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## Nitride passivation of the interface between high-k dielectrics and SiGe

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*In-situ* direct ammonia (NH<sub>3</sub>) plasma nitridation has been used to passivate the Al<sub>2</sub>O<sub>3</sub>/SiGe interfaces with Si nitride and oxynitride. X-ray photoelectron spectroscopy of the buried Al<sub>2</sub>O<sub>3</sub>/SiGe interface shows that NH<sub>3</sub> plasma pre-treatment should be performed at high temperatures (300 °C) to fully prevent Ge nitride and oxynitride formation at the interface and Ge out-diffusion into the oxide. C-V and I-V spectroscopy results show a lower density of interface traps and smaller gate leakage for samples with plasma nitridation at 300 °C. © *2016 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4939460]

To address the demand for scaling CMOS technology, novel device architectures such as fin field effect transistors (FinFETs) and nanowire FETs (NW-FETs) are proposed, which require thinner high-k dielectrics as well as channel materials with higher electron and hole mobility.<sup>1,2</sup> Silicon-Germanium (SiGe) alloys have shown a great promise for use as FinFETs and NW-FETs channels due to tunability of their carrier mobilities and band gaps by variation in Ge content and tensile/compressive stresses.<sup>3,4</sup> However, to ensure full integration of SiGe into the future CMOS technology, deposition of thin high-k dielectrics with low leakage and high interface quality on these alloys is crucial.<sup>5,6</sup>

*In-situ* nitridation is an efficient technique to passivate the high-k oxide/semiconductor interfaces that has been extensively investigated for Ge MOS device.<sup>7–9</sup> Remote plasma nitridation is known to terminate the oxide/Ge interface with Ge nitride or oxynitride, resulting in low density of interface traps (D<sub>it</sub>) and high thermal stability.<sup>8,10</sup> For Al<sub>2</sub>O<sub>3</sub>/ SiGe, electron cyclotron resonance (ECR) N<sub>2</sub> plasma nitridation showed better performance in post-nitridation processing during which a 1 nm thick Al<sub>2</sub>O<sub>3</sub> is deposited first to prevent the plasma damage.<sup>11</sup> Despite low D<sub>it</sub>, even for HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> bilayers, post-nitridation limits the equivalent oxide thickness (EOT) scaling to 3.0 nm.<sup>12</sup> This may be related to the challenge for fully nitriding Ge atoms in the presence of the more reactive Si atoms.

The present study demonstrates *in-situ* remote ammonia  $(NH_3)$  plasma treatment, prior to atomic layer deposition (ALD), as an effective method to passivate the interface

between  $Al_2O_3$  (as a model high-k dielectric) and SiGe(001) with minimal plasma damage. Oxide insulating properties and interface quality were evaluated by electrical characterization where nitrided interfaces showed a lower leakage current and a lower density of interface traps compared with samples with only HF wet clean. Chemical characterization of high-temperature NH<sub>3</sub> plasma-treated surfaces and buried interfaces by X-ray photoelectron spectroscopy (XPS) revealed selective nitridation of Si at the interface and strong suppression of Ge out-diffusion from the substrate into the oxide.

Metal-oxide-semiconductor capacitors (MOSCAPs) were fabricated on 12 nm thick p-type Si<sub>0.7</sub>Ge<sub>0.3</sub> (001) layers epitaxially grown on p-type Si(001) substrates (Applied Materials, Inc.). The native oxides on SiGe surfaces were removed by cyclic HF cleaning using 2% HF solution and Deionized (DI) water for 1 min in each solution for 2.5 cycles, ending with HF dip. ALD was performed in a Beneq TFS-200 continuous flow reactor, with Ar carrier gas. To deposit Al<sub>2</sub>O<sub>3</sub> on SiGe, 20 cycles of 45-ms trimethylaluminum (TMA) pre-pulses were followed by 30 cycles of 200 ms of TMA and 50 ms of H<sub>2</sub>O. After each TMA and H<sub>2</sub>O pulse, a 6-s Ar purge was employed. Prior to ALD, an in-situ clean/passivation was performed using RF NH<sub>3</sub> plasma at 25 W with 1:3 NH<sub>3</sub>:Ar ratio. Note that the plasma is within a few centimeters of the surface and thus prone to damage the substrates; these conditions were selected after testing over 20 processing conditions to determine the operating parameters for minimal plasma damage. MOSCAP fabrication was completed by thermal evaporation of Ni gate metal and Al back contacts. After fabrication, MOSCAPs were annealed in forming gas (5% H<sub>2</sub>, 95% N<sub>2</sub>) at 250 °C for 15 min.

Capacitance-Voltage (C-V) and Conductance-Voltage (G-V) spectroscopy were performed using AC modulation

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FIG. 1. C-V characteristics of HFtreated ((a) and (b)) versus NH<sub>3</sub>-treated ((c) and (d))  $Al_2O_3$ -SiGe(001) MOSCAPs with ALD at 120 °C and 300 °C. The C<sub>ox</sub> values were estimated by quasi-static C-V simulations. The vertical dotted lines indicate flat band voltage (V<sub>FB</sub>).

amplitude of 30 mV, in the gate bias range of -2 to 2 V, at multiple frequencies from 2 kHz to 1 MHz. Gate leakage vs. gate bias was measured in the same bias range. The chemical compositions of the Al<sub>2</sub>O<sub>3</sub>/Si<sub>0.7</sub>Ge<sub>0.3</sub>(001) interfaces were determined by VG Theta Probe angle resolved XPS (AR-XPS) using an Al-K $\alpha$  excitation source (1486.7 eV). AR-XPS measurements were performed on samples with 8 cycles of Al<sub>2</sub>O<sub>3</sub> ALD (with no gate metal) at various take-off angles from 26.75° to 71.75° with 7.5° steps.

Fig. 1 shows the C-V characteristics of the Al<sub>2</sub>O<sub>3</sub> deposited on SiGe(001) surfaces at 120 °C and 300 °C with and without *in-situ* NH<sub>3</sub> plasma treatment prior to ALD. In the absence of NH<sub>3</sub> plasma (Figs. 1(a) and 1(b)), an increase in ALD temperature resulted in higher frequency dispersion in capacitance near flat band voltage ( $0 V < V_g < 0.5 V$ ) as a result of larger Dit.<sup>13,14</sup> It should be noted that large frequency dispersion in accumulation at 300 °C is due to the higher leakage of the oxide rather than a greater density of near-interface or border traps (N<sub>BT</sub>).<sup>15</sup> Using NH<sub>3</sub> plasma treatment reversed the trend for D<sub>it</sub> vs. temperature, resulting in smaller frequency dispersion near flat band voltage (Figs. 1(c) and 1(d))

for 300 °C in comparison with 120 °C. Increasing the plasma treatment temperature reduced the oxide capacitance ( $C_{ox}$ ) by 0.3  $\mu$ F/cm<sup>2</sup> consistent with the formation of a nitride or oxynitride at the Al<sub>2</sub>O<sub>3</sub>/SiGe interface. Therefore, qualitatively, *insitu* NH<sub>3</sub> treatment at 300 °C reduced the density of the interface traps (shorter D<sub>it</sub> bump) by forming a thicker interfacial layer (IL) than at 120 °C causing a drop in C<sub>ox</sub>.

Results for the qualitative analysis of the C-V characteristics are shown in Fig. 2.  $D_{it}$  versus energy profiles (Fig. 2(a)) were extracted from capacitance- and conductance-voltage characteristics using full interface state model.<sup>16,17</sup> In all samples,  $D_{it}$  peaks near the edge of the valence band (E-E<sub>v</sub> = 0.25–0.35 eV) in agreement with the observation of  $D_{it}$  maxima in C-V curves close to the flat band voltage. The maximum  $D_{it}$  for samples without NH<sub>3</sub> treatment increased with ALD temperature from 2.9 × 10<sup>12</sup> cm<sup>-2</sup> eV<sup>-1</sup> at 120 °C to 4.9 × 10<sup>12</sup> cm<sup>-2</sup> eV<sup>-1</sup> at 300 °C. In contrast, when NH<sub>3</sub> plasma pre-treatment is used, a reduction in maximum  $D_{it}$  (from 3.1 × 10<sup>12</sup> cm<sup>-2</sup> eV<sup>-1</sup> to 2.4 × 10<sup>12</sup> cm<sup>-2</sup> eV<sup>-1</sup>) is observed as process temperature is raised from 120 °C to 300 °C. NH<sub>3</sub> plasma also made the  $D_{it}$  peaks near the edge of the valence band more asymmetric with wider



FIG. 2. (a) Density of interface trap as a function of energy relative to the valence band edge for sample prepared by *ex-situ* HF clean only as well as samples with *in-situ* NH<sub>3</sub> plasma treatment. (b) Equivalent oxide thickness (EOT) for the four samples prepared with and without *in-situ* NH<sub>3</sub> plasma prior to Al<sub>2</sub>O<sub>3</sub> ALD at 120 °C and 300 °C.

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FIG. 3. I-V gate leakage characteristics for SiGe MOSCAPs with and without NH<sub>3</sub> treatment with ALD at 120 °C and 300 °C.

distribution of interface traps towards the mid-gap. This is consistent with the different bonding at the interface in the presence of plasma nitridation compared with the interfaces that are treated by only HF clean.

Fig. 2(b) displays the EOT as a function of ALD temperature and surface treatment. Raising the ALD temperature from  $120 \,^{\circ}$ C to  $300 \,^{\circ}$ C in the absence of NH<sub>3</sub> plasma treatment resulted in a small change in EOT (only 0.1 nm difference), while for NH<sub>3</sub> plasma pre-treated samples, this temperature increase results in an increase in EOT by 0.45 nm. The larger EOT for samples NH<sub>3</sub> plasma pre-treated at 300  $^{\circ}$ C is consistent with the formation of an IL of Si or Ge nitride or oxynitride.<sup>8</sup> Therefore, high temperature NH<sub>3</sub> results in lower D<sub>it</sub> at the expense of 0.5 nm increase in EOT. However, it should be noted that EOT of 2.55 nm is  $\sim 0.5$  nm smaller than the lowest EOT values reported for Al<sub>2</sub>O<sub>3</sub> on SiGe prepared by *in-situ* plasma post nitridation.<sup>11,12</sup>

Leakage current characteristics of the ALD Al<sub>2</sub>O<sub>3</sub> with and without in-situ NH3 plasma pre-treatment are shown in Fig. 3. The leakage current in accumulation ( $V_g < -1.0 V$ ) is greater than in depletion because the high density of majority carriers at the Al<sub>2</sub>O<sub>3</sub>/SiGe interface in accumulation increases the current leakage through the oxide. With no plasma pretreatment, there is an order of magnitude decrease in the leakage current by lowering the ALD temperature from 300 °C to 120 °C. When NH<sub>3</sub> plasma pre-treatment is used, leakage current in accumulation becomes almost independent of ALD temperature and the absolute current density is more than  $10 \times$ smaller than samples with no plasma treatment. Therefore, it can be hypothesized that NH<sub>3</sub> plasma treatment reduces the leakage current either by improving the Al<sub>2</sub>O<sub>3</sub> ALD nucleation density (removing pinholes within the oxide<sup>18</sup>) or by forming thicker oxides. For 120 °C ALD, the EOTs with and without plasma treatment are nearly identical (Fig. 2(b)); therefore, the data are consistent with the primary effect of NH<sub>3</sub> treatment being an increase in nucleation density.

To determine the changes in interface composition by surface treatment and processing temperature, AR-XPS was performed on samples with 0.8 nm thick Al<sub>2</sub>O<sub>3</sub> on SiGe with ALD at 120 °C–300 °C. Due to the limited escape depth, thicker Al<sub>2</sub>O<sub>3</sub> layers would prevent a large majority of photoelectrons from reaching the analyzer. Ge3d and Si2p spectra at two different take-off angles (26.75° and 71.75°) are displayed in Fig. 4. At 120 °C, NH<sub>3</sub> plasma pre-treatment increased the intensity of the high-binding-energy shoulder for Si2p peaks (101–103 eV), with 0.5 eV shift to higher



FIG. 4. Si2p and Ge3d peaks measured by AR-XPS at 26.75° and 71.75° take-off angles on Al<sub>2</sub>O<sub>3</sub>/SiGe samples with and without NH<sub>3</sub> plasma treatment followed by 8 cycles of ALD at 120°C ((a) and (b)) and 300°C ((c) and (d)).

TABLE I. Ge to Si oxide or oxynitride for the HF-treated and  $NH_3$ -plasma treated SiGe surfaces with 8 cycles of  $Al_2O_3$  ALD.

Surface treatment	$T^{\mathbf{a}}$	(GeON/Ge)/(SiON/Si) <sup>b</sup>
HF	120 °C	0.88
HF	300 °C	1.10
NH <sub>3</sub>	120 °C	0.54
NH <sub>3</sub>	300 °C	0.11

<sup>a</sup>Temperature at which Al<sub>2</sub>O<sub>3</sub> ALD was performed.

<sup>b</sup>Ratio between GeON/Ge (or GeOx/Ge) and SiON/Si (or SiOx/Si) extracted from Si2p and Ge3d XPS spectra.

binding energies compared with the sample with no plasma treatment. This is consistent with the formation of  $Si_3N_4$  (BE = 101.8–102.2 eV) and possibly  $SiO_xN_y$  (or SiON, BE = 102–103 eV).<sup>19</sup> The fraction of Si atoms with nitrogen and oxygen bonding increased by 60% by including the NH<sub>3</sub> plasma step. Similarly, NH<sub>3</sub> pre-treatment at 120 °C slightly increased the intensity of high-binding-energy shoulder for Ge3d peak (Fig. 4(b)) with 0.4–0.5 eV = higher BE than GeO, which can be explained by the formation of small amounts of GeO<sub>x</sub>N<sub>y</sub> (or GeON) or Ge<sub>3</sub>N<sub>4</sub> during low-temperature plasma nitridation.<sup>10</sup>

By using NH<sub>3</sub> plasma treatment at 300 °C, larger Si<sub>3</sub>N<sub>4</sub> and SiO<sub>x</sub>N<sub>y</sub> (i.e., SiON) components were observed compared with plasma treatment at 120 °C (Fig. 4(c)). At 300 °C, the SiON to Si ratio was  $3 \times$  higher than that in the sample without plasma treatment. In addition, NH<sub>3</sub> plasma treatment at 300 °C nearly eliminated the high-binding-energy shoulder for Ge3d peaks at both take-off angles (Fig. 4(d)). Considering the greater N1s signal (supplementary material)<sup>20</sup> measured on the NH<sub>3</sub>-treated surfaces at 300 °C, it can be hypothesized that at 300 °C, SiN<sub>x</sub> or SiON is selectively formed on SiGe surfaces, resulting in a Si-rich interfacial layers between  $Al_2O_3$  and SiGe(001). In order to demonstrate the nitridation selectivity, the angle resolved Si2p and Ge3d XPS signals were fitted to determine the ratio between GeON/Ge and SiON/Si ratios as functions of ALD temperature and surface treatment as shown in Table I. Nitridation at 300°C resulted in approximately  $5 \times$  lower amount of GeON at the interface. This is consistent with the lower bond enthalpy for Ge-N (257 kJ/mol) vs. Si-N (355 kJ/mol) that makes Si-N more stable at higher temperatures.<sup>21</sup> At similar temperatures,  $NH_3$  plasma pre-treatment yields more Si/Ge selectivity compared with ECR N<sub>2</sub> plasma post-nitridation with a screen oxide, where a large GeON component was present in the interfacial nitride layer.<sup>11</sup> It is noted that this may be due to the higher reactivity of atomic N from the N<sub>2</sub> plasma than the  $NH_x$  from the  $NH_3$  plasma.

A common challenge in processing Ge-containing substrates is Ge out-diffusion that occurs as a result of GeO<sub>x</sub> instability even at low processing temperatures, leading to MOS devices with low reliability and large D<sub>it</sub>.<sup>22,23</sup> In order to determine the distribution of Ge within Al<sub>2</sub>O<sub>3</sub>, Ge2p peaks were measured by AR-XPS on 0.8-nm Al<sub>2</sub>O<sub>3</sub>/SiGe samples at 3 different take-off angles: 26.75°, 49.25°, and 71.75° (Fig. 5). Since Ge2p photoelectrons have an inelastic mean free path (IMFP) of only 0.85 nm,<sup>24</sup> a large portion of Ge2p signal originates from the interior of the oxide or oxide top surface. When no plasma pre-treatment is used, Ge2p peak at both 120 °C and 300 °C (black and blue lines) has a large GeO<sub>2</sub> component that becomes more dominant as take-off angles become more grazing, consistent with the presence of Ge and GeO<sub>2</sub> on the top of and within the  $Al_2O_3$  layer as a result of out-diffusion.

For NH<sub>3</sub> pre-treatment at 120 °C, Ge2p peaks (red line) have a large GeO<sub>2</sub> component at all take-off angles. This might be due to the instability of the interfacial GeON in the presence of H<sub>2</sub>O in the ALD process. The presence of H<sub>2</sub>O during the ALD process is reported to facilitate GeON decomposition and incorporation into the gate oxide.<sup>25</sup> Alternatively, the thinner SiON layer formed by the NH<sub>3</sub> plasma at 120 °C may provide an insufficient diffusion barrier to H<sub>2</sub>O so that during ALD additional GeO<sub>x</sub> was formed which diffused to the top of the oxide. This could also explain the higher D<sub>it</sub> for samples processed by plasma nitridation at 120 °C (Fig. 2(a)). Conversely, Ge2p peaks for NH<sub>3</sub> pre-treatment at 300 °C showed no GeO<sub>2</sub> component at all the three take-off angles and a very small total Ge2p signal for 71.75°. From these results, it can be inferred that NH<sub>3</sub> pre-treatment at 300 °C forms a good quality nitride interfacial layer that acts as a diffusion barrier for Ge out-diffusion from SiGe substrate into the gate oxide. It is noted in the detailed XPS studies on SiON/Si interfaces, formed at high



FIG. 5. Ge2p peaks for 0.8-nm Al<sub>2</sub>O<sub>3</sub>/SiGe samples with and without NH<sub>3</sub> plasma treatment and ALD at 120 °C and 300 °C measured by AR-XPS at (a) 26.75°, (b) 49.25°, and (c) 71.75° take-off angles.

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temperatures, that a nearly pure  $Si_3N_4$  layer forms on top of the Si which would provide a good diffusion barrier for Ge.<sup>26,27</sup>

In conclusion, NH<sub>3</sub> plasma treatment has been investigated as an *in-situ* technique to clean and passivate the SiGe surfaces prior to high-k oxide ALD. Nitridation by NH<sub>3</sub> plasma is shown to be more efficient at passivating the oxide/SiGe interface at temperatures as high as 300 °C by selectively terminating the SiGe surfaces with Si<sub>3</sub>N<sub>4</sub> and SiON. This selective interface nitridation greatly reduces the amount of Ge out-diffusion from the SiGe substrate into the oxide consistent with SiN<sub>x</sub> being a good diffusion barrier. It is noted that the diffusion barrier may be for H<sub>2</sub>O diffusing to the SiGe surface and/or diffusion of GeOx from the semiconductor surface into the gate oxide. Si<sub>3</sub>N<sub>4</sub> and SiON interface passivation improves the electronic characteristics of the Al<sub>2</sub>O<sub>3</sub>/SiGe MOS capacitors: reducing the density of interface traps near the valence band edge along with more than 10× reduction in oxide leakage current while maintaining EOT of no larger than 2.6 nm.

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