface (green curve). STS of the ordered rows on the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface shows no defect states in the band gap and a Fermi level position slightly above midgap identical to the clean surface and consistent with removal of the surface dipole from-OH termination. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bound. This difference in STM imaging is consistent with STM simulations previously shown on the  $H_2O_2(g)$  dosed Ge(100) surface [45]. The red box highlights the small portion of the surface that remains unreacted leaving undercoordinated surface atoms with dangling bonds which have a high tunneling current and image as very bright spots.

During the dosing of  $H_2O_2(g)$ , background  $H_2O(g)$  is present. However,  $H_2O(g)$  has a very low reactivity with the Ge(100) surface at room temperature [46]. It is hypothesized that the background  $H_2O(g)$  did not affect the reaction of  $H_2O_2(g)$  with the SiGe(100) surface. If  $H_2O(g)$  dissociatively chemisorbed to the SiGe surface, the reaction Ge-H +  $H_2O_2(g) \rightarrow$  Ge-OH +  $H_2O(g)$  would quickly occur eliminating the Ge-H bond due to the difference in bond strength of Ge-O (659 kj/mol) vs Ge-H (327 kj/mol) [47].

STS curves were taken on the  $H_2O_2(g)$  dosed  $Si_{0.6}Ge_{0.4}(001)$  surface and are shown in Fig. 2(C). As shown by the red arrow,  $H_2O_2(g)$  shifts the Fermi level toward the valence band edge consistent with the oxygen containing adsorbates shifting the Fermi level toward the valence band edge due to the large dipole on the surface [48].

After  $H_2O_2(g)$  dosing onto the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface, XPS was employed to verify that the surface was terminated with Ge atoms and show the progression of SiGe(001) surface bonding as the



**Fig. 6.** XPS of  $5 \times 10^4$  L of TMA dosed on a SiGe(100) surface that was predosed with  $4 \times 10^5$  L of  $H_2O_2(g)$  vs. annealing temperature. XPS showing elements on the SiGe surface after a 25 °C 4 × 10<sup>5</sup> L of  $H_2O_2(g)$  and  $5 \times 10^4$  L of TMA 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 (Si2p + Ge3d) peak feature intensity.



**Fig. 7.** Ge 3d and Si 2p spectrum of TMA/H<sub>2</sub>O<sub>2</sub>/SiGe(001) (left) Ge 3d spectrum showing complete reduction of Ge – O – Al bonding (red peak) after a 310 °C anneal indicating Ge – Si place exchange occurring. (right) Si 2p spectrum showing increase of Si – O – Al bonding (red peak) after a 310 °C anneal indicating Ge – Si place exchange fully occurring.

annealing temperature was raised. Fig. 3 shows the evolution of the Ge 3d and Si 2p peaks after a variety of surface treatments. Fig. 3(A) shows the Ge 3d and Si 2p peaks after repeated cycles of sputtering and annealing until the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) sample was free of contaminants. The cleanliness was verified by STM imaging and verified as contaminant free in XPS. The  $Si_{0.6}Ge_{0.4}(001)$  surface was subsequently dosed with  $2 \times 10^5$  L of  $H_2O_2(g)$  at RT. While the Ge 3d peak on the clean Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface in Fig. 3(A) only shows a bulk-like component, H<sub>2</sub>O<sub>2</sub>(g) dosing at room temperature (RT) generated a higher binding energy peak which is assigned as GeO<sub>x</sub>H<sub>v</sub>. As previously shown, dosing  $H_2O_2(g)$  onto a Ge surface results in a variety of bonding configurations involving a complete – OH and – O termination [45]. Therefore, the resulting bonding configurations on the surface have been collectively assigned as a single broad GeO<sub>x</sub>H<sub>y</sub> peak centered at ~1.5 eV higher than the bulk Ge feature. However, the RT  $H_2O_2(g)$  dose has no effect on the Si 2p peak shown in Fig. 3(B). This is consistent with the sputter cleaned  $Si_{0.6}Ge_{0.4}(001)$  surface being completely terminated with Ge - Ge dimers and indicates that H<sub>2</sub>O<sub>2</sub>(g) dosing at RT results in no subsurface oxidation of  $Si_{0.6}Ge_{0.4}(001)$ .

The sample was subsequently annealed at 180 °C inducing a large reduction in the GeO<sub>x</sub>H<sub>v</sub> peak and formation of a SiO<sub>x</sub>H<sub>v</sub> peak (see Fig. 3(C)). This is consistent with the – OH and – O adsorbates pulling the subsurface Si atoms to the surface to form Si-OH or Si-O bonds upon heating to 180 °C. This phenomenon has been seen in a similar system where Cl atoms on a Ge terminated SiGe surface induce place exchange when annealed resulting in Si – Cl bonding [49]. Fig. 3(D) shows the XPS spectra of  $H_2O_2/Si_{0.6}Ge_{0.4}(001)$  after a 300 °C anneal; there are no Ge-OH nor Ge-O bonds remaining on the surface consistent with complete Si/Ge place exchange. The complete Si/Ge place exchange is also consistent with the growth of the  $SiO_xH_v$  peak in Fig. 3(D) compared to Fig. 3(c). This place exchange results from the difference in bond strengths between Ge-O (659.4 kj/mol) and Si-O (799.6 kj/mol) bonds [47]. The ability to manipulate the H<sub>2</sub>O<sub>2</sub>(g) dosed SiGe(001) surface from Ge termination to Si termination is beneficial for device fabrication because the Si-OH terminated surface should form stable strong bonds to high-k ALD metal precursors. Furthermore, if any dangling bonds persist after oxide deposition, the dangling bonds will be on Si which can be passivated using forming gas thereby minimizing D<sub>it</sub> [22–25].

Once the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface was functionalized via  $H_2O_2(g)$  dosing, TMA was dosed in order to emulate typical ALD processing for growth of Al<sub>2</sub>O<sub>3</sub>; afterward, STM and STS measurements were preformed. Fig. 4(A) shows an STM image of a  $Si_{0.6}Ge_{0.4}(001)$ surface dosed with  $4 \times 10^5$  L of H<sub>2</sub>O<sub>2</sub>(g) and subsequently dosed with  $5 \times 10^4$  L of TMA and annealed at 230 °C for 20 min. Vertical rows are observed along the SiGe dimer row direction demonstrating chemisorption of the TMA onto the  $H_2O_2/SiGe(001)$  surface. The TMA/ $H_2O_2/$ SiGe STM image has inferior resolution than the clean SiGe surface due to the many weakly bound adsorbates covering the surface making it difficult to maintain high resolution STM tip stability; however, line trace analysis, STS, XPS, and DFT (shown below) can be employed for definitive structure identification. Line trace analysis was performed on 20 different locations on the image; for each of the 20 traces, the spacing over at least 3 rows was measured to increase accuracy. The average row spacing was 8.3 Å with a standard deviation of 1.0 Å and with a standard error of 0.023 Å. Fig. 4(B) shows four line trace profiles taken on the STM image showing consistent spacing of the ordered rows which corresponds with the dimer row spacing on the clean Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface.

STS measurements were used to analyze the electronic structure of the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface and are shown in Fig. 5. By dosing the H<sub>2</sub>O<sub>2</sub>/SiGe surface (Fig. 2C red curve) with TMA, the Fermi level is shifted back to a position identical to that on the clean surface as shown by the good agreement in Fermi level position between the clean SiGe surface (Fig. 5 blue curve) and the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface (Fig. 5 green curve).

Fig. 6 shows XPS analysis of a SiGe(100) sample dosed with  $4 \times 10^5$  L of H<sub>2</sub>O<sub>2</sub>(g) and subsequently dosed with  $5 \times 10^4$  L of TMA and annealed at 230 °C for 20 min. The sample was subsequently annealed at 310 °C for 20 min. As the sample is headed to 310 °C, XPS shows that the carbon signal decreases consistent with methyl desorption. Annealing the sample may also slightly reduce the oxygen signal while the aluminum signal remains constant. This is consistent with Al–O–Si bonds being stable up to 310 °C demonstrating thermal stability after H<sub>2</sub>O<sub>2</sub>(g) and TMA dosing.

Although both precursors were dosed at RT then subsequently annealed, XPS peak shape analysis verifies that the Ge-Si place exchange still occurs during annealing even when TMA chemisorbates are present on the surface resulting in only Si-O-Al bonding at 310 °C. Fig. 7 shows XPS peak shape analysis of the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe surface as a function of annealing temperature. The spectra presented in Fig. 7A show that both the Si 2p (purple) and Ge 3d (green) spectra have a small higher binding energy peak (red) indicating that both Si and Ge are bonded to -O-Al at 230 °C. However, unlike what was seen with  $H_2O_2(g)$  only dosing, the higher binding energy peak has less of an energy shift due to the TMA chemisorbates, particularly Al, donating electrons to oxygen reducing the impact on the Si 2p and Ge 3d higher binding energy features. Although this higher binding energy peak (red, Ge/Si-O-Al) is less pronounced, it is clear that, upon annealing the sample to 310 °C (Fig. 7B), the feature grows on the Si 2p spectra and is completely eliminated on the Ge 3d spectra indicating the place exchange has fully occurred resulting in purely Si-O-Al bonding.

#### 5. Density functional theory simulations

DFT modeling was performed to verify proposed bonding configurations and to study the thermodynamic stability of the bonding configuration of the  $H_2O_2/SiGe$  during annealing. The DFT models were established by placing -OH or -O groups from dissociated  $H_2O_2(g)$  onto the SiGe(100) surface, with either Si or Ge termination, followed by a relaxation. Multiple bonding configurations were modeled and the lowest energy models are presented. Fig. 8 shows a side view of six different bonding configurations calculated for the reaction products of  $H_2O_2(g)$  on the Si<sub>0.5</sub>Ge<sub>0.5</sub>(001) surface. Note that the experiments



**Fig. 8.** DFT models and total energy of the  $H_2O_2/SiGe$  system. DFT models and total energies of (Column A) clean SiGe(001) surface Ge dimer terminated (top) or Si dimer terminated (bottom) (Column B) two hydroxyls bonded to each Ge dimer terminated SiGe(001) (top) or Si dimer terminated SiGe(001) (bottom) (Column C) two hydroxyls with an inserted bridge bonded oxygen atom on each Ge dimer terminated SiGe(001) (top) or Si dimer terminated SiGe(001) (bottom). The total energies of all the systems are compared showing that the clean surface is more thermodynamically stable with Ge termination while the  $H_2O_2(g)$  dosed surface is more stable with Si termination.

were performed on  $Si_{0.6}Ge_{0.4}(001)$  while the DFT model is for  $Si_{0.5}Ge_{0.5}(001)$  to simplify the calculations; the differences are not expected to be important. The top row of DFT models shows the

SiGe(001) surface with Ge termination on (A) the clean surface, (B) the -OH passivated surface, and (C) the -OH passivated surface with an additional -O atom inserted into the Ge dimer bond. The



**Fig. 9.** DFT model and DOS of TMA/H<sub>2</sub>O<sub>2</sub>/SiGe(001) DFT model and DOS of the H<sub>2</sub>O<sub>2</sub>(g) dosed SiGe(100) surface bonded to MMA species and relaxed to the lowest energy configuration. Yellow circles correspond to silicon atoms, 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. 5 (green curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

bottom row of DFT models shows the same three surface bonding configurations on SiGe(001) but instead with Si termination.

In order to compare the relative thermodynamic stability of each system, gas phase species were added to ensure that each system has the same number of atoms. Column (A) compares the total energy of the clean SiGe(001) surface terminated in either Ge dimers or Si dimers. As shown Fig. 8, the clean Ge terminated surface has a lower total energy than the Si terminated surface. This is consistent with the surface being more thermodynamically stable with Ge dangling bonds; since Ge bonds are weaker than Si bonds, it is reasonable that the thermodynamically preferred under-coordinated atoms are Ge. Columns (B&C) compare the total energy of the SiGe(001) surface in the two most stable H<sub>2</sub>O<sub>2</sub>(g) dosed SiGe(001) bonding configurations. In contrast to the clean surface, the systems are now more stable when they are terminated with Si atoms (bottom row) rather than Ge atoms (top row). This is due to the stronger bond that is formed during Si-OH or Si-O bonding compared to Ge-OH or Ge-O bonding. While the total energy calculations are slightly different due to the bottom most layer being either Ge-H vs. Si-H terminated, the difference in energy value of these bonds does not affect the overall trend presented herein.

DFT simulations were performed to verify the bonding configuration and DOS of TMA dosed onto the  $H_2O_2(g)$  functionalized SiGe surface and are shown in Fig. 9. This model was developed by bonding monomethylaluminum (MMA) to the oxygen species on the OH-Si-O-Si-OH structure shown in the bottom row of column C in Fig. 8. The model was subsequently relaxed. During relaxation, the aluminum atoms pulled the oxygen that had previously inserted into the Si/Ge dimer bond out of the dimer bond to form an oxygen bridge bonded between two aluminum atoms above the dimer. This structure is consistent with the STM image and line traces of TMA/H<sub>2</sub>O<sub>2</sub>/SiGe (Fig. 4 A&B) with row spacing identical to the clean surface. The DOS of this structure was calculated and shows no states in the band gap, consistent with STS results in Fig. 5 (green curve) verifying that the TMA/H<sub>2</sub>O<sub>2</sub>/SiGe structure provides an electrically passive unpinned interface with no mid-gap defect states. The band gap of the DFT calculated DOS is smaller than the actual band gap of the system due to the standard PBE band gap underestimation. Note that the exact atomic positions of all atoms in the DFT models presented herein are included in the supplementary material.

#### 6. Conclusion

 $H_2O_2(g)$  was employed to functionalize and passivate the Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface. The clean Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface is terminated with Ge dimers; RT dosing of  $H_2O_2(g)$  onto the clean surface results in either two or three oxygen species per surface Ge dimer successfully passivating the dangling bonds on the surface Ge dimers. When the RT H<sub>2</sub>O<sub>2</sub>/Si<sub>0.6</sub>Ge<sub>0.4</sub>(001) surface is annealed above ~150 °C, the atoms near the surface undergo a "flip" or place exchange pushing Ge atoms subsurface while bringing Si to the surface. This occurs because, upon thermal activation, it is most thermodynamically favorable for Si to bond to oxygen containing adsorbates. This phenomenon allows for manipulation of the H<sub>2</sub>O<sub>2</sub>/SiGe interface by annealing. By "flipping" the Ge and Si surface atoms and terminating the SiGe(001) surface in Si-OH and Si-O, high-k ALD precursors can directly react to the Si terminated surface. Once the surface has been functionalized with  $H_2O_2(g)$ , TMA is dosed resulting in a high nucleation density of Al-O bonds. Dosing TMA onto the  $H_2O_2/Si_{0.6}Ge_{0.4}(001)$  surface results in an electrically passive thermally stable monolayer of Al-O-Si bonds which serves as an ideal template for further high-k deposition. DFT modeling verified the bonding configuration of the  $H_2O_2(g)$  only and  $TMA + H_2O_2(g)$  dosed Si<sub>0.5</sub>Ge<sub>0.5</sub>(001) surface, and the total energy calculations were consistent with experimental data demonstrating the Ge-Si "flip" phenomenon on the  $H_2O_2/SiGe$  surface. Using  $H_2O_2(g)$  as an oxidant precursor provides a high density of reactive oxygen containing adsorbates which nucleate Al<sub>2</sub>O<sub>3</sub> growth when dosed with TMA. It is expected that the Si – OH functionalized surface can directly form strong bonds to most high-k ALD metal precursors and, if any unpassivated sites remain on this Si terminated surface after oxide deposition, they can be passivated via forming gas anneal.

#### Acknowledgments

This work was supported by the Semiconductor Research Corporation (Task 2051.001) in coordination with Applied Materials (Task 2181.001) and Global Foundries (Task 2451.001). The SiGe wafers were provided by Applied Materials.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.susc.2014.08.027.

### References

- [1] J. Welser, J. Hoyt, J. Gibbons, IEEE (1992) 1000.
- [2] J. Welser, J. Hoyt, S.-I. Takagi, J. Gibbons, IEEE (1994) 373.
- [3] S. Datta, J. Brask, G. Dewey, M. Doczy, B. Doyle, B. Jin, J. Kavalieros, M. Metz, A. Majumdar, M. Radosavljevic, IEEE (2004) 194.
- [4] K.J. Kuhn, A. Murthy, R. Kotlyar, M. Kuhn, ECS Trans. 33 (2010) 3.
- [5] M. Caymax, G. Eneman, F. Bellenger, C. Merckling, A. Delabie, G. Wang, R. Loo, E. Simoon, I. Mitard, R. Do Logar, IEEE (2000) 1
- Simoen, J. Mitard, B. De Jaeger, IEEE (2009) 1. [6] K. Kita, S. Wang, M. Yoshida, C. Lee, K. Nagashio, T. Nishimura, A. Toriumi, IEEE (2009) 1.
- [7] C. Lee, T. Nishimura, N. Saido, K. Nagashio, K. Kita, A. Toriumi, IEEE (2009) 1.
- [8] C.H. Lee, T. Nishimura, K. Nagashio, K. Kita, A. Toriumi, IEEE Trans. 58 (2011) 1295.
- [9] C.H. Lee, T. Tabata, T. Nishimura, K. Nagashio, K. Kita, A. Toriumi, ECS Trans. 19 (2009) 165.
- [10] F. LeGoues, R. Rosenberg, B. Meyerson, Appl. Phys. Lett. 54 (1989) 644.
- [11] P. Zimmerman, G. Nicholas, B. De Jaeger, B. Kaczer, A. Stesmans, L.-A. Ragnarsson, D. Brunco, F. Leys, M. Caymax, G. Winderickx, IEEE (2006) 1.
- [12] J. Mitard, B. De Jaeger, F. Leys, G. Hellings, K. Martens, G. Eneman, D. Brunco, R. Loo, D. Shamiryan, T. Vandeweyer, Record ION/IOFF performance for 65 nm Ge pMOSFET and novel Si passivation scheme for improved EOT scalability, 2008. 873.
- [13] L. Gomez, C. Ni Chléirigh, P. Hashemi, J. Hoyt, IEEE 31 (2010) 782.
- [14] R. Pillarisetty, B. Chu-Kung, S. Corcoran, G. Dewey, J. Kavalieros, H. Kennel, R. Kotlyar, V. Le, D. Lionberger, M. Metz, IEEE 6.7 (2010) 1.
- [15] C. Ni Chleirigh, O. Olubuyide, J. Hoyt, IEEE (2005) 203.
- [16] S. Chatterjee, S. Samanta, H. Banerjee, C. Maiti, Thin Solid Films 422 (2002) 33.
- [17] G. Lucovsky, H. Yang, Y. Wu, H. Niimi, Thin Solid Films 374 (2000) 217.
- [18] B. Cheng, M. Cao, R. Rao, A. Inani, P. Vande Voorde, W.M. Greene, J.M. Stork, Z. Yu, P.M. Zeitzoff, J.C. Woo, IEEE Trans. 46 (1999) 1537.
- [19] J. Zhang, J. Yuan, Y. Ma, Solid State Electron. 44 (2000) 2089.
- [20] J. Zhang, J. Yuan, Y. Ma, A. Oates, Solid State Electron. 44 (2000) 2165.
- [21] H. Zhang, R. Solanki, B. Roberds, G. Bai, I. Banerjee, J. Appl. Phys. 87 (2000) 1921.
- [22] E. Cartier, J. Stathis, D. Buchanan, Appl. Phys. Lett. 63 (1993) 1510.
- [23] K.L. Brower, Phys. Rev. B 38 (1988) 9657.
- [24] K.L. Brower, S. Myers, Appl. Phys. Lett. 57 (1990) 162.
- [25] M.L. Reed, J.D. Plummer, J. Appl. Phys. 63 (1988) 5776.
- [26] S. Swaminathan, M. Shandalov, Y. Oshima, P.C. McIntyre, Appl. Phys. Lett. 96 (2010) (082904–082904–3).
- [27] H.-B. Wang, D.-Y. Ma, F. Ma, K.-W. Xu, J. Vac. Sci. Technol. B 30 (2012) 040601.
- [28] D. Wu, J. Lu, E. Vainonen-Ahlgren, E. Tois, M. Tuominen, M. Östling, S.-L. Zhang, Solid State Electron. 49 (2005) 193.
- [29] S.L. Manatt, M.R. Manatt, Chem. Eur. J. 10 (2004) 6540.
- [30] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
- [31] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- [32] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
- [33] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
- [34] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) (1396–1396).
- [35] J. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1996) 1396.
- [36] G.G. Jernigan, P.E. Thompson, C.L. Silvestre, Surf. Sci. 380 (1997) 417.
- [37] D. Godbey, M. Ancona, J. Vac. Sci. Technol. B 11 (1993) 1120.
- [38] D. Godbey, M. Ancona, Appl. Phys. Lett. 61 (1992) 2217.
- [39] D. Godbey, M. Ancona, J. Vac. Sci. Technol. B 11 (1993) 1392.
- [40] R.M. Feenstra, J.A. Stroscio, A. Fein, Surf. Sci. 181 (1987) 295.
- [41] N. Lang, Phys. Rev. B 34 (1986) 5947.
- [42] J. Tersoff, D. Hamann, Phys. Rev. B 31 (1985) 805.
- [43] O. Gurlu, H.J. Zandvliet, B. Poelsema, Phys. Rev. Lett. 93 (2004) 066101.
- [44] L. Kipp, R. Manzke, M. Skibowski, Solid State Commun. 93 (1995) 603.
- [45] T. Kaufman-Osborn, E.A. Chagarov, A. Kummel, J. Chem. Phys. 140 (2014) 204708.
  [46] L. Papagno, D. Frankel, Y. Chen, L. Caputi, J. Anderson, G. Lapeyre, Surf. Sci. 248 (1991) 343.
- [47] J. Kerr, D. Lide, CRC Handbook of Chemistry and Physics, 81st ed. CRC Press, Boca Raton, FL, USA, 2000.
- [48] T.J. Grassman, S.R. Bishop, A.C. Kummel, Surf. Sci. 602 (2008) 2373.
- [49] D.-S. Lin, S.-Y. Pan, M.-W. Wu, Phys. Rev. B 64 (2001) 233302.