Formation of atomically ordered and chemically selective Si—O—Ti monolayer on Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) for a MIS structure via H\textsubscript{2}O\textsubscript{2}(g) functionalization

Sang Wook Park, Jong Yoon Choi, Shariq Siddiqui, Bhagawan Sahu, Rohit Galatage, Naomi Yoshida, Jessica Kachian, and Andrew C. Kummel

Materials Science and Engineering Program, University of California, La Jolla, San Diego, California 92093, USA
TD Research, GlobalFoundries USA Inc., 257 Fuller Road, Albany, New York 12203, USA
Applied Materials, Inc., Santa Clara, California 95054, USA
Department of Chemistry and Biochemistry, University of California, La Jolla, San Diego, California 92093, USA

(Received 11 July 2016; accepted 19 October 2016; published online 14 November 2016)

Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) surfaces were passivated and functionalized using atomic H, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), and either tetrakis(dimethylamino)titanium (TDMAT) or titanium tetrachloride (TiCl\textsubscript{4}) and studied in situ with multiple spectroscopic techniques. To passivate the dangling bonds, atomic H and H\textsubscript{2}O\textsubscript{2}(g) were utilized and scanning tunneling spectroscopy (STS) demonstrated unpinning of the surface Fermi level. The H\textsubscript{2}O\textsubscript{2}(g) could also be used to functionalize the surface for metal atomic layer deposition. After subsequent TDMAT or TiCl\textsubscript{4} dosing followed by a post-deposition annealing, scanning tunneling microscopy demonstrated that a thermally stable and well-ordered monolayer of Ti\textsubscript{O} was deposited on Si\textsubscript{0.5}Ge\textsubscript{0.5}(110), and X-ray photoelectron spectroscopy verified that the interfaces only contained Si—O—Ti bonds and a complete absence of GeO\textsubscript{x}. STS measurements confirmed a TiO\textsubscript{x} monolayer without mid-gap and conduction band edge states, which should be an ideal ultrathin insulating layer in a metal-insulator-semiconductor structure. Regardless of the Ti precursors, the final Ti density and electronic structure were identical since the Ti bonding is limited by the high coordination of Ti to O. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4966690]

I. INTRODUCTION

As the size of Si-based complimentary metal-oxide semiconductor (CMOS) devices decreases, new materials have been developed to enhance device performance. Silicon-germanium (SiGe) has received much attention due to its ability to maintain good performance in CMOS devices while being compatible with the existing Si infrastructure. SiGe has been utilized in n-type MOS transistors to improve electron mobility by applying a biaxial tensile stress into Si channels. Alternatively, when SiGe materials were employed in the source or drain areas, a compressive stress was utilized for the enhancement of hole mobility in p-type MOS transistors. Furthermore, due to the higher mobility of SiGe compared to silicon, SiGe has been employed as a channel material in p-type MOS transistors. However, to utilize SiGe in the source and drain in very large scale integrated (VLSI) technology, source/drain resistance must be minimized.

While few studies have looked at passivation of SiGe as a contact material, many studies have reported passivation of SiGe and Ge as channel materials. Extensive studies have been reported to passivate the channel surfaces with low interface state density (D\textsubscript{i}) and unpinned Fermi level. Passivation of Ge via ozone oxidation below 400 °C resulted in low D\textsubscript{i} by suppressing the formation of Ge suboxide in favor of GeO\textsubscript{2}. Lee et al. demonstrated that water (H\textsubscript{2}O) was effective in passivating Ge(001) surfaces as verified by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements. Recent studies verified that hydrogen peroxide vapor (H\textsubscript{2}O\textsubscript{2}(g)) formed a more stable passivation layer and a higher nucleation density for atomic layer deposition (ALD) than H\textsubscript{2}O\textsubscript{2}(g) on Ge(001). SiGe(001), and SiGe(110) surfaces, thereby improving the formation of high-k dielectrics.

Extremely thin insulator interfaces have been used to form unpinned contacts on Ge and SiGe substrates. Kobayashi et al. deposited an ultrathin tunnel barrier of Si\textsubscript{3}N\textsubscript{4} between the contact metal and a Ge substrate to form a metal-insulator-semiconductor (MIS) structure. However, the insulating layer of Si\textsubscript{3}N\textsubscript{4} introduced a large tunneling resistance due to the significant conduction band offset (CBO) to the Ge substrate. Lieten et al. formed a thin Ge\textsubscript{3}N\textsubscript{4} layer on Ge substrates for ohmic contacts, and this layer passivated Ge surface states. Lin et al. employed a 7.1 nm-thick TiO\textsubscript{2} interfacial layer in a MIS structure to reduce the tunneling resistance by having nearly zero CBO. The TiO\textsubscript{2} films deposited on SiGe(001) for MIS capacitors minimized D\textsubscript{i} as demonstrated by capacitance-voltage and conductance-voltage measurements.

In this report, the topological, electronic, and chemical properties of Si\textsubscript{0.5}Ge\textsubscript{0.5}(110) were studied for the application as a MIS structure. Exposure of atomic H or H\textsubscript{2}O\textsubscript{2}(g) passiv-
ated the dangling bonds on sputter-cleaned Si$_{0.5}$Ge$_{0.5}$(110) with hydrogen atoms or hydroxyl groups resulting in an unpinned Fermi level. H$_2$O$_2$(g) also was utilized to form a high density of OH sites which is advantageous for the formation of a high density ultrathin insulating layer in a MIS structure. Subsequent tetakis(dimethylamino)titanium (TDMAT) or titanium tetrachloride (TiCl$_4$) dosing via ALD functionalized the hydroxyl-terminated Si$_{0.5}$Ge$_{0.5}$(110) with Ti atoms, thereby forming a monolayer of TiO$_x$ on Si$_{0.5}$Ge$_{0.5}$(110) surfaces. Annealing studies demonstrated the thermal and electronic stability of a TiO$_x$ monolayer on Si$_{0.5}$Ge$_{0.5}$(110) surfaces and the complete absence of GeO$_x$ at the interface; instead the interface was composed solely of Si—O—Ti bonds. Each experimental process was probed using in situ STM, STS, and X-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL

P-type Si$_{0.5}$Ge$_{0.5}$(110) films with 10$^{15}$ cm$^{-3}$ B doping grown on Si(110) wafers were provided by GLOBAL-FOUNDRIES and diced into 10.5 $\times$ 5.5 mm$^2$ pieces. Each sample was repeatedly cleaned via a degassing method using acetone, methanol, and deionized water then dried with N$_2$ gas. Samples were loaded into a customized Omicron ultra-high vacuum (UHV) preparation chamber with a base pressure of 1 $\times$ 10$^{-10}$ Torr and prepared by combined sputtering and annealing processes. The sputtering process utilized a 1.5 kV argon ion (Ar$^-$) beam (Model 1403 ion gun, Nonsequitur Technologies) with a current of 0.9 $\mu$A and an Ar gas pressure of 6 $\times$ 10$^{-7}$ Torr for 30 min, while the sample temperature was maintained at 500 °C using resistive pyrolytic boron nitride (PBN) heating. An annealing process was performed at a sample temperature of 500 °C for 30 min. After repeated sputter and annealing cycles, the chemical, topological, and electronic characteristics were studied via in situ XPS, STM, and STS.

Sputter-cleaned Si$_{0.5}$Ge$_{0.5}$(110) samples were reacted with atomic hydrogen in the UHV preparation chamber using a thermal gas cracker (Atomic Hydrogen Source, Veeco). The gas pressure was controlled via a leak valve and measured with an ion gauge; the exposure was calculated in terms of Langmuirs (1 Langmuir (L) = 1 $\times$ 10$^{-6}$ Torr 1 s). During the atomic hydrogen dose, the temperature of filament was maintained between 1800 and 2200 °C while the temperature of Si$_{0.5}$Ge$_{0.5}$(110) samples was maintained at 300 °C; the cracking efficiency was expected to be 30%, but the reported amount of atomic H dose was estimated based solely on the H$_2$ pressure, so the actual amount of atomic H dose should be smaller compared to the reported value. During the experiment, H$_2$ was dosed at 1 $\times$ 10$^{-5}$ Torr for 360 s; this is reported below as 3600 L of atomic H.

To avoid air exposure, samples were transferred to an in situ ALD chamber with a base pressure of 1 $\times$ 10$^{-7}$ Torr. H$_2$O$_2$(g), TDMAT, and TiCl$_4$ were dosed at 25 °C surface temperature by filling the dosing chamber at 25 °C without a carrier gas. As a control experiment, Si$_{0.5}$Ge$_{0.5}$(110) samples were also dosed with H$_2$O(g) at 25 °C. To achieve saturated nucleation on Si$_{0.5}$Ge$_{0.5}$(110) surfaces, a 30% solution of H$_2$O$_2$(aq) (Fisher Scientific), TDMAT (99%, Strem Chemicals), and TiCl$_4$ (99%, Strem Chemicals) were utilized. In this paper, the “H$_2$O$_2$(aq)” refers to the mixture of H$_2$O(g)/H$_2$O(g); the H$_2$O$_2$(aq) solution was composed of both components and the H$_2$O$_2$(g) reaction should be dominant due to its high reactivity. Based on a previous report, a 30% solution of H$_2$O$_2$(aq) resulted in a vapor of 2.67% H$_2$O$_2$(g) at 25 °C; therefore, the actual amount of H$_2$O$_2$(g) involved in the chemical reaction should be smaller than the reported amount of total vapor below.

During the experiment, H$_2$O$_2$(aq) was dosed at 30 mTorr for 150 s to provide 4.5 $\times$ 10$^6$ L of total vapor from H$_2$O$_2$(aq); the maximum amount of H$_2$O$_2$(g) should be 120 000 L. Before the samples were transferred to the ALD chamber, the chamber was baked overnight by heating the chamber walls to 120 °C to minimize the background O and H$_2$O contaminations. In addition, several cycles of H$_2$O$_2$(g), TDMAT, and TiCl$_4$ were pre-dosed to minimize the chemical reaction with the stainless-steel chamber walls during the actual experiments.

Chemical properties from each experimental step were studied with an in situ monochromatic XPS (XM 1000 MkII/SHERA, Omicron Nanotechnology). For the XPS studies, an Al K$_\alpha$ source (1486.7 eV) was utilized as an anode material; spectra were measured with a constant analyzer-energy (CAE) mode with a pass energy of 50 eV and a step width of 0.1 eV. The take-off angle between the analyzer axis and the sample normal was 60° and the analyzer-acceptance angle was 7°. For peak shape analysis, a CASA XPS v.2.3 program was utilized via a Shirley background subtraction.

The samples were transferred to an in situ STM chamber (LT-STM, Omicron Nanotechnology) with a base pressure of 1 $\times$ 10$^{-11}$ Torr to probe the topological and electronic properties on the Si$_{0.5}$Ge$_{0.5}$(110) surface after each experimental process. Constant-current mode ($I_{sp}$ = 200 pA) STM was performed with a sample bias between −2.0 and −1.8 V to obtain filled-state STM images. Variable-z mode STS was performed with a modulation signal (0.1 V, 650 Hz) through an external lock-in amplifier (SR830 DSP, Stanford Research Systems) to directly obtain the $dI/dV$ along with the I/V spectra while varying the sample bias from −1.5 to +1.5 V and simultaneously moving the tip position forward then backward during the scan to increase the sensitivity with regard to small currents. As described in a previous report, the raw I/V data were smoothed through a low-pass filter with energy width of (3.0 eV)/2π (frequency parameter value in filter of (3.0 eV)$^{-1}$). This smoothing step led to a broadened I/V, denoted as (I/V), which forms a suitable normalization quantity for dI/dV. For the precise STS measurements, at least 5 individual spectra of (dI/dV)/(I/V) were resealed from 0 to 1 and subsequently averaged into a single spectrum in the STS images. Since the (dI/dV)/(I/V) spectrum has the property that band onsets have a linear dependence on the sample bias, they were fit with a linear function to extract the band edge energies. Based on previous STS studies, a fitting method was performed to extract the band edge energies for the (dI/dV)/(I/V) spectra using
a linear function depending on both operational temperature and alternating current (AC) modulation. The calculated linear fits for each STS measurement were included as the solid lines and the onsets of the linear fits corresponding to the band edge energies were calculated with error ranges. The obtained error ranges from the fitting method were standard errors of the least-squares fits and did not reflect thermal broadening nor inaccuracies due to band edge states. Note that the resolution of the bias step from the experimental STS measurements was lower than the extracted error ranges from the linear fits. These results from the linear fits using a very large number of data points; therefore, the small reported error is the uncertainty in the fit to the data and does not reflect systematic errors in the measurements and fittings such as small band tail states and the work function of the tip.

III. RESULTS AND DISCUSSION

To understand the intrinsic surface reactivity, a clean Si0,5Ge0,5(110) surface without carbon and oxygen should be prepared. However, several cleaning procedures utilizing aqueous HCl24 or HF25–27 cleaning left SiGe surfaces with oxygen and carbon contaminations. Conversely, it was demonstrated that a combined sputtering and annealing process produces clean SiGe surfaces without carbon and oxygen.3,14 Si0,5Ge0,5(110) surfaces were cleaned via several cycles of sputtering with an Ar gas pressure of 6 × 10−2 Torr for 30 min and annealing at 500 °C, and the cleanliness of the surfaces was verified by an in situ XPS showing no carbon and oxygen at the surfaces. As explained in the supplementary material, a sputter-cleaned Si0,5Ge0,5(110) should be terminated with adatoms, which induce a pinned Fermi level due to the half-filled dangling bonds. To form an unpinned Fermi level, 3600 L of atomic H was dosed onto Si0,5Ge0,5(110) while the substrate temperature was maintained at 300 °C. Afterwards, sputter-cleaned or atomic H dosed Si0,5Ge0,5(110) samples were transferred to an in situ ALD chamber to functionalize the surfaces with hydroxyls. For the saturation reaction, 4.5 × 106 L of vapor from H2O2(gaq), which was composed of approximately 120 000 L H2O2(g) and the balance H2O(g), was dosed onto the samples at 25 °C and this amount was expected to be a saturation dose which would fully react with Si0,5Ge0,5(110) surfaces.

To understand the surface reaction after atomic H or H2O2(g) dosing of Si0,5Ge0,5(110) surfaces, schematic models were proposed based on the XPS studies in the supplementary material. XPS data showed that a full saturation dose of H2O2(g) at 25 °C resulted in an O/(Si + Ge) ratio of 19%, which corresponded to ~1.05 monolayers (see Fig. S3 in the supplementary material). For a 25 °C H2O2 dose on H-terminated Si0,5Ge0,5(110), the O/(Si + Ge) ratio was identical to 25 °C H2O2/Si0,5Ge0,5(110) demonstrating a stronger reactivity of 25 °C H2O2(g) on H-terminated Si0,5Ge0,5(110) to replace H atoms with hydroxyls. In addition, the chemical shifts of Ge—O and Si—O on 25 °C H2O2/Si0,5Ge0,5(110) and 25 °C H2O2/300 °C atomic H/Si0,5Ge0,5(110) surfaces mainly corresponded to Ge2+ and Si2+ (see Fig. S5 in the supplementary material). Fig. 1 presents schematic diagrams for 25 °C H2O2(g) reactions with clean or H-terminated Si0,5Ge0,5(110) surfaces. As shown in Fig. 1(a), a saturation H2O2(g) dose on a clean Si0,5Ge0,5(110) surface, which was terminated with half-filled dangling bonds from adatoms, formed hydroxyls on dangling bonds along with oxygen inserted into adatom backbonds with H2(g) as a byproduct. Similarly, when a H-terminated Si0,5Ge0,5(110) surface was dosed with a saturation H2O2(g) at 25 °C, H2O2(g) was sufficiently reactive to replace H atoms with hydroxyls on Si0,5Ge0,5(110) and to insert additional oxygen atoms into Si—Ge backbonds, producing H2O(g) as a byproduct as shown in Fig. 1(b). In sum, when a clean or H-terminated Si0,5Ge0,5(110) surface was exposed to a saturation dose of H2O2(g) at 25 °C, the top surface should be terminated with hydroxyls and additional oxygen atoms were likely to break the backbonds resulting in oxygen insertion consistent with

![Diagram](image)

FIG. 1. Proposed models of clean and H-terminated Si0,5Ge0,5(110) surfaces dosed with 25 °C H2O2(g). (a) A schematic diagram of a 25 °C H2O2(g) dosing of a clean Si0,5Ge0,5(110) surface terminated with dangling bonds (red). The surface was terminated with hydroxyls with O insertion into backbonds and the byproduct is H2(g). (b) A schematic diagram of a 25 °C H2O2(g) dose on a H-terminated Si0,5Ge0,5(110) surface. H2O2(g) was sufficiently reactive to form hydroxyl termination at the surface with H2O(g) as a byproduct.

![Diagram](image)

FIG. 2. STS of H2O2 dosed Si0,5Ge0,5(110) surfaces STS spectra with fits to estimate VB and CB edges. After a 25 °C H2O2(g) dose, the electronic structures are nearly identical with an unpinned Fermi level regardless of an atomic H dose.
the XPS intensities and chemical shifts corresponding to Ge$^{2+}$ and Si$^{2+}$ in the supplementary material.

The electronic properties of 25 °C $\text{H}_2\text{O}_2$/Si$_{0.5}$Ge$_{0.5}$(110) and 25 °C $\text{H}_2\text{O}_2$/300 °C atomic H/Si$_{0.5}$Ge$_{0.5}$(110) surfaces were studied through STS measurements in Fig. 2. STS measurements of $(\text{d}I/\text{d}V)/(I/V)$ are known to be proportional to the local density of states (LDOS). Therefore, STS measurements were performed to understand the electronic structures of the surfaces. STS spectra of 25 °C $\text{H}_2\text{O}_2$/Si$_{0.5}$Ge$_{0.5}$(110) surface (black) demonstrated the nearly identical electronic structure to 25 °C $\text{H}_2\text{O}_2$/300 °C atomic H/Si$_{0.5}$Ge$_{0.5}$(110) surface (yellow) with ±0.1 V difference with regard to valence band maximum (VBM) and conduction band minimum (CBM), respectively. While the clean p-type Si$_{0.5}$Ge$_{0.5}$(110) surface had a Fermi level pinned near mid-gap (as demonstrated in Fig. S2 in the supplementary material), the Fermi levels of 25 °C $\text{H}_2\text{O}_2$/Si$_{0.5}$Ge$_{0.5}$(110) and 25 °C $\text{H}_2\text{O}_2$/300 °C atomic H/Si$_{0.5}$Ge$_{0.5}$(110) surfaces were positioned closer to the VB edge consistent with Fermi level unpinning. In addition, the bandgaps were decreased due to the increased density of states near VB and CB edges. Based on STS analysis, it was demonstrated that a 25 °C $\text{H}_2\text{O}_2$ doping on clean or H terminated Si$_{0.5}$Ge$_{0.5}$(110) resulted in electronically identical surfaces.

To functionalize the surfaces with Ti atoms for the TiO$_2$ formation, the 25 °C $\text{H}_2\text{O}_2$/Si$_{0.5}$Ge$_{0.5}$(110) and 25 °C $\text{H}_2\text{O}_2$/300 °C atomic H/Si$_{0.5}$Ge$_{0.5}$(110) surfaces were dosed with 4.5 × 10$^5$ L of TDMAT or 4.5 × 10$^5$ L of TiCl$_4$ without carrier gas at 25 °C in an in situ ALD chamber. Fig. 3 shows the chemical compositions after a saturation

FIG. 3. XPS chemical compositions and Si 2p and Ge 3d spectra of TDMAT or TiCl$_4$ dosed Si$_{0.5}$Ge$_{0.5}$(110) surfaces. (a) Chemical intensities normalized to Si 2p + Ge 3d peaks upon a 25 °C TDMAT dose. Ti:O:C ratios were 1:3:2 with error ranges of ±0.02 and no N peak was observed. After 300 °C annealing, Ti and O ratios were constant consistent with a thermally stable TiO$_x$ monolayer while C was decreased due to desorption of methanes or ethanes. (b) Ge 3d (green) and Si 2p (purple) peaks upon a 25 °C TDMAT dose followed by 300 °C PDA. After a TDMAT dose at 25 °C, XPS showed shoulder peaks (red) on both Ge 3d and Si 2p peaks corresponding to Ge—O—Ti and Si—O—Ti components. After annealing at 300 °C, C atomic H/TiCl$_4$ removed GeO$_2$ and increased SiO$_2$/Si resulting in exclusively Si—O—Ti bonds increased. The shoulder peak of Si was shifted toward the higher binding energy by 1.0 eV after 300 °C PDA. (c) Table shows the ratios of GeO$_2$/Ge and SiO$_2$/Si with standard errors after 25 °C TDMAT dose and 300 °C PDA. 300 °C PDA removed GeO$_2$ and increased SiO$_2$/Si resulting in exclusively Si—O—Ti termination on Si$_{0.5}$Ge$_{0.5}$(110). (d) Chemical intensities normalized to Si 2p + Ge 3d peaks upon a 25 °C TiCl$_4$ dose. Ti:O:C ratios were 1:3:2 and after 300 °C annealing, Ti and O ratios were constant while Cl was decreased due to a HCl(g) desorption. These data were consistent with a thermally stable TiO$_x$ monolayer while Cl was decreased due to the desorption of HCl. (e) XPS spectra upon a 25 °C TiCl$_4$ dose followed by 300 °C PDA. The change in shoulder peaks after 300 °C PDA was identical with (b). (f) The table shows the ratios of GeO$_2$/Ge and SiO$_2$/Si with standard errors after 25 °C TiCl$_4$ dose and 300 °C PDA. The surface was also composed of Si—O—Ti bonds after 300 °C PDA.
dose of TDMAT or TiCl₄ followed by 300 °C post-deposition annealing (PDA); the Ge 3d and Si 2p peaks are also presented. Based on the Hartree-Slater model, all elemental intensities were corrected using photoelectron cross sections (Si 2p-0.817, Ge 3d-1.42, Ti 2p-7.81, O 1s-2.93, C 1s-1, Cl 2p-2.29) and normalized to the combination of Si 2p and Ge 3d peaks to estimate the ratios of each chemical component on the surfaces. As shown in Fig. 3(a), when 25 °C TDMAT was dosed onto 25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110) surface, the ratios of Ti:O:C were 1:3:2 and no N signal was observed. In addition, the shoulder peaks of Si 2p and Ge 3d in Fig. 3(b) had the identical binding energies as those on the H₂O₂ dosed Si₀.₅Ge₀.₅(110) surfaces (shown in Fig. S5 in the supplementary material); this demonstrated that Si—O—Ti and Ge—O—Ti bonds formed by H₂O remained intact after low temperature TDMAT dosing.

After 300 °C PDA, the ratio of Ti and O remained constant demonstrating a thermally stable TiOₓ monolayer while the C ratio was decreased. To explain these results, it was proposed that, upon annealing, Ti—O—Ti bonds were formed allowing C₂H₆ desorption. In addition, the shoulder peak of Si 2p was increased while the shoulder peak Ge 3d was disappeared consistent with the Si₀.₅Ge₀.₅(110) surfaces being terminated with only Si—O—Ti bonds. It was expected that the thermal energy at 300 °C activated the Si atoms to diffuse to the top surface to bond with oxygen atoms and drove the Ge atoms to the subsurface due to the stronger bonds between Si and O compared to the bonds between Ge and O. Furthermore, the shoulder peak of Si 2p was shifted toward the higher binding by 1.0 eV after 300 °C PDA (between 101.5 and 102.5 eV) corresponding to Si²⁺ on 300 °C anneal/25 °C TDMAT/25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110); this was consistent with the Si atoms making additional Si—O bonds upon annealing.

TiCl₄, an inorganic precursor, was also dosed onto 25 °C H₂O₂/Si₀.₅Ge₀.₅(110) surface at 25 °C to provide a comparison between an inorganic precursor and TDMAT, an organometallic precursor. Fig. 3(d) showed that the ratios of Ti:O:Cl were 1:3:2 after a TiCl₄ dose at 25 °C on 25 °C H₂O₂/Si₀.₅Ge₀.₅(110) consistent with the results of TDMAT dosed 25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110). Moreover, the shoulder peaks of Si 2p and Ge 3d in Fig. 3(e) had identical binding energies as 25 °C TDMAT/25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110) in Fig. 3(c). This demonstrated that each Ti atom was likely to form Ti—O bonds by replacing two ligands with two oxygen atoms at the surface regardless of Ti precursors.

For the 25 °C TiCl₄/25 °C H₂O₂/Si₀.₅Ge₀.₅(110), a subsequent PDA at 300 °C demonstrated that the monolayer of TiOₓ was thermally stable as shown by the constant Ti and O ratios; however, the ratio of Cl was decreased due to the desorption of Cl₂(g). In addition, as demonstrated in Fig. 3(e), the shoulder peaks of Si spectra showed a shift to higher binding energy while the shoulder peaks of Ge spectra were removed from the interface upon 300 °C PDA consistent with the results of 300 °C anneal/25 °C TDMAT/25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110) in Fig. 3(b).

In Fig. 4, STS and XPS chemical shift measurements were performed to understand the electronic and chemical characteristics of a TiOₓ monolayer on Si₀.₅Ge₀.₅(110) surfaces. STS measurements in Fig. 4(a) verified identical electronic properties for 300 °C anneal/25 °C TDMAT/25 °C H₂O₂/300 °C atomic H/Si₀.₅Ge₀.₅(110) and 300 °C anneal/25 °C TiCl₄/25 °C H₂O₂/Si₀.₅Ge₀.₅(110) surfaces. The Fermi level was positioned closer to VB edge on both surfaces consistent with the band edge states. The reported VB positions are for the inner band gap. (b) Ti 2p peaks of TDMAT or TiCl₄ dosed Si₀.₅Ge₀.₅(110). The Ti 2p 3/2 peaks on both surfaces were positioned at 459.2 eV corresponding to Ti²⁺.
dosed with a 25 °C H₂O₂(g), the STS spectra after TDMAT or TiCl₄ dosing showed that state density near CB edge decreased; while consistent with the formation of a wide band monolayer of TiOₓ, a detailed understanding of this change requires density functional theory (DFT) calculations. A bilinear fit was performed to determine the onset VB edges and the inner VB onsets were reported in Fig. 4(a). The increase in the bandgap after TiOₓ formation is consistent with the formation for a wide bandgap TiOₓ layer.

Fig. 4(b) presented XPS spectra of Ti 2p peaks on TDMAT or TiCl₄ dosed Si₁₀.₅Ge₀.₅(110) surfaces to investigate the oxidation states. The positions of Ti 2p 3/2 and 1/2 spin-orbit components between two different Si₁₀.₅Ge₀.₅(110) surfaces were almost the same with an error range of ±0.1 eV. Furthermore, the positions of Ti 2p 3/2 peaks were located in 459.3 eV, and this binding energy corresponded to Ti⁴⁺ consistent with a proposed model of Ti atoms bonded to two O atoms with two other Ti—O or Ti—Cl bonds, which have stronger electronegativity than Ti atoms, as shown in detail below. Note that a pass energy of 50 eV was employed to achieve high intensity counts of the Ti 2p peak from a monolayer of TiOₓ. This pass energy causes the broadening in the Ti 2p peak, and it was not possible to uniquely deconvolute the Ti 2p peak, and it was not possible to uniquely deconvolute the Ti 2p spectra into several distinct contributions. Therefore, it is possible that the broadening of the Ti 2p peak might be partially attributed to chemical states other than Ti⁴⁺.

Proposed models of TDMAT or TiCl₄ dosed Si₁₀.₅Ge₀.₅(110) surfaces followed by 300 °C PDA are shown in Fig. 5. A proposed model in Fig. 5(a) shows that TDMAT molecules reacted with surface hydroxyl groups forming one Ti atom bonded to two oxygen atoms on Si₁₀.₅Ge₀.₅(110) surface, two other ligands reacted with weakly bound hydroxyl groups from the surface forming two Ti—O—CH₃ bonds, and NH(CH₃)₃ or NH₂(CH₃)₂ desorbed as byproducts; note that it was proposed that the back bonded oxygens remained intact and this was consistent with the XPS peak intensities and shifts in Figs. 3 and 4. Moreover, a proposed model including Ti—O—CH₃ bonds was consistent with the previous report. After 300 °C PDA, O≡Ti—CH₃ bonds and additional Si—O—Si bonds were formed and C₂H₆(g) desorbs as a byproduct consistent with the XPS peak intensities and shifts; however, the experimental ratio between Ti:O was 1:3, while the proposed model in Fig. 3 had a Ti:O ratio of 1:5. In order to explain the ratio difference, a model must consider that many of oxygens are located at the subsurface and the emitted electrons should be affected by an exponential attenuation function according to the depth. The electron escape depths for Ti and O peaks are 2 nm at normal incidence and decreased to 1 nm at 60° take-off angle, which is the experimental condition during the XPS measurements. Based on the proposed model in which the depths of oxygen are assumed to be 0, 3, and 6 Å, a simple attenuation estimate using the electron escape depth of 1 nm provides a Ti and O ratio of 1:4, which is closer to the experimental results.

A model is also provided for the TiCl₄ reaction, as shown in Fig. 5(b), and TiCl₄ molecules reacted with hydroxyl...
groups resulting in the formation of one Ti atom bonded to two oxygen atoms on Si_{0.5}Ge_{0.5}(110) surface while a HCl(g) desorbed as a byproduct. After 300 °C PDA, annealing induced the formation of Ti—O—Ti bonds allowing Cl_{2}(g) desorption and surface Si atoms formed additional Si—O backbonds. Note that proposed models were highly simplified to provide explanations with regard to the chemical compositions.

To compare the topology of Si_{0.5}Ge_{0.5}(110) surfaces dosed with TDMAT or TiCl_{4} followed by 300 °C PDA, STM images and line trace analyses are presented in Fig. 6. In Fig. 6(a), 300 °C anneal/25 °C TDMAT/25 °C H_{2}O_{2}/300 °C atomic H/Si_{0.5}Ge_{0.5}(110) surface showed consistent vertical rows. To analyze the row spacing, four different areas in the STM image were analyzed and line traces were performed as shown in Fig. 6(b). Line traces of 300 °C anneal/25 °C TDMAT/25 °C H_{2}O_{2}/300 °C atomic H/Si_{0.5}Ge_{0.5}(110) surface showed an average row spacing of 18.0 Å with a standard deviation of 1.7 Å and a standard error of 0.60 Å. This row spacing was more than twice the 8.0 Å of adatom spacing on a sputter-cleaned Si_{0.5}Ge_{0.5}(110) surface consistent with the proposed models in Fig. 5(a), in which one Ti atom is bonded to two oxygen atoms on Si_{0.5}Ge_{0.5}(110) surface with the oxygen backbond insertion. In comparison, Fig. 6(c) shows the STM image of 300 °C anneal/25 °C TiCl_{4}/25 °C H_{2}O_{2}/Si_{0.5}Ge_{0.5}(110) surface. The line traces in Fig. 6(d) show an average row spacing of 18.2 Å with a standard deviation of 1.3 Å and a standard error of 0.47 Å. Therefore, there is an identical row spacing for TDMAT and TiCl_{4} dosing followed by PDA within an error range demonstrated the formation of TiO_{x} monolayer with the same surface structure independent of precursors. Compared to the 11.8 Å average row spacing of a monolayer of Al_{2}O_{3} on Si_{0.5}Ge_{0.5}(110) surface, in which one Al atom was bonded to one oxygen atom with the ratio of Al:O to be 2:3 on Si_{0.5}Ge_{0.5}(110), the TiO_{x} row spacing was larger as shown in the proposed model in Figs. 5(a) and 5(b) for Ti making two bonds to surface O atoms.

IV. CONCLUSIONS

Clean or H-terminated Si_{0.5}Ge_{0.5}(110) surfaces were dosed with H_{2}O_{2}(g) at 25 °C to functionalize the surfaces with hydroxyls. STS measurements demonstrated that H_{2}O_{2}(g) resulted in the identical electronic and –OH terminated...
molecular structures on both clean and H-terminated Si_{10.5}Ge_{0.5}(110) surfaces. To form a monolayer of TiOₓ on hydroxyl-terminated Si_{10.5}Ge_{0.5}(110) surfaces, TDMAT or TiCl₄ were subsequently dosed at 25 °C on 25 °C H₂O₂/300 °C atomic H/Si_{10.5}Ge_{0.5}(110) and 25 °C H₂O₂/Si_{10.5}Ge_{0.5}(001) surfaces. XPS indicated that the ratio between Ti and O was 1:3 and remained constant upon 300 °C PDA demonstrating a thermally stable monolayer of TiOₓ regardless of Ti-based precursors. STM images showed that the row spacing of TiOₓ monolayer on Si_{10.5}Ge_{0.5}(110) surfaces was more than twice the adatom spacing on a clean Si_{10.5}Ge_{0.5}(110) verifying a proposed chemisorption model. XPS analysis verified that a monolayer of TiOₓ was composed of only Si—O—Ti bonds after PDA indicating the complete segregation of Si atoms. Furthermore, STS measurements were consistent with the monolayer of TiOₓ having no mid-gap and CB edge states, which should be an ideal ultrathin insulating layer for a MIS structure.

SUPPLEMENTARY MATERIAL

See supplementary material for the properties of Si_{10.5}Ge_{0.5}(110) surfaces.

ACKNOWLEDGMENTS

This work was supported in part by the Center for Low Energy Systems Technology (LEAST), one of the six centers of STARnet, a Semiconductor Research Corporation program (Grant No. 2013-VJ-2451) sponsored by MARCO and DARPA, NSF DMR 1207213, GLOBALFOUNDRIES, and Applied Materials. The Si_{10.5}Ge_{0.5} wafers were provided by GLOBALFOUNDRIES.  