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HfO_2 as gate dielectric on Ge: Interfaces and deposition techniques

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Abstract

To fabricate MOS gate stacks on Ge, one can choose from a multitude of metal oxides as dielectric material which can be deposited by many chemical or physical vapor deposition techniques. As a few typical examples, we will discuss here the results from atomic layer deposition (ALD), metal organic CVD (MOCVD) and molecular beam deposition (MBD) using HfO_2/Ge as materials model system. It appears that a completely interface layer free HfO_2/Ge combination can be made in MBD, but this results in very bad capacitors. The same bad result we find if $HfGe_y$ (Hf germanides) are formed like in the case of MOCVD on HF-dipped Ge. A GeO_x interfacial layer appears to be indispensable (if no other passivating materials are applied), but the composition of this interfacial layer (as determined by XPS, TOFSIMS and MEIS) is determining for the *C*/*V* quality. On the other hand, the presence of Ge in the HfO_2 layer is not the most important factor that can be responsible for poor *C*/*V*, although it can still induce bumps in *C*/*V* curves, especially in the form of germanates (Hf–O–Ge). We find that most of these interfacial GeO_x layers are in fact sub-oxides, and that this could be (part of) the explanation for the high interfacial state densities. In conclusion, we find that the Ge surface preparation is determining for the gate stack quality, but it needs to be adapted to the specific deposition technique.

Keywords: Hafnium oxide; Germanium; Metal–oxide–semiconductor structures; Gate stack; Atomic layer deposition; Metal organic vapor deposition; Molecular beam deposition

1. Introduction

Germanium as alternative, high mobility MOS channel material requires a deposited gate dielectric, because of the unstable character of thermally grown GeO_2 [1]. Initially, the high-k metal oxides and their deposition processes as developed for Silicon CMOS seemed to offer a quick solution for this problem. Interfacial passivation for Si /high-k systems was basically "just" a matter of creating and maintaining a minimum of SiO_2 and preventing silicide formation. For Ge however this is less straightforward due to the unstable character of GeO_2. Because of this, several alternative passivation techniques have been proposed and tested such as nitridation by NH_3 annealing [2] or SiH_4 annealing [3] which is similar to Si deposition [4]. Although the best Ge MOS transistor results so far published have been obtained in Si-passivated structures, in this overview, we will limit ourselves to interfacial passivation based on Ge oxide or oxide–nitride layers formed either ex situ or in situ, in combination with HfO_2 layers deposited by either atomic layer deposition (ALD), metal organic chemical vapor deposition (MOCVD) or molecular beam deposition (MBD). We will show that GeO_2-like interfacial layers can be better than expected, and that other factors can be responsible for poor *C*/*V* characteristics.

2. Experimental methods

HfO_2 deposition was done by atomic layer deposition (ALD) in an ASM Pulsar® 2000 reactor from $HfCl_4$ and H_2O at 300 °C. This Pulsar® reactor is part of a 200 mm reactor cluster Polygon® 8200, including amongst others an Epsilon® style nitride module which is basically a lamp heated, single wafer horizontal flow reactor with a quartz tube equipped with NH_3, O_2 and other gases. MOCVD is performed in a 200 mm Applied Materials Centura® MOCVD reactor module. We use tetrakis

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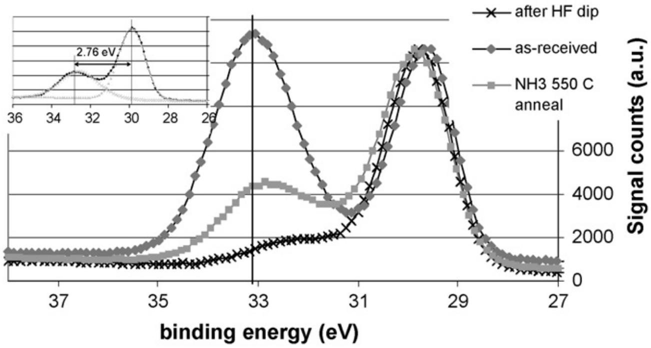

Fig. 1. XPS analysis of Ge substrate: Ge 3d spectrum of Ge surface as-received, after an HF dip and after NH_3 anneal at 550 °C. The inset shows a de-convolution of the NH_3-annealed sample spectrum.

di-ethyl amido hafnium (TDEAH) and O_2 as precursor gases at a standard temperature of 485 °C. Part of this Centura cluster is an ISSG rapid thermal oxidation chamber. Molecular beam deposition (MBD) is carried out in an 2 in. ultra-high vacuum (UHV) MBE tool. For MBD, the native oxide was desorbed under UHV for 15 min at 360 °C (until clear (2 × 1) Ge surface reconstruction was visible in RHEED) and HfO_2 was grown with atomic Hf and O beams at 225 °C. O was supplied from a remote RF plasma source.

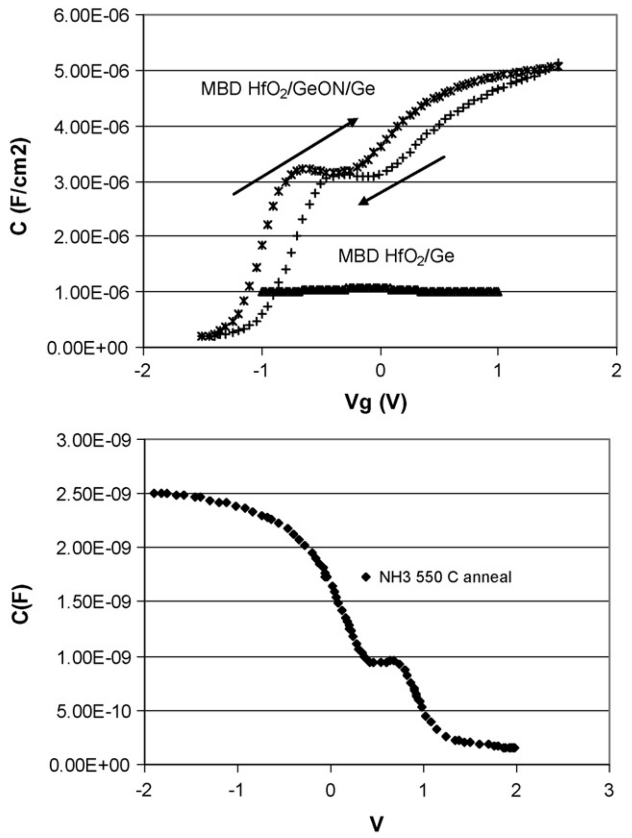

Fig. 2. *C*/*V* curves of TiN metal dot capacitors on MBD (upper panel) and MOCVD (lower panel) deposited HfO_2. The samples in the upper panel contain 4.5 nm HfO_2 on either HF-dipped Ge (lower curve) or on a GeON layer (upper curves). The latter ones, measured at 100 kHz, show a shift in the flat-band voltage (hysteresis) of 200–250 mV for back-and-forth voltage sweeps.

3. Results

Ge wafers out-of-the-box are covered by a ~1.7 nm thick native oxide (as measured by X-ray photo-electron spectroscopy, XPS), comprising mainly GeO_2, see the XPS Ge 3d spectrum showing the Ge^0 and Ge^{4+} states in Fig. 1 (“as-received”). Stripping the native oxide in an H_2O/HF solution leaves ~0.3 nm GeO_x (same figure). De-convoluting the spectra (see by way of example the inset in Fig. 1, showing the de-convoluted spectrum after NH_3 anneal) allows to estimate the binding energy shift between the elemental and the oxidized Ge peak. In the as-received sample, this shift is 3.38 eV, which is very close to the shift of 3.4 eV assigned to Ge^{4+} (GeO_2) as determined by Schmeisser et al. [5]. The Ge sub-oxide peak in the HF dipped sample shows a shift of ~2.18 eV. According to [5], this would mean this 0.3 nm sub-oxide layer is comprised of a mixture of Ge^{2+} and Ge^{3+} with respective shifts of 1.8 and 2.6 eV.

The MBD (Fig. 2) and MOCVD (not shown) layers typically resulted in flat *C*–*V* curves and suffered from very high leakage (not shown). The ALD layers on the other hand showed not

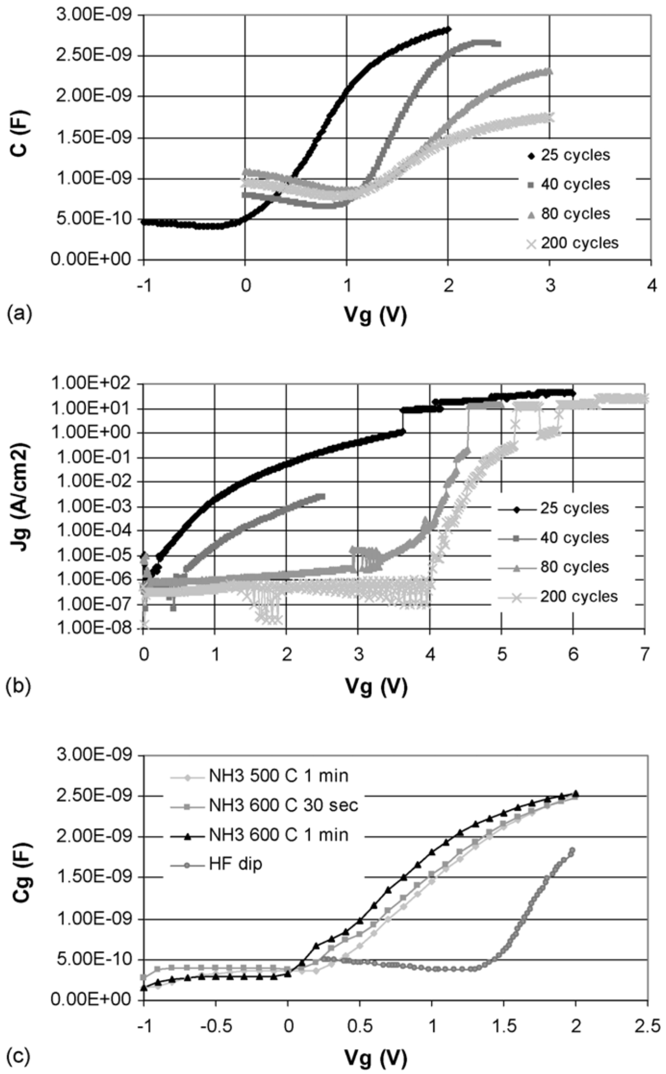

Fig. 3. *C*/*V* (a) and *I*/*V* (b) analysis of ALD HfO_2 on HF dipped and NH_3-annealed (c) Ge.

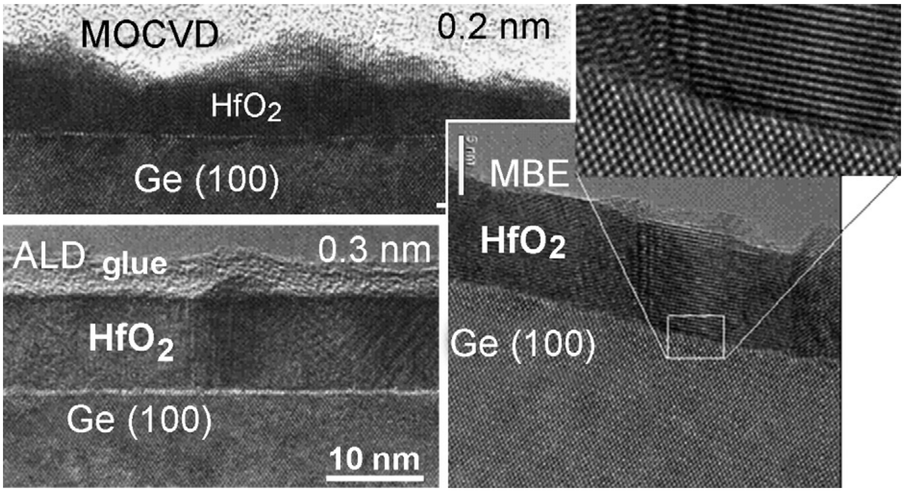

Fig. 4. x-TEM images of HfO_2 layers on Ge, deposited by MOCVD, ALD and MBD. The interfacial layer thickness is also indicated.

perfect but still quite reasonable *C–V* and *I–V* curves with a capacitance and leakage that scale with the thickness of the HfO_2 layer, see Fig. 3.

The interface between the MBD HfO_2 grown straight on the (2 × 1) reconstructed Ge surface appears to be very sharp without any noticeable interfacial layer according to cross-sectional TEM (x-TEM) (Fig. 4). The HfO_2 layer surface shows some roughness which seems to be correlated to crystallization. XPS of the Ge 3p core electrons (Fig. 5, middle panel) shows a clean spectrum with the Ge $3p_{1/2}$ and Ge $3p_{3/2}$ peaks, without any additional bump that could indicate oxidized Ge. Also TOFSIMS (Fig. 7, middle panel) shows a sharp interface between the Ge substrate and the HfO_2 layer, with almost no out-diffusion of Ge into the HfO_2.

The MOCVD layer on the HF-dipped Ge substrate shows a very rough surface in the x-TEM images in Fig. 4 while the ALD layer (also on HF-dipped Ge) is very smooth. In contrast to this, both the ALD and MOCVD layers grown on HF-dipped Ge show a thin, smooth and well-defined interfacial layer of 0.2–0.3 nm.

The Ge 3s spectrum of the ALD layer (XPS, Fig. 5, upper panel) can be resolved completely with only two peaks, one for the metallic Ge of the substrate at 182.2 eV and another one at 184.9 eV, which corresponds to the Ge^{4+} oxidation state, i.e. GeO_2. Similarly to the MBD layer, TOFSIMS (Fig. 7, lower panel) cannot find almost any Ge inside the HfO_2 layer, even not after a 600 °C O_2 anneal. According to medium ion scattering spectroscopy (MEIS, Fig. 6, panel a) the ALD interfacial layer is mainly composed of Ge and O (with quite some Cl contamination), with only a minor trace of Hf. The MOCVD HfO_2 layer on HF-dipped Ge is quite different: TOFSIMS (Fig. 7, upper panel) shows strong Ge in-diffusion from the substrate into the HfO_2 layer. According to MEIS (Fig. 6, panel b), the HfO_2 layer indeed looks more like a mixed HfO_2/GeO_2 layer, and at the interface there is a strong indication for a Hf Germanide phase (Hf–Ge mix, without the presence of O).

A possible passivation of the surface is nitridation of the Ge surface such as by annealing in NH_3 [2]. Fig. 1 shows an XPS

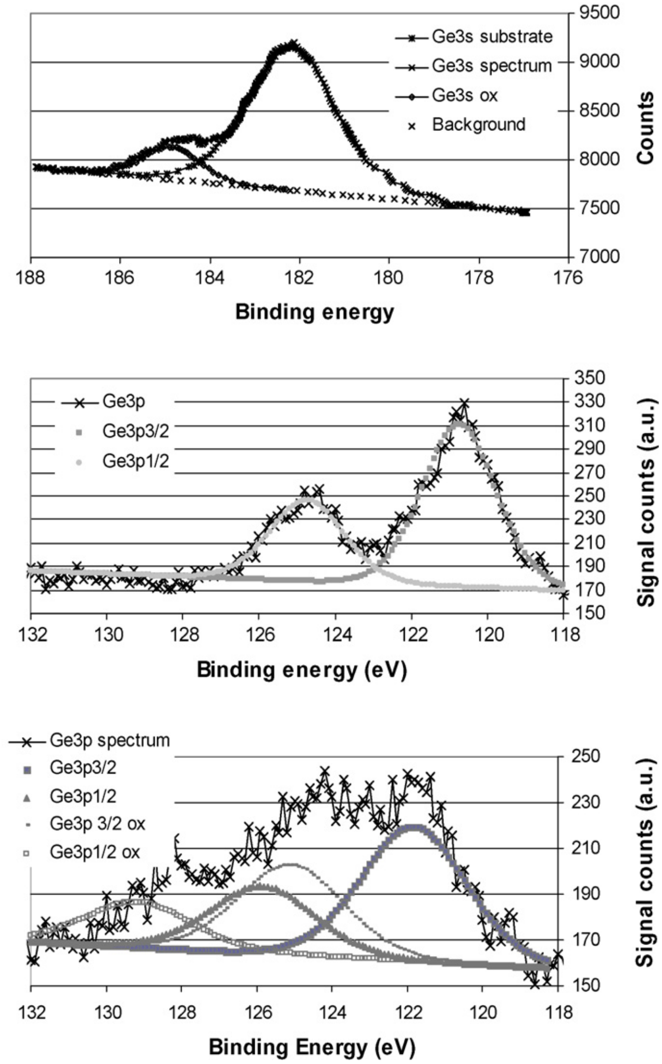

Fig. 5. XPS Ge 3p spectrum of ALD HfO_2 on Ge after HF dip (upper), MBD HfO_2 on Ge (middle) and on GeON/Ge (lower figure).

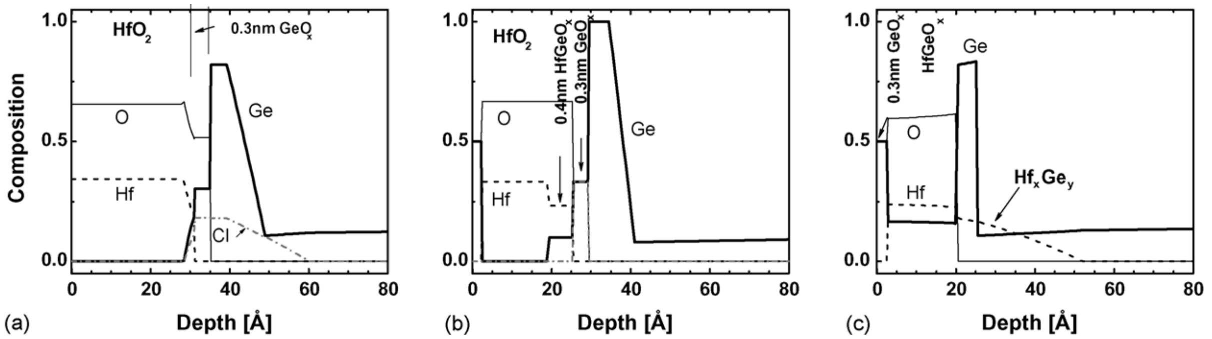

Fig. 6. MEIS spectra fittings for ALD (a) and MOCVD (b) HfO_2 on HF-dipped Ge, and MOCVD HfO_2 on NH_3-annealed Ge (c).

spectrum of the Ge surface after a 1 min NH_3 550 °C anneal, which results in a Ge–O–N type of bond with a reduced peak shift of the oxidized Ge peak as compared to the fully oxidized Ge^{4+}. For MOCVD HfO_2 deposition on such a surface, TOFSIMS shows that the Ge in-diffusion in the HfO_2 layer is reduced with an order of magnitude (Fig. 7, upper panel). MEIS shows a strong change in the MOCVD case, in that the Hf germanide interface now is replaced by a $HfGeO_x$ layer with a graded Hf content (Fig. 6, panel c). Capacitors on these MOCVD layers on nitrided Ge show a pretty decent *C*/*V* shape albeit with some bump in depletion that could be due to interfacial states (Fig. 2, lower panel). Also their leakage current is considerably reduced (not shown) in contrast to the poor behavior on HF-dipped Ge. For *C*/*V* on ALD oxide layers (Fig. 3c), we notice no specific changes in the *C*/*V* shape except a strong shift in V_{FB}, likely due to fixed charges because of the presence of N [6].

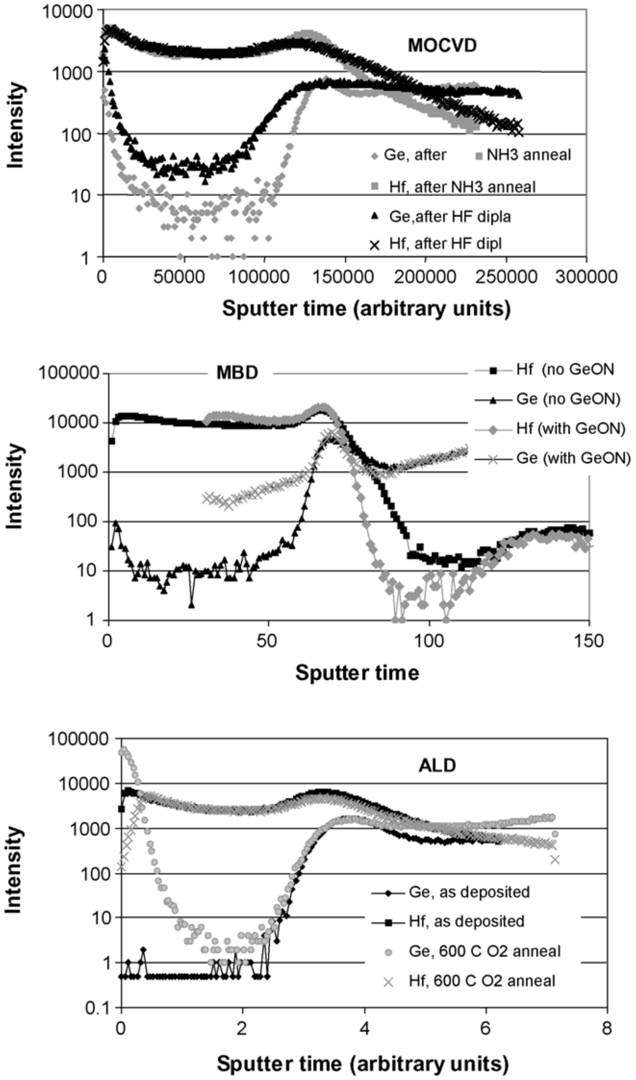

Fig. 7. TOFSIMS profiles of Hf and Ge in HfO_2 layers: MOCVD (upper panel, HfO_2 on Ge after HF dip and after NH_3 550 °C anneal), MBD (middle panel, HfO_2 on Ge, HfO_2 on GeON/Ge), ALD (lower panel, as-deposited HfO_2 on HF-dipped Ge, and after 600 °C O_2 anneal).

In the case of MBD, we deposited in situ a GeO_xN_y layer (further-on denoted as GeON) with combined beams of Ge and/or O atoms [7] immediately followed by the HfO_2 layer. Similar to MOCVD, the interfacial passivating layer has a dramatic effect on improving the *C*/*V* characteristics, see Fig. 2, from which an interfacial state density $N_{it} \sim 5 \times 10^{12}\ cm^{-2}$ can be extracted. Switching the device from inversion to accumulation and back to inversion shows a flat-band voltage shift of about 200–250 mV (measurement frequency is 100 kHz). This hysteresis effect could be due to trapping/de-trapping defects in either the HfO_2 bulk or at the interface. In this respect, it is interesting to note that TOFSIMS shows quite some Ge in this HfO_2 layer, in contrast to HfO_2 deposited straight on bare Ge after an oxide desorption step (Fig. 7, middle panel). We speculate the presence of Hf in the interfacial layer is due to the unstable nature of the GeON layer which “dissolves” in the growing HfO_2 layer. From XPS (Fig. 5, lower panel, Ge 3p spectrum) we know this GeON layer is not GeO_2 but some form of Ge sub-oxide (Ge^{1+}, Ge^{2+}, Ge^{3+}), the exact oxidation state of which however is difficult to determine on the 3p peak. The 3d peak would be better suited for this, if it were not for an interfering overlap between the Ge 3d and the Hf 4f from the HfO_2 overlayer.

In another experiment, we deposited a tiny amount of HfO_2 (0.3–1.5 nm) by means of either ALD or MOCVD on Ge and annealed these in O_2 at 550 °C for 15 min [8]. Careful AR-XPS showed a homogeneous, mixed oxide layer and a Ge^{4+} peak shifting in the direction of sub-oxides. A similar shift of the Hf peak shows that this newly formed bond is a Hf germanate (Hf–O–Ge). *C*/*V* and *I*/*V* measurements on these layers showed high leakage and – more important – an interfacial density of states that increases with the amount of Hf–O–Ge bonds.

4. Discussion

A first striking feature is the different behavior of HfO_2 layers deposited with different techniques on a bare Ge surface. The abrupt interface in the MBD case (x-TEM) probably involves a high density of dangling bonds because of the mismatch between the two crystalline structures of Ge and HfO_2 (if not epitaxial), which could explain the poor *C*/*V*. In the case of MOCVD on HF-dipped Ge, the formation of a metallic-like germanide observed in MEIS can cause Fermi level pinning, so hindering modulation of the surface potential. None of these fatal errors occurs in the ALD case, which consequently results in decent *C*/*V*. It is worthwhile to mention here that the interface in the ALD case is characterized as GeO_2 by XPS.

By inserting a “passivation” layer between the HfO_2 and the Ge, these fatal errors can be prevented: for MOCVD, the GeON layer made by NH_3 anneal prevents the formation of Hf germanide (as indicated by MEIS measurements), whereas the in situ deposited amorphous GeON layer in MBD prevents the formation of HfO_2 crystalline phases in direct contact with the Ge crystalline phase, which helps saturating any dangling bonds. Electron spin resonance [9] was not able to show significant ($\leq 10^{12}$ cm^{-2}) densities of dangling bond type of defects in GeO_x interfaces made in various ways.

An interesting observation is that the mere presence of Ge inside the high-k layer is not really a killer problem: MBD HfO_2 on GeON/Ge clearly shows an important Hf trace inside the HfO_2, but still gives reasonable *C*/*V* albeit with some bumps. As mentioned, we noticed that Hf–O–Ge (germanate) bonds which were formed in trace amounts of HfO_2 on a thermal GeO_2 layer after a long 550 °C anneal in O_2 also induce bumps in the *C*/*V* curve, the magnitude of which scales with the amount of Hf. So, it is not unlikely that the presence of Ge inside the HfO_2 can create an enhanced interfacial state density depending on the thermal history. Additionally, the presence of Ge inside the HfO_2 film could be related to the observed hysteresis, but this statement is rather speculative at this time. Finally, although we have not been able to index unambiguously the different Ge oxidation states underneath HfO_2, it appears that also the lower oxidation states of Ge, i.e. the sub-oxides, are able to generate bumps in the *C*/*V* curves.

5. Conclusion

We have studied MOS capacitors made in HfO_2 on Ge as a materials model system made with several different deposition techniques. By a close inspection of physical characterization results of the interfacial layers, we have found indications for some different root causes of failing gate stacks, all for HfO_2 layers made directly on pristine Ge surfaces. By introducing either in situ or ex situ a passivation layer that screens the HfO_2 from the Ge, the *C*/*V* and *I*/*V* results can be strongly improved. We find that a GeON-like interfacial layer is quite effective in passivating the Ge surface, contrary to what originally was believed. Still, the best interfacial state densities we have seen so far in the HfO_2/Ge system is around 5×10^{12} cm^{-2}, which needs further improvement. We speculate that a better control of the interface, especially the Ge oxidation state which should be as much as possible Ge^{4+}, could be very important here.

Whereas there is probably no such thing as the ultimate high-k material, from this HfO_2/Ge model material system it may be clear, that the Ge surface preparation and the high-k material deposition technique must be matched to each other, and cannot be combined arbitrarily.

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