Hafnium oxide gate dielectrics on sulfur-passivated germanium

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Sulfur passivation of Ge(100) is achieved using aqueous ammonium sulfide (NH$_4$)$_2$S(aq). The passivation layer is largely preserved after atomic layer deposition of the high-$\kappa$ dielectric material HfO$_2$ when sufficiently low growth temperatures (e.g., 220 °C) are employed. Oxygen incorporation is moderate and results in an electrically passivating GeOS interface layer. The HfO$_2$/GeOS/Ge gate stack exhibits lower fixed charge and interface state density than a more conventional HfO$_2$/GeON/Ge gate stack fabricated via an ammonia gas treatment. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338751]

Metal-oxide-semiconductor field-effect transistors (MOSFETs) incorporating Ge channels are an attractive option to further increase complementary MOS (CMOS) logic performance, since Ge offers bulk electron (hole) mobilities about three (four) times higher than Si. The main issue that has so far prevented the fabrication of competitive Ge-based devices is the poor electrical quality and low chemical stability of native germanium oxides, analogous to similar gate dielectric issues on compound semiconductors.

A good quality deposited dielectric is therefore needed. The recent advent of high-permittivity (“high-$\kappa$”) dielectrics on Si (Refs. 4–7) offers a new opportunity. Hafnium-based oxides are the most promising high-$\kappa$ dielectrics for Si CMOS. These films are usually grown by chemical vapor deposition (CVD) or atomic layer deposition (ALD). Of these techniques, ALD has the advantage of intrinsic monolayer thickness control and excellent film conformality.

While electrically insulating gate stacks can be fabricated by HfO$_2$ growth on Ge wet chemically precleaned using, e.g., water, HCl(aq), or HF(aq), their current-voltage (C-V) characteristics usually indicate charge trapping and fixed charge. This is likely caused by undesirable HfO$_2$/Ge interface reactions, made possible by the absence of a stable, passivating native oxide on Ge. Direct interaction of ALD-grown HfO$_2$ with wet-cleaned Ge is supported by the observation of epitaxial registry of HfO$_2$ with the Ge(100) and the lack of a substantial interfacial GeO$_2$ layer. For CVD-grown HfO$_2$, Ge can diffuse through the high-$\kappa$ layer.

To prevent uncontrolled interface reactions, Ge treatment with a stronger passivant than oxygen seems desirable. Most work so far has concentrated on nitridation using atomic N exposure or an NH$_3$ gas treatment. Indeed, Ge oxyynitride layers thus formed are more effective passivants, as evidenced by amorphous ALD-grown HfO$_2$ films and reduced Ge migration into HfO$_2$. The electrical quality of HfO$_2$/Ge gate stacks is somewhat improved but they still exhibit interface state densities $D_{it}$ $>$ 10$^{12}$ cm$^{-2}$ and fixed charge, as shown below. The only other Ge passivation scheme that has been reported is a strong passivating HBr(aq) etch. However, poor HfO$_2$ nucleation was found, implying islanded gate dielectrics.

Sulfur is an attractive alternative passivant, since it electrically passivates III-V compound surfaces and grain boundaries in polycrystalline Ge. Ge surface passivation is achieved, for example, using aqueous ammonium sulfide (NH$_4$)$_2$S(aq). A less than 3 ML thick, air-stable germanium sulfide (GeS$_x$) layer is thus formed, incorporating (1–2) $\times$ 10$^{15}$ cm$^{-2}$ S atoms. In this letter, we show that sulfur passivation can be substantially preserved during high-$\kappa$ dielectric growth and that it improves the electrical properties of HfO$_2$/Ge stacks.

First, we report experimental results showing S passivation of Ge(100) and compare our observations to what has been reported in the literature. Epiready n-Ge(100) was degreased by sonication in acetone and methanol, cleaned in 5:1 H$_2$SO$_4$:H$_2$O for 2 min, rinsed with water, and then etched in 10% HF(aq) for 10 min. Finally, the substrates were immersed into 10% (NH$_4$)$_2$S(aq) at 70–80 °C for 15 min, followed by a water rinse and a N$_2$ blow dry. The results of medium-energy ion scattering (MEIS) and x-ray photoelectron spectroscopy (XPS) analyses of these samples are shown in Fig. 1, along with data from native-oxide-covered Ge and from Ge that received a 25% HF(aq) clean.

![FIG. 1. (Color online) (a) XPS data in the Ge 3d region from native-oxide-covered Ge(100) compared to HF and (NH$_4$)$_2$S(aq) treatment; (b) MEIS data from the same samples; (c) XPS data in the S 2p region from Ge(100) after (NH$_4$)$_2$S(aq) treatment and after subsequent ultrahigh vacuum anneals.](image-url)
The XPS data in the Ge 3d region [Fig. 1(a)] demonstrate that the (NH₄)₂S-treated surface is predominantly composed of Ge in the oxidation state 0 (signal at 30.1 eV), with only traces of oxidized Ge (signal at 32.5–33.0 eV). In this respect, it is similar to the HF-etched Ge surface and distinctively different from native-oxide-covered Ge. As shown by the MEIS feature at 93.75 keV [Fig. 1(b)] and by an XPS S 2p signal at 162.1 eV [Fig. 1(c)], S is present with an areal density of 1.0 × 10¹⁵ cm⁻², consistent with literature data. Assuming germanium monosulfide (GeS) or disulfide (GeS₂) stoichiometry, this corresponds to a passivation layer thickness of 4–5 Å. A MEIS signal at 88.1 keV [Fig. 1(b)] shows that oxygen is present due to air exposure, with similar areal density of 8.5 × 10¹⁴ cm⁻². While S passivation thus reduces the amount of surface O to only 60% of what is observed for air-exposed HF-etched Ge [Fig. 1(b)], the surface stoichiometry is more accurately denoted as GeOS. The thermal stability was determined by recording XPS spectra after 2–3 min anneals to successively higher temperatures in ultrahigh vacuum [Fig. 1(c)]. Most S is retained on the Ge surface up to 260 °C, while it is desorbed at temperatures of >320 °C, consistent with previous studies.

Now, we turn to gate stacks on S-passivated Ge. HfO₂ was grown in an ASM Pulsar3000™ ALD reactor using alternating exposures of HCl₂ and H₂O in a N₂ carrier gas at 220 °C. Conventionally, HfO₂ from these precursors is grown on Si at 300 °C. However, as indicated by the results above, such high temperature would lead to loss of the S passivation, while at 220 °C one may expect most S to be preserved. The structure of Al/HfO₂/Ge stacks is illustrated by the transmission electron microscopy (TEM) images in Fig. 2, comparing 77 Å ALD HfO₂ deposited at 220 °C (92 ALD cycles, i.e., ~0.84 Å HfO₂ per cycle) onto HF-etched Ge [Fig. 2(a)] and onto S-passivated Ge [Fig. 2(b)]. A relatively sharp Ge–HfO₂ interface results when HF-etched Ge is used: at most 2 ML of interfacial material such as GeO₂ is visible, in line with previous observations for growth at 300 °C. In some locations, HfO₂ is in epitaxial registry with the Ge (though less so than at 300 °C), indicating intimate chemical interaction. We have observed nearly identical growth characteristics on HCl-etched Ge. For the S-passivated sample [Fig. 2(b)], we employed a treatment with 50% (NH₄)₂S(aq) at 70–80 °C for 10 min (the 50% concentration being higher than the 10% utilized for the XPS analysis). The stack then contains an ~2 nm thick interlayer with lower average nuclear mass than for HfO₂, based on the TEM contrast, indicating that the passivation layer remains in place during HfO₂ growth. HfO₂ epitaxy is prevented [Fig. 2(b)], consistent with a rather stable barrier layer. Due to the high (NH₄)₂S concentration used, the GeOS layer in Fig. 2(b) is thicker than that obtained on bare Ge(100) described previously, and thicker than would be desirable for MOSFET applications. However, it is conceivable that the GeOS layer could be thinned while maintaining its passivation benefits.

To obtain depth-dependent chemical information, secondary ion mass spectrometry (SIMS) data were recorded by sputtering (2.5 keV Cs⁺) through the gate stack. A S-implanted SiO₂ standard was used for quantification. Taking the similarity of the SiO₂ and HfO₂ matrices and the expected high S⁻ ion yield under Cs⁺ bombardment into account, we estimate that the S quantification is accurate within a factor of ~2. Regarding the high-κ dielectric, HfO₂ ions were detected as they exhibit a higher ion yield than H⁺. The inset in Fig. 3(b) shows the SIMS depth profiles of Al, S, Ge, and HfO₂. Despite signal broadening, it is clear that the centroid of the S distribution is located below the HfO₂ layer. The total areal density of S is ~5 × 10¹⁴ cm⁻², confirming that a substantial fraction of the S is preserved.

We now compare the electrical characteristics of HfO₂/Ge gate stacks fabricated with sulfur passivation to stacks fabricated using the more conventional NH₃ gas treatment. The NH₃ treatment is appropriate for reference, since it results in better characteristics than HF and HCl cleans. Dual-sweep current-voltage (C–V) characteristics of Al dot capacitors with 77 Å HfO₂ grown at 220 °C on n-Ge(100) are shown in Fig. 3(a) for S-passivated Ge [50% (NH₄)₂S(aq), 70–80 °C, and 5 min] and Fig. 3(b) for NH₃-annealed Ge (1 atm, 650 °C, and 1 min). Charge trapping by interface and bulk states in the dielectric film is evidenced by C–V stretch out and hysteresis between up and down sweeps. The hysteresis is slightly larger for the S-passivated sample, possibly due to increased charge injection into the HfO₂ due to the lack of a wide band gap interfacial layer, or due to trapping in the GeOS.

A significant advantage of the S-passivated Ge is revealed by the flatband voltage V₉. At 100 kHz, the average between up and down sweeps, we find V₉ = −0.15 V with S passivation, compared to V₉ = −1.35 V with an NH₃ anneal. The flatband voltage of the S-passivated samples is close to the ideal value of V₉ = +0.08 V and to V₉ of Al/HfO₂/SiON/Si control.
samples (not shown). This indicates that S introduces much less fixed positive oxide charge than nitrogen.

Finally, $D_n$ was measured using the frequency-dependent conductance method and the high-low capacitance method. For the former technique, admittance measurements were performed as a function of frequency, and the loss, defined as the ratio of the effective parallel capacitance to the frequency, $G_p/\omega$, was plotted versus frequency [4(a) and 4(b)]. The loss curves show typical interface state behavior, where the frequency corresponding to the peak $G_p/\omega$ value changes exponentially with bias. The value of $D_n$ was extracted according to $D_n = 2.5 \times (G_p/\omega)_{\text{max}}/qA$, where $(G_p/\omega)_{\text{max}}$ is the peak loss value, $q$ is the electronic charge, and $A$ is the area. In Fig. 4(c), the extracted $D_n$ is plotted as a function of energy relative to the valence band edge ($D_n$ values corresponding to peak frequencies $<1$ kHz have been eliminated, where conductance associated with bulk traps is significant). For the sample with S passivation, the minimum $D_n$ extracted from the conductance method ($2.4 \times 10^{12}$ cm$^{-2}$/eV) is less than half of the value determined for the NH$_3$-annealed substrate ($5.9 \times 10^{12}$ cm$^{-2}$/eV). This trend is confirmed by the high-low capacitance results, albeit with slightly higher absolute $D_n$ values. The $D_n$ advantage of the S-passivated sample appears mainly to occur near the valence band, whereas near the conduction band, $D_n$ is slightly higher. This result is consistent with the higher frequency dispersion of the S-passivated sample in accumulation and also with recent temperature-dependent admittance spectroscopy measurements.

In conclusion, sulfur passivation of Ge(100) using (NH$_3$)$_2$S(aq) can be largely preserved during high-$\kappa$ dielectric growth at sufficiently low temperatures, e.g., at $220\ ^\circ C$. The resulting HIO$_3$/GeOS/Ge stacks exhibit lower fixed charge and interface state density than what is achieved with conventional NH$_3$-annealed Ge substrates, and may therefore constitute an important subject of further study. Future work needs to concentrate on gate stack capacitance scaling and reduction of charge trapping.


