Atomic layer deposition of hafnium oxide on germanium substrates

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Germanium combined with high-k dielectrics has recently been put forth by the semiconductor industry as potential replacement for planar silicon transistors, which are unlikely to accommodate the severe scaling requirements for sub-45-nm generations. Therefore, we have studied the atomic layer deposition (ALD) of HfO2 high-k dielectric layers on HF-cleaned Ge substrates. In this contribution, we describe the HfO2 growth characteristics, HfO2 bulk properties, and Ge interface. Substrate-enhanced HfO2 growth occurs: the growth per cycle is larger in the first reaction cycles than the steady growth per cycle of 0.04 nm. The enhanced growth goes together with island growth, indicating that more than a monolayer coverage of HfO2 is required for a closed film. A closed HfO2 layer is achieved after depositing 4–5 HfO2 monolayers, corresponding to about 25 ALD reaction cycles. Cross-sectional transmission electron microscopy images show that HfO2 layers thinner than 3 nm are amorphous as deposited, while local epitaxial crystallization has occurred in thicker HfO2 films. Other HfO2 bulk properties are similar for Ge and Si substrates. According to this physical characterization study, HfO2 can be used in Ge-based devices as a gate oxide with physical thickness scaled down to 1.6 nm. © 2005 American Institute of Physics. [DOI: 10.1063/1.1856221]

I. INTRODUCTION

Germanium is a high-performance device material due to its narrow band gap, high mobility and low dopant activation temperatures. It has recently been put forth by the semiconductor industry as a potential replacement for planar silicon transistors, which are unlikely to accommodate the severe scaling requirements for sub-45-nm transistor generations. However, a major technological drawback to the use of Ge is the difficulty in growing an insulating oxide comparable to SiO2 in Si technology. Deposited high-k materials may provide a solution for the gate dielectric of Ge-based transistors. Indeed, the successful use of a ZrO2 dielectric film in Ge field-effect transistors (FETs) has recently been demonstrated.1 The low-field mobility for the Ge/ZrO2 FETs was twice that of Si/SiO2 FETs.1

High-performance devices in the sub-45-nm technology mode should reach the equivalent oxide thickness (EOT) targets below 0.8 nm. For ZrO2 and HfO2 dielectrics with a k value of 20–25, this means that films thinner than 4 nm should be deposited. Atomic layer deposition (ALD) is a suitable technique to deposit uniform films in the nanometer thickness range.2,3 In order to function as a gate dielectric, the layer should also be smooth and contain no holes. As the ALD growth behavior can depend on the substrate,4–8 it is important to investigate and compare the growth characteristics and morphology of the dielectric films on the specific substrates. At least two ALD growth characteristics are affected by the substrate. A first growth characteristic is the growth per cycle or growth rate, defined as the total amount of material deposited per reaction cycle.6 The growth per cycle can be expressed as thickness increment (nm) or as increase of areal density (number of atoms/nm²).6 A second growth characteristic influenced by the substrate is the growth mode,9 which refers to the way the deposited material is arranged on the substrate; the material can be deposited as islands, or in a more favorable case as a closed two-dimensional layer.

For the ALD of HfO2 on Si substrates, using HfCl4 and H2O precursors, both growth per cycle and growth mode have been investigated for different surface preparations.4,8,10–15 The growth per cycle can accurately be determined by means of a Rutherford backscattering spectroscopy (RBS) as the number of Hf atoms/nm². The growth per cycle as thickness can be obtained from the RBS Hf coverage assuming a value for the HfO2 density,6 or from ellipsometry if the layers are thinner than about 10 nm.16,17

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On the other hand, the experimental determination of the growth mode is less straightforward. Essentially, we want to monitor the composition of the top surface of the sample and observe how fast the substrate intensity decreases as a function of the Hf coverage. Therefore, very surface sensitive techniques, such as low-energy ion scattering (LEIS) or time-of-flight secondary-ion-mass spectrometry (TOFSIMS) should be used. The combination of RBS and TOFSIMS has shown that the growth per cycle dependence on the substrate can give a first indication of the growth mode. Strong inhibition effects in the first ALD cycles have been associated with islandlike morphology and poor electrical properties of the dielectric layer. Growth inhibition is very pronounced on hydrogen-terminated Si substrates and may be related to the low reactivity of the HfCl₄ precursor with Si–H bonds. The introduction of more reactive Si–OH groups, for example, by chemical oxidation or by remote plasma treatments, leads to a more constant growth per cycle and a more two-dimensional growth mode. LEIS has demonstrated HfO₂ layer closure after ten reaction cycles for ALD on chemical oxide substrates.

In this contribution, we investigate the ALD of HfO₂ on Ge substrates by means of several complementary analysis techniques. Both growth per cycle and growth mode are studied using RBS, TOFSIMS, and LEIS. The Ge interface will be particularly important with respect to device performance. Therefore, the Ge interface is also investigated by means of x-ray photoelectron spectroscopy (XPS) and medium energy ion scattering (MEIS). Cross-sectional transmission electron microscopy (TEM), x-ray diffraction (XRD), and TOFSIMS depth profiling further characterize the HfO₂ layer on Ge substrates.

II. EXPERIMENTAL DETAILS

A. HfO₂ layer growth

Prior to deposition, 100-mm Ge(100) substrates were cleaned for 5 min in a 2% HF solution, rinsed in de-ionized water, and dried in clean room air. Both Ge(100) and miscut Ge(100) substrates were used. The miscut was 5.7° towards (111). The results for miscut Ge(100) were not different from the results for Ge(100). HfO₂ was deposited in an ASM ALCVD™ Pulsar 2000 reactor, integrated on a Polygon™ 8200 platform. All depositions were performed at 300 °C with HfCl₄ and H₂O precursors. The pressure in the reactor was 1 Torr. The cycle numbers ranged between 1 and 300. The pulse and purge times were optimized for HfO₂ films grown in tens to hundreds of ALD reaction cycles. The optimized process gave uniform HfO₂ films over the 100-mm Ge wafers. Reactant doses below that needed for saturation caused a sharp thickness decrease at the back end of the wafer. Small changes in the pulse and purge times did not affect the amount of material deposited. Uniform film thickness and low sensitivity towards pulse and purge times indicated that surface saturation was obtained and ALD conditions prevailed.

B. XPS

Ge/HfO₂ samples were analyzed by XPS after several weeks of air exposure. XPS measurements were performed in a Quantum 2000 from Phi (Q1) using a monochromatic Al Kα radiation in a high-power mode (100 W, measuring spot 100 μ, scanned over 1400 × 500 μ²). The angle between the axis of the analyzer and the sample surface was 90°. The amount of C was found to be ~10 at. %, which is a normal contamination level for samples stored in ambient air. The Ge2p line, corresponding to a kinetic energy of 260 eV, was detectable only for HfO₂ samples of less than 60 cycles. Thicker HfO₂ layers attenuate the Ge2p signal too much. Due to a strong overlap between the O2s (from HfO₂) and the Ge3d peak, this region could not be used to analyze the oxidation of the Ge interface. The Ge3s lines gave chemical information about the bottom interface. Standard sensitivity factors were used to convert peak areas to atomic concentrations. The thickness of the GeO₂ and HfO₂ layers was estimated by means of a three-layer model calculation. The escape mean free paths of the photoelectrons was calculated using the Tanuma–Powell–Penn (TPP2) formula.

The HF-cleaned Ge substrate was also characterized by XPS. The air exposure between cleaning and XPS measurement was limited to less than 15 min. The Ge3d lines were analyzed.

C. RBS

RBS was performed in a RBS400 Endstation (Charles Evans and Associates) which is installed around a 6SDH-12MV tandem (National Electrostatics Corporation). The measurements were performed with a 1-MeV He⁺ beam in a rotating random mode. The scatter angle was 168°. The accumulation dose was 20 μC. Beam current was limited to 5 nA to avoid pile up in the electronics. A beamchopper was used for normalization. The RUMP simulation code was applied to calculate the areal density of Hf (number of atoms/cm²).

D. LEIS

LEIS measurements were performed with 3-keV ⁴He⁺ and ²⁰Ne⁺. First a ⁴He⁺ measurement was performed to get a general impression of the surface composition, using an ion dose of 2.1 × 10¹³ ions/cm² to measure one spectrum. Measurements with 3-keV ²⁰Ne⁺ were performed directly after the ⁴He⁺ measurements using an ion dose of 1.1 × 10¹³ ions/cm². For each sample the analysis was based upon an average of three spectra to obtain adequate statistics. There was a linear dependency between the Hf and Ge intensities, which allows a reliable determination of maximum Hf and Ge intensities by extrapolation. The surface fractions of Hf and Ge were calculated by dividing the Hf and Ge intensity by their maximum intensities.

Cleaning the sample surface prior to LEIS analysis is inevitable as organics, adsorbed during air exposure between sample preparation and LEIS analysis, diminish the surface spectrum intensity. Two different cleaning methods prior to LEIS analysis were used: low-energy atomic oxidation and calcination. Low-energy atomic oxidation was performed at
room temperature with $10^{-4}$-mbar oxygen pressure. The minimum time needed to obtain a clean surface by atomic oxidation was determined for a sample consisting of 5-cycles HfO$_2$ deposited on a HF-cleaned Ge. An increase of the complete spectrum intensity was observed with increasing oxidation time, indicating a decreasing content of organics. Extrapolation of the results after 0, 3, 6, and 9-min oxidation indicated that 15 min was sufficient to obtain a clean surface. In a second cleaning method, samples were first calcined for 20 min at 300 °C using an oxygen pressure of 200 mbar. After calcination, samples were oxidized using atomic oxygen. Subsequent atomic oxidation treatments did not change the LEIS spectrum, suggesting a fully cleaned surface. Only minor top surface carbon contamination was detected. In a second cleaning method, atomic oxidation only, will therefore be used for analysis of the HfO$_2$ growth mode.

### E. TOFSIMS

All TOFSIMS measurements were performed using an Ion TOF-IV instrument using a 10-keV Ar$^+$ analysis ion beam. Normalized intensities were calculated by dividing the Measured Intensity by the Signal measured on a pure HfO$_2$ or Ge surface. For the depth profiles, a dual beam setup with a 500-eV Ar$^+$ ion beam was used.

### F. MEIS

The MEIS instrument (High Voltage Engineering B.V., Amersfoort, the Netherlands) has been described in detail elsewhere. Protons with an energy of 98.80±0.08 keV were used. Backscattered ion energies were analyzed with a high-energy-resolution toroidal electrostatic detector ($\Delta E/E \sim 0.1\%$). Depth profiles of the elements were obtained from simulations of the measured backscattered ion energy distribution assuming that the film densities are known or can be extrapolated from known data. The scattering geometry used had the incident beam aligned in the [001] direction, deviating $\sim 5^\circ$ from macroscopic surface normal, due to the miscut of the Ge substrate wafer. Therefore, the data were acquired at a scattering angle of $130.7^\circ$. Prior to MEIS analysis, the samples were exposed to air for several days. Only minor top surface carbon contamination was detected.

### G. TEM

Cross-sectional TEM specimens were prepared by conventional ion milling and observed in Jeol 200CX and Philips CM30 TEMs at 200 and 300 kV, respectively.

### H. XRD

A high-temperature grazing incidence x-ray diffraction (HT-GI-XRD) was performed with a θ-θ XRD diffractometer (3003 TT Seifert, Ahrensburg, Germany) using a Cu Kα source radiation and an incidence angle of $3^\circ$. The diffractometer is equipped with a parabolic multilayer mirror for parallel beam optics and a furnace for in situ high-temperature XRD tests. The sample was heated from room temperature to a test temperature, at which a scan in the 2θ range from 20 to 40 takes about 30 min. After the scan, the sample was heated to a higher temperature for a new scan with the same schedule.

### III. RESULTS

#### A. XPS

First, XPS measurements were performed to characterize the uncleaned and HF-cleaned Ge substrate. The Ge3d lines (spectrum not shown) were measured at binding energy between 28 and 35 eV and were separated into substrate Ge and oxidized Ge. After HF clean, the binding energy of the oxidized Ge peak significantly reduced in intensity and shifted from 33 to 32 eV. This indicates that the native oxide on the uncleaned Ge wafer, consisting mainly of GeO$_2$, was etched during HF clean. Only a limited amount of suboxide ($0.2–0.3$ nm) was present after the HF clean (Table I).

Second, XPS was used to characterize the Ge interface of samples with 40, 60, and 80 cycles of HfO$_2$. The Ge3s were separated into substrate Ge (at 182.2 eV) and interfacial GeO$_2$ (at 184.9 eV) [Fig. 1(a)]. As expected, the intensity of the Ge signal decreased with increasing Hf coverage. The thickness of the GeO$_2$ interfacial layer, as deduced from a three-layer model, was small ($0.3$ nm) (Table I). The Hf4f peaks consisted of one single doublet with a peak position at 17.2 eV [Fig. 1(b)]. No indications for metallic Hf or Hf suboxides were observed.

#### B. RBS

The RBS Hf content as a function of the number of ALD cycles is shown in Fig. 2. The growth per cycle in the first ten ALD reaction cycles is shown in Fig. 3. The ALD growth was enhanced by the Ge substrate; the growth per cycle was higher in the first reaction cycles than in the steady regime. The amount of Hf deposited in the first reaction cycle is $7.6$ Hf/nm$^2$. This corresponds to almost one monolayer of HfO$_2$ ($9.15$ Hf/nm$^2$), as calculated from the bulk density of HfO$_2$ ($9.68$ g cm$^{-3}$). Within few cycles, the growth per cycle decreased to a steady value of about $1.1$ Hf/nm$^2$ or $0.040$ nm assuming the bulk density. Thus, the steady growth is similar as the case of HfO$_2$ growth on Si substrates.

### Table I. XPS and MEIS GeO$_2$ thickness (nm). * not measured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS thickness (nm)</th>
<th>MEIS thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-cleaned Ge</td>
<td>0.2–0.3</td>
<td>*</td>
</tr>
<tr>
<td>HF-cleaned Ge+30-cycles HfO$_2$</td>
<td>* 0.3</td>
<td></td>
</tr>
<tr>
<td>HF-cleaned Ge+40-cycles HfO$_2$</td>
<td>0.3 *</td>
<td></td>
</tr>
<tr>
<td>HF-cleaned Ge+60-cycles HfO$_2$</td>
<td>0.4 0.3</td>
<td></td>
</tr>
<tr>
<td>HF-cleaned Ge+80-cycles HfO$_2$</td>
<td>0.4 *</td>
<td></td>
</tr>
</tbody>
</table>
C. LEIS

Figures 4(a) and 4(b), respectively, show the $^{4}\text{He}^+$ and $^{20}\text{Ne}^+$ LEIS spectra measured after atomic oxidation on samples with different number of HfO$_2$ cycles. Peaks of O, Ge, and Hf were clearly visible. No other elements were observed. The surface of the pure Ge wafer (0 cycles) was oxidized, as shown by the O peak in the LEIS spectrum [Fig. 4(b)]. With increasing number of cycles, the Ge peak decreased and the Hf peak increased. After 25 cycles, the Ge surface was fully covered by HfO$_2$, as shown by the absence of a Ge peak in the $^{20}\text{Ne}^+$ spectrum [Fig. 4(b)]. From this point, the Hf peak in the $^{4}\text{He}^+$ spectrum substantially broadens to the low-energy side. Asymmetric broadening originates from ion scattering of Hf atoms below the surface.$^{27}$

The HfO$_2$ and Ge surface fractions, calculated by normalizing the LEIS Hf and Ge signals, are shown in Fig. 5. The HfO$_2$ surface fraction increased and the Ge surface fraction decreased with the number of ALD reaction cycles, as expected. After 25 cycles; the HfO$_2$ film covers the surface completely.

D. TOFSIMS

Figure 6 shows the evolution of the normalized Hf and Ge intensities at the top surface, as measured by TOFSIMS. Similarly as in LEIS, the HfO$_2$ intensity increased and the Ge intensity decreased with the number of cycles. The TOFSIMS Hf signal follows the same trend as LEIS, with saturation around 25 reaction cycles.

TOFSIMS was also used to achieve a depth profile of the Hf, Cl, and Ge intensities (Fig. 7). No significant amount of Ge was observed in the HfO$_2$ bulk. The shape of the Cl profile for HfO$_2$ deposition on Hf-cleaned Ge is similar to that for HfO$_2$ deposited on Si substrates,$^{28}$ with a Cl peak at the bottom HfO$_2$ interface.

E. MEIS

MEIS was used to estimate film composition and interfacial oxide thickness. Figure 8 shows a proton backscatter-
ing energy spectrum from an as-deposited 3-nm-thick HfO$_2$ film. Both 3- and 6-nm HfO$_2$ spectra can be fitted with very thin \(0.3 \text{ nm}\) GeO$_x$ interfacial oxides (Table I). The HfO$_2$/GeO$_2$/Ge interfaces are likely to be sharp, the position of the Ge peak indicating that there is not much Hf–Ge–O intermixing. In addition, Cl concentrations of about \(10^{15}\) atoms/cm$^2$ were detected close to the Ge interface, attributed to the use of the HfCl$_4$ precursor in the ALD process. Probably, this Cl is distributed in several monolayers located close to the Ge interface. MEIS angular distribution profiles show no evidence for crystallinity, both 3- and 6-nm HfO$_2$ films appearing to be amorphous.

Cross-sectional TEM images of samples with 12-, 40-, and 200-cycles HfO$_2$ deposited on an HF-cleaned Ge substrate are shown in Fig. 9. The Ge interface was smooth. A bright contrast layer was observed at this interface. This contrast is most probably due to the presence of a thin interfacial oxide layer, as indicated by XPS and MEIS. The thin HfO$_2$ layers both were amorphous as deposited. The 200-cycles HfO$_2$ layer was 9.0 nm thick and polycrystalline. Some crystals were formed in epitaxy with the Ge substrate; one can see the continuation of the (111) Ge crystallographic planes through the interface.

The HfO$_2$ thickness deduced from TEM is shown in Table II. HfO$_2$ densities were calculated for the three samples by combining the TEM HfO$_2$ thickness and RBS Hf coverage.

G. XRD

XRD measurements were performed on as-deposited samples with 100-, 200-, and 300-cycles of HfO$_2$, which
correspond to 5-, 9-, and 14-nm, respectively. Figure 10 shows the results for 14-nm HfO$_2$. The as-deposited layer is partially crystalline and is composed of 10 vol % cubic, 10 vol % monoclinic, and 80 vol % amorphous phase. At 400 °C, a fully crystalline layer forms. With the increase of temperature, the cubic phase, which is metastable in the temperature range of the test, transforms into a monoclinic phase. A similar phase transformation occurs for HfO$_2$ on Si substrates. At 800 °C, only a very small amount of cubic phase remains. The spectra shown in Fig. 10 reveal m(200) and (002) textures, or the intensities of the peaks are higher than in powder diffraction. This indicates the epitaxial orientation of the crystallites.

XRD indicated that thinner HfO$_2$ layers (5 and 9 nm) were amorphous as deposited, and crystallize at a temperature between 300 and 400 °C. The phase transformation from cubic to monoclinic is also observed.

IV. DISCUSSION

A. Reactive sites at the Ge substrate

The chemical composition of the substrate can influence both growth per cycle and growth mode of the atomic layer deposition. Therefore, we have characterized the Ge substrate after HF clean with XPS. A small amount of suboxide remains present on Ge after HF clean (Table I). Prior to HfO$_2$ deposition, this substrate is conditioned in the ALD reactor at 300 °C in 1 Torr of N$_2$. At this temperature, H starts to desorb from the Ge$_{100}$ substrate. High-resolution electron energy-loss spectroscopic (HREELS) studies have shown that the dihydride and monohydride coverage decreases to zero at 300 and 380 °C, respectively. It has been shown that coadsorbed O creates little perturbation to the H desorption kinetics of Ge. Above 300 °C, O is proposed to be present in the form of a bridge-bonded species, although

<table>
<thead>
<tr>
<th>Number of ALD cycles</th>
<th>TEM thickness (nm)</th>
<th>HfO$_2$ density (10$^{22}$ HfO$_2$/cm$^3$)</th>
<th>% of HfO$_2$ bulk density</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1.6</td>
<td>1.59</td>
<td>58</td>
</tr>
<tr>
<td>40</td>
<td>2.6</td>
<td>2.22</td>
<td>80</td>
</tr>
<tr>
<td>200</td>
<td>9.0</td>
<td>2.69</td>
<td>97</td>
</tr>
</tbody>
</table>

TABLE II. Density of HfO$_2$ layers deduced from the TEM thickness (Fig. 9) and the RBS Hf coverage (Fig. 2).

substrates. At 800 °C, only a very small amount of cubic phase remains. The spectra shown in Fig. 10 reveal m(200) and (002) textures, or the intensities of the peaks are higher than in powder diffraction. This indicates the epitaxial orientation of the crystallites.

XRD indicated that thinner HfO$_2$ layers (5 and 9 nm) were amorphous as deposited, and crystallize at a temperature between 300 and 400 °C. The phase transformation from cubic to monoclinic is also observed.
OH groups may also be present. Thus, monohydrides, oxygen bridges as well as OH groups could be present at the Ge substrate before ALD.

For HF-cleaned Si(100), on the other hand, no significant amount of oxide is present. Both mono-, di-, and trihydrides are present at the HfO$_2$ ALD process temperature, as H desorption occurs only at temperatures above 500 °C. Si–H is known to be a very low-activity site for as H desorption occurs only at temperatures above 500 °C.33,34 Si–H is known to be a very low-activity site for as H desorption occurs only at temperatures above 500 °C.

Thus, the active sites for ALD on HF-cleaned Ge probably are OH groups, possibly also the Ge–O–Ge bridge configuration, probably not Ge–H. As the reactive sites at HF-cleaned Ge and Si substrates clearly are very different, we can expect a different growth behavior on HF-cleaned Ge and Si substrates. This will indeed be shown in the following paragraphs.

B. Analysis of the HfO$_2$ growth mode

The normalized intensities of the substrate and the deposited HfO$_2$ layer (obtained from LEIS and TOFSIMS) give information about the growth mode when they are combined with the total amount of HfO$_2$ deposited (as measured by RBS). In the two-dimensional growth mode (also called layer-by-layer growth and Frank van der Merwe growth), the surface fraction of the substrate first decreases linearly with the amount of material deposited. From the point where one HfO$_2$ monolayer (9.15 Hf/nm$^{-2}$) is present, it is zero. On the other hand, an approximately exponential decay of the substrate surface fraction is expected in the random deposition mode. In this growth mode, all surface sites have the same probability of deposition. If the substrate intensity decay is even slower than in the random deposition mode, island growth is prevailing. We will compare LEIS and TOFSIMS results with the theoretical models in order to determine the growth mode.

The interpretation of LEIS results is straightforward because the measured intensity comes from the first atomic layer and, as such, directly gives the surface fraction. Theoretical surface fraction curves for two-dimensional and random deposition were calculated, as described in Ref. 7, using the growth per cycle curve shown in Fig. 3. The LEIS surface fractions for HfO$_2$ growth on HF-cleaned Ge deviate significantly from the theoretical surface fraction curves, both for two-dimensional and random deposition [Fig. 11]. According to the two-dimensional growth, the HfO$_2$ layer should be closed already at about 9.15 Hf/nm$^{-2}$, much earlier than observed by LEIS, about 40 nm$^{-2}$. The closure point measured with LEIS for HfO$_2$ deposition on HF-cleaned Ge is similar as expected on the basis of random deposition. However, before closure we observe a significant deviation between the measured and calculated curves; LEIS systematically shows higher Ge and lower HfO$_2$ surface fractions. This demonstrates that island growth (Volmer–Weber growth) takes place. Another possibility is that Hf mixes with Ge, forming a HfGeO$_x$ layer.

The interpretation of the TOFSIMS substrate intensities is more complicated than LEIS, as not only the outermost surface but the first few atomic layers can determine the TOFSIMS intensity. An exponential decay of the substrate intensity is often observed

\[ I(t) = I_0 \exp(-tl/\lambda) \]

Here, $t$ is the film thickness. $\lambda$ can be considered as a parameter that qualitatively describes how fast the layer closes. For HfO$_2$ growth on Si chemical oxide, which is close to two dimensional, the TOFSIMS Si signal decays exponentially with $\lambda \approx 0.2$ nm. This decay curve is shown in Fig. 12 together with the TOFSIMS Ge decay curve for HfO$_2$ deposition on HF-cleaned Ge. Up to 12 ALD cycles, the Ge intensity decays much slower as compared to the two-dimensional reference. The data points can be fitted with an exponential function with $\lambda = 0.6$ nm. This high $\lambda$ value again points to island growth. The TOFSIMS decay of the Ge substrate signal accelerates after 12 ALD reaction cycles (Figs. 6 and 12).

Although LEIS and TOFSIMS both suggest the formation of islands, islands are not directly visible with TEM. For 12-cycles HfO$_2$, LEIS shows that only 60% of the substrate is covered by HfO$_2$. However, the HfO$_2$ layer visible on the cross-sectional TEM image appears to be closed and rather smooth [Fig. 9(a)]. The islands and voids between islands are expected to be of much smaller dimensions than the thickness of the TEM cross section (50–100 nm). Therefore, it is not possible to distinguish them individually in the cross-section TEM image.
section view due to the dark contrast of HfO₂. Plan view TEM, on the other hand, gives a “top view” of the sample. However, plan view TEM (not shown) also could not confirm the presence of the HfO₂ islands because the thin HfO₂ layer gave a too weak contrast.

The islandlike growth on HF-cleaned Ge must be distinguished from the island growth, for example, on HF-cleaned Si. First, it goes together with the growth enhancement instead of the growth inhibition observed on HF-cleaned Si.⁴,⁸,¹⁰ Second, the HfO₂ layer closure on HF-cleaned Ge is faster as compared to HF-cleaned Si; the HfO₂ layer on Ge closes after about 1.6 nm, while for Si more than 4 nm must be deposited.³⁷ The faster layer closure can indicate that there are more nucleation sites at the HF-cleaned Ge substrate (e.g., OH, see Sec. IV A), as compared to HF-cleaned Si. A higher island density can then be expected, resulting in faster layer closure.

C. Analysis of growth enhancement

Growth enhancement in the first reaction cycles is not common for ALD processes, although in some cases it has been observed.¹²,¹⁴,³⁸,³⁹ The Ge surface is very smooth, so the high growth per cycle cannot be attributed to surface roughness or even a microporous structure such as, e.g., in the ALD growth of Al₂O₃ on SILK.³⁸

The possible reactions involved in the chemisorption of HfCl₄ on the Ge substrate can be analyzed by means of a recent model of growth per cycle in ALD.⁶ The model is based on the mass balance of chemisorption and assumes a two-dimensional arrangement of the adsorbed ligands. The amount of Hf adsorbed in the first reaction cycles is directly obtained from the growth per cycle as 7.6 nm⁻² [Fig. 3]. During the HfCl₄ reaction, each Hf atom brings along four Cl ligands (using the HfCl₄ precursor). Thus, according to mass balance, about 30 Cl ligands nm⁻² arrive to the surface. The maximum number of Cl ligands remaining on a flat surface when steric hindrance prevails can be estimated from the van der Waals radius of Cl [0.175 nm (Ref. 40) as 9.4 nm⁻²].⁶ Therefore, according to the growth per cycle model, at least (30–9.4) ≈ 21 Cl ligands nm⁻² must have been removed from the surface. The typical mechanism for removing Cl ligands is ligand exchange in which Cl is released into the gas phase according to the following reaction:

\[ 2\text{OH}^* + \text{MCl}_4 \rightarrow 2\text{Cl}^* + \text{MCl}_2(\text{OH})_2 \]

\[ \text{MCl}_2(\text{OH})_2 \rightarrow \text{MO}_2^* + 2\text{HCl} \]

This process is often referred to as agglomeration.⁴²,⁴³ This agglomeration process may occur when metal halide precursors are used, for example, for the TiCl₄/H₂O TiO₂ and ZrCl₄/H₂O ZrO₂ ALD processes.⁴⁴-⁴⁹ The transport of oxygen from the substrate to the growing metal oxide particle might be explained by an intermediate MCl₂(OH)₂ species, moving OH groups from the substrate to the formed metal chloride surface species. No clear evidence has been presented for agglomeration reactions in HfO₂ ALD on Si substrates. However, agglomeration could occur more easily on Ge substrates, as the Ge–O bond is weaker than the Si–O bond, facilitating the release of O necessary for the formation of the agglomerates.

Some support for the agglomeration mechanism comes from the growth studies of HfO₂ on an O-free Ge substrate. The XPS spectrum clearly demonstrated that no GeO₂ or suboxide was present on this substrate before HfO₂ deposition. The growth per cycle for HfO₂ deposition on O-free Ge was significantly lower as compared to HF-cleaned Ge substrates (Fig. 3), indicating that the growth enhancement is related to the presence of oxygen at the Ge substrate. Furthermore, agglomeration has usually been associated with chlorination of the substrate. According to MEIS and TOFSIMS, there was indeed a significant amount of CI present close to the Ge interface for deposition on HF-cleaned Ge. TOFSIMS indeed indicates that the CI peak at the bottom interface is higher for HfO₂ deposition on Ge substrates, as compared to Si substrates (see also Sec. IV D).

D. HfO₂ bulk properties on Ge substrates

1. Density

The density of the HfO₂ layers (Table II) depends on the layer thickness. A similar dependence was also observed for ALD HfO₂ on Si substrates¹⁷,⁵⁰ and for metal-organic...
chemical-vapor deposition (MOCVD) HfO$_2$ on Si substrates. The low density of the thinnest layers could reflect their island morphology. For closed HfO$_2$ layers on Ge substrates, a density of more than 80% of the bulk density is obtained. This is in agreement with the density of ALD HfO$_2$ deposited on Si substrates with similar thickness.

2. Ge/Hf intermixing

TOFSIMS depth profiles (Fig. 7) indicate no significant concentration of Ge in the HfO$_2$ bulk, in contrast to what is observed, for example, for HfO$_2$ deposited by MOCVD on HF-cleaned Ge substrates.

3. Impurities

Both TOFSIMS and MEIS show some Cl in the ALD HfO$_2$ films due to the use of the HfCl$_4$ precursor. TOFSIMS indicates a similar bulk Cl content for Ge and Si substrates. However, the Cl peak at the bottom interface is higher for Ge substrates. This could be due to substrate chlorination reactions associated with the agglomeration process. MEIS indicates a Cl content close to the Ge interface of about 10 Cl/nm$^2$. As this Cl content corresponds to about one monolayer, the Cl is probably distributed in several monolayers located close to the Ge interface.

4. Crystallization behavior

Cross-sectional TEM, XRD, and MEIS show that thin HfO$_2$ layers (<9 nm) are amorphous as deposited. XRD shows that a 14-nm-thick HfO$_2$ layer is partially crystalline, with some HfO$_2$ grains oriented in epitaxy with the Ge substrate (Fig. 10). XRD and TEM disagree on the critical HfO$_2$ thickness at which crystallization starts to occur. With TEM, crystals are already observed in a 9-nm HfO$_2$ layer. On the other hand, XRD shows no diffraction peaks for a 9-nm HfO$_2$, but they appear for a 14-nm HfO$_2$ layer. The sensitivity of XRD is probably not sufficient to detect a limited amount of crystalline phase. Alternatively, the crystallites observed in a 9-nm layer by TEM might have grown in such an orientation that grazing incidence XRD cannot detect them.

The fact that thin films are amorphous implies that also thicker layers are amorphous in the first stages of the deposition process. As such, epitaxial crystallization occurs in a later stage of the ALD process, not during the ALD gas-substrate reactions itself. The presence of small amounts of O or Cl at the Ge interface and the lattice mismatch between the Ge and HfO$_2$ probably locally hinders full epitaxial crystallization of the HfO$_2$ film. Local epitaxial ZrO$_2$ crystals were also observed for a 5.5-nm ZrO$_2$ layer deposited by ALD on HF vapor-cleaned Ge(100) substrates and for HfO$_2$ deposited by MOCVD on Ge.

The crystallization behavior as a function of temperature, as studied by means of XRD, is similar for Ge and Si chemical oxide substrates. A fully crystalline layer forms during a thermal treatment at low temperature. With the increase of temperature, the transformation from cubic to monoclinic phase is observed. The main difference for Ge and Si substrates is that no epitaxial crystallization was observed on Si.

E. The Ge interface

The interface between HfO$_2$ and the Ge channel will be particularly important in regard to device performance. First, the presence of low-quality Ge oxide or suboxide may degrade the electrical performance. Second, the thickness of the interfacial layer (with low-$\kappa$ value) directly adds to the equivalent oxide thickness (EOT) of the high-$\kappa$ stack. It should therefore be as thin as possible if subnanometer EOT targets are aimed for.

The cross-sectional TEM images (Fig. 9) show a smooth Ge interface with no obvious indication of an interfacial layer. XPS and MEIS investigations both indicate the presence of a thin (about 0.3 nm) oxide interfacial layer. Moreover, the XPS binding energy of the Ge3s lines indicates that the chemical composition of the interfacial layer is GeO$_2$.

The stability of the interfacial oxide layer during air exposure is important in case the gate is subsequently deposited ex situ. For nonclosed HfO$_2$ layers deposited on Ge, ellipsometer measurements show a thickness increase during air exposure due to interfacial oxide growth. LEIS also indicates that nonclosed HfO$_2$ layers on Ge are not stable during calcinations at 300 °C. For ZrO$_2$ and Al$_2$O$_3$ layers deposited on Si substrates, it has also been reported that interfacial oxide forms easily during air exposure when the high-$\kappa$ layers are not fully closed. Closed HfO$_2$ layers on Ge, on the other hand, are stable during air exposure.

V. CONCLUSIONS

We have demonstrated the atomic layer deposition of HfO$_2$ on HF-cleaned Ge substrates using the HfCl$_4$ and H$_2$O precursors. According to this physical characterization study, the physical thickness of HfO$_2$ dielectric layers grown on HF-cleaned Ge can be scaled down to about 1.6 nm. Optimization of the surface preparation resulting in a more two-dimensional growth mode may allow the further scaling of dielectrics layers to less than 1.6 nm. A second critical issue for the ultimate scaling of the Ge/high-$\kappa$ stacks is the interfacial layer. A promising observation for HfO$_2$ stacks deposited on HF-cleaned Ge is that the bottom interfacial layer is less than 0.4 nm thin. The scaling potential combined with the high mobility of the Ge substrate makes the Ge/high-$\kappa$ stacks promising for high-performance complementary metal-oxide semiconductor (CMOS) applications.

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41 For example, the RBS Hf coverage and LEIS HfO2 surface fraction in the first cycle can be reproduced assuming a cylindrical shape of the HfO2 islands with height of 1 nm and radius 0.3 nm, with a distribution of one island per nm2. The cylindrical configuration would allow a much higher maximum Cl coverage, of about 23 Cl/nm2.