The physical properties of metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) deposited HfZrO4 films have been analyzed in detail by atom probe tomography, X-ray photoelectron spectroscopy, Rutherford backscattering spectrometry, transmission electron microscopy, atomic force microscopy, variable angle spectroscopic ellipsometry as well as temperature dependent grazing incidence X-ray diffraction. In addition we extend our recently presented electrical 32nm device results with MOCVD and ALD deposited HfZrO4 gate dielectrics by further evaluating 32 nm high performance logic devices on silicon on insulator (SOI) substrates with respect to interface trap charge densities $D_{it}$ and time dependent dielectric breakdown (TDDB) reliability. All investigated parameters revealed a comparable behavior between ALD and MOCVD and therefore MOCVD is demonstrated to be a promising alternative to ALD in high volume manufacturing in this work.

Introduction

High-k (HK) dielectrics with metal gate (MG) electrodes are required for future scaling of complementary metal oxide semiconductor (CMOS) technology to realize higher gate capacitances and low gate leakage currents [1]. During the last decade there was an industry-wide effort to find the best material. Due to their relatively high dielectric constants, large band gap and conduction band offset to Si and their thermodynamic stability with Si, hafnium-based dielectrics and particularly HfO2 are considered to be the most promising candidates to replace SiON in high volume manufacturing [2-4]. However, compared to SiO2, HfO2 dielectrics suffer from mobility degradation and charge trapping as well as reliability degradation [5,6]. Recently HfZrO4 gate dielectrics have been demonstrated to be beneficial compared to HfO2 [7-11]. Addition of ZrO2 to HfO2 forming HfZrO4 helps to partially stabilize tetragonal phase being associated with higher k- and lower CET values [7]. Additionally a more uniform film quality, smaller and more uniform grains, a tighter leakage distribution, lower CV hysteresis, less charge...
trapping, lower $D_{it}$ values, higher transconductance and drive currents, reduced SILC and longer product reliability lifetimes have been reported among other things for HfZrO$_4$ compared with HfO$_2$ [7-11]. But on the other hand disadvantages like smaller band gap (~0.4 eV) and lower conduction band offsets resulting in increased leakage have been presented as well [7]. In the scientific literature up to now atomic layer deposition (ALD) [7-10] as well as physical vapor deposition (PVD) [11] have been explored to form the HfZrO$_4$ layers. As metal-organic chemical vapor deposition (MOCVD) stands out due to excellent manufacturability and high throughputs, we have recently shown first electrical 32 nm SOI high performance logic CMOS device data of HfZrO$_4$ gate dielectrics deposited with MOCVD and ALD [12]. Based on the electrical data presented, a comparable behavior between ALD and MOCVD was demonstrated and particularly with regard to manufacturability and cost of ownership MOCVD was shown to be a real promising alternative in high volume manufacturing. In this publication we extend our previous work by presenting a detailed physical characterization of MOCVD and ALD deposited HfZrO$_4$ layers. The composition of the HfZrO$_4$ films has been analyzed in detail by atom probe tomography (APT). Subsequently the results were confirmed by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). Temperature dependent grazing incidence X-ray diffraction (GI-XRD) has been used to investigate the crystallization temperature and the crystalline phase of very thin HfZrO$_4$ films ranging from 2nm to 6nm thickness. Brightfield high resolution transmission electron microscopy (HRTEM) pictures of high temperature annealed HfZrO$_4$ samples have been taken to confirm the crystallinity after an annealing step. Besides the impact of a high temperature annealing on physical properties has been explored by directly comparing annealed and as deposited HfZrO$_4$ samples via atomic force microscopy (AFM) and variable angle spectroscopic ellipsometry (VASE). Recently presented electrical results [12] based on 32 nm high performance logic devices covering gate leakage current, capacitance equivalent thickness, threshold voltage, and performance as well as reliability (bias temperature instability and hot carrier injection) data are extended in this work. A determination of the interface trap density by means of charge pumping and the correlation with long channel mobility will be shown. Complementary to the HCI/BTI reliability data presented so far, the results of time dependent dielectric breakdown tests will be displayed.

**Experimental**

On standard 300 mm wafers a nitrided chemical base oxide was formed with a SC1/SC2 based wet chemistry and an interface nitridation step. Optical measurements of this base oxide revealed a thickness of ~8 Å with a negligible wafer to wafer variation of less than 0.1Å ensuring an equal quality of the incoming material. Subsequently 20-60 Å thick HfZrO$_4$ layers were deposited via MOCVD and ALD. In case of ALD monolayers of HfO$_2$ and ZrO$_2$ have alternately been deposited using an HfCl$_4$ and ZrCl$_4$ based ALD process. For the MOCVD single wafer process a Hafnium t-butoxide / Zirconium t-butoxide premix chemistry (ratio 1:1) was used. A detailed analysis of physical properties has been performed after the HfZrO4 deposition. The composition of the as deposited HfZrO4 films has been analyzed by atom probe tomography (APT). Basics of this method are described in [13, 14]. For the APT measurement material to be analyzed must be brought in the shape of a tip. To this end
the high-k material was sharpened in a FEI Strata 400™ Dual-Beam-FIB (Focused Ion Beam). The preparation closely follows the procedure given by [15]. For protection of the samples during the sample preparation in FIB, a capping layer stack consisting of 6 nm Cr / 100 nm Si / 50 nm Ni was deposited with electron beam deposition on top of the high-k layer. During the APT measurement a constant high voltage was applied to the tip. With additional laser pulses the atoms at the surface of the tip were ionized and field-evaporated in a controlled way. The surface of the tip was projected on a 2-dimensional detector and so the position of each atom at the tip surface was recorded. The third dimension was obtained from the sequential field-evaporation of the atoms. For each atom the time between the laser pulse, leading to evaporation, and arrival at the detector, was recorded. With this time-of-flight and the known distance between tip and detector the mass of each ion leaving the tip was determined. Finally, a reconstruction was performed to obtain the chemical composition and the 3-dimensional information of the analyzed material. The measurements were performed on a LEAP 3000 X Si™ instrument with 0.2 nJ laser energy and at specimen temperature of 97 K. Additionally the APT results were confirmed by RBS and XPS. The RBS measurements have been carried out by means of a van-de-Graaff-accelerator with a 1.2 MeV He beam at a scattering angle of 170°. The sample was in random orientation. XPS data were acquired using a ThermoFisher Theta 300 instrument equipped with a monochromated Al Ka source (hi = 1486.6 eV). The measurements were carried out with an energy step size of 0.1 eV and a pass energy of 80 eV. The energy scale of the instrument was calibrated with respect to the Au 4f 7/2 signal at a binding energy of 84.0 eV and the Au Fermi level. Furthermore the crystalline phase and the crystallization temperature of HfZrO4 layers in the range between 20 Å and 60 Å have been identified using X-ray diffraction (XRD). The XRD experiments have been performed on a Bruker D8 Discover diffractometer equipped with a standard Cu-tube, a 3rd generation Goebel mirror for beam parallelization, a Soller collimator as secondary optics and a scintillation counter. For temperature depending high temperature grazing incidence X-ray diffraction (HT GI-XRD) measurements in nitrogen atmosphere a BTS solid furnace with a hemispherical Be window (mri Leitz) mounted on the diffractometer was used. During the experiments, a 2θ range between 23° and 34° was scanned repeatedly while the temperature constantly increased at a heating rate of 5 K/min up to 780°C. In order to study the impact of a high temperature annealing the HfZrO4 samples have been annealed at 1050°C under Ar ambient for 10 sec. Afterwards Brightfield-HRTEM pictures have been taken with a FEI Titan 80-300 system at 300 kV acceleration voltage, to check the crystalline behavior after the annealing step. The optical properties of the annealed and as deposited films were characterized by VASE on a Woollam M-2000D ellipsometer in a spectral range of 193 to 1000 nm. The angle of incidence was varied from 45° to 85°. A Tauc-Lorentz oscillator was used to model the dielectric function of the HfO2 layer. The amplitude, gap energy and HfO2 thickness were chosen as fit parameters. The thickness of the SiON interlayer was held constant at 8 Å for the as deposited samples and 16 Å for the annealed ones respectively. The surface roughness of annealed and as deposited films and the mean grain size values have been determined via AFM with a Veeco Instruments D5000 AFM metrology system in tapping mode. In order to generate electrical data, 32nm high performance logic CMOS SOI devices have been fabricated. Therefore SOI Wafers were processed with standard 32nm pre gate modules like Shallow Trench Isolation (STI) and pre gate implantations. Afterwards the same processes as described above have been used
to form the SiON base oxide and the MOCVD and ALD deposited HfZrO4 gate dielectrics, having a thickness range between 18 Å and 29 Å. The thickness was determined by optical inline measurements. Afterwards a 32nm high-k metal gate CMOS SOI process has been applied to fabricate high performance transistors. Finally the high performance transistors were electrically characterized in detail to directly compare both deposition methods.

**Results and Discussion**

The results of a detailed analysis of the physical properties are presented in this chapter. Since current 32nm technologies require gate oxide thicknesses below 20 Å the focus was laid on thin 20Å HfZrO4 films if compatible with the particular analysis method.

**Composition Analysis**

A detailed film composition analysis of 20Å HfZrO4 films deposited with MOCVD and ALD has been performed using the atom probe tomography (APT) method [13,14].

Figure 1. 3-dimensional atom probe tomography-image of the analyzed high-k stack. Atoms are color-coded. The Hf and Zr atoms are homogeneously distributed in the high-k film.

As an example figure 1 shows the 3-dimensional APT-image of the analyzed MOCVD HfZrO4 stack. The Hf and Zr atoms are homogeneously distributed within the high-k material. For ALD (not shown) similar results were found. In figure 2 the APT depth profiles are displayed in detail for MOCVD and ALD. The Hf, Zr and O concentration profiles for MOCVD and ALD deposited HfZrO4 samples are almost identical. These APT results have been confirmed with RBS and XPS analysis by comparing the Hf/Zr ratio. In case of APT the Hf/Zr ratio has been determined by integrating over the Hf and Zr APT depth profiles (figure 2) and subsequently calculating the quotient of the corresponding integrals. For the RBS the ratio has been determined by evaluating the Hf
and Zr area densities via an integration over the RBS depth profiles (not shown here) and calculating the corresponding quotient afterwards. XPS data quantification was carried out using sensitivity factors corrected with RBS data in a previous measurement on a different set of samples. The Hf/Zr ratios determined with three different independent methods are shown in TABLE I. Compared with Zr a slightly higher Hf content has been found for both deposition methods. The comparison between the analysis techniques did not reveal any significant differences.

Figure 2. HfZrO₄ depth profile obtained with APT. The depth profiles for O, Hf and Zr are in agreement.

TABLE I. Hf/Zr ratio determined with three different independent methods. An excellent agreement between MOCVD and ALD for all three different analysis techniques is demonstrated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hf/Zr ratio</th>
<th>Hf/Zr ratio</th>
<th>Hf/Zr ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>APT</td>
<td>RBS</td>
<td>XPS</td>
</tr>
<tr>
<td>MOCVD HfZrO₄</td>
<td>1.04 ± 0.03</td>
<td>1.06 ± 0.04</td>
<td>1.08 ± 0.01</td>
</tr>
<tr>
<td>ALD HfZrO₄</td>
<td>1.05 ± 0.07</td>
<td>1.08 ± 0.04</td>
<td>1.04 ± 0.01</td>
</tr>
</tbody>
</table>

In addition precursor residuals inside the high-k layer have been analyzed using APT, too. In figure 3 the depth profiles are shown for MOCVD and ALD deposited HfZrO₄ samples. Due to the application of HfCl₄ and ZrCl₄ for the ALD deposition, Cl residuals are detected in ALD deposited samples. In contrast to that in MOCVD deposited samples no Cl was detected even if the detection limit for Cl is better than 0.1 at%. Although an organic precursor was used for MOCVD HfZrO₄ deposition no remarkable difference in terms of C concentration was found between MOCVD and ALD as shown in figure 3. Note that the C observed at the interface high-k / Cr is due to surface contamination before capping the high-k material. Here the amount is similar for both deposition methods. The amount of C is increasing towards the interface high-k / Si substrate to 1-2 at% for ALD as well as MOCVD. Note: the amount of Zr less than 1 at% in the cap material is an analysis artifact and is due to mass peak overlap between Zr and Cr from the cap material.
Figure 3. Depth profiles obtained from APT measurements. Precursor residuals are plotted for the two different deposition methods. Not all atoms are shown for clarity.

**Crystallization Behavior**

To determine the crystallization temperature and the crystalline phase temperature dependent GI-XRD scans have been carried out for the 20Å and 40Å HfZrO$_4$ samples. In figure 4 the scans for the 20Å HfZrO$_4$ films are shown.

Figure 4. Temperature dependent grazing incidence X-ray diffraction scans for 20Å HfZrO$_4$ samples deposited with MOCVD and ALD. As indicated by the appearance of a characteristic peak (increase in intensity) the crystallization temperature was found to be ~680°C for MOCVD and ~660°C for ALD.
The crystallization temperatures between MOCVD and ALD are similar and found to be ~680°C for MOCVD and ~660°C for ALD deposited films, indicated by the appearance of characteristic peaks (increase in intensity). For 40Å HfZrO₄ films the crystallization temperatures are determined to be ~410°C for MOCVD and 440°C for ALD (scans are not shown here). The GI-XRD spectra for MOCVD and ALD deposited films after the high temperature GI-XRD scans are shown in figure 5. In addition the peak positions of cubic ZrO₂ are inserted as well. In general MOCVD and ALD show a comparable behavior. As shown in figure 5, a cubic or tetragonal phase of the HfZrO₄ was stabilized in the case of all 20Å and 40Å thick films confirming earlier results for ALD deposited HfZrO₄ [7]. A reduced grain size which corresponds to the film thickness leads to a significant peak broadening in case of the thin 20Å films. Independent of the deposition technique all 20Å and 40Å thick films did not show any peaks after the deposition (not shown in figure 5) indicating an amorphous state for all as deposited films.

![GI-XRD Spectra](image)

Figure 5. GI-XRD spectra for the 20Å and 40Å MOCVD and ALD deposited films after the high temperature GI-XRD. MOCVD and ALD exhibit a similar behavior at same thickness. Besides a cubic or tetragonal phase of the HfZrO₄ was stabilized.

**Annealing Impact**

20Å HfZrO₄ samples have been annealed at 1050°C as described before. Due to the considerably lower crystallization temperatures the samples are expected to be in a crystalline phase afterwards. For confirmation Brightfield-HRTEM pictures have been taken after the annealing shown in figure 6. As expected both MOCVD and ALD deposited samples exhibit a crystalline condition after the annealing. According to the TEM pictures, the original thickness of the SiON base oxide (~8Å based on optical measurements) has doubled during the annealing process to a thickness of approximately 16Å for MOCVD and ALD deposited samples. This is allocated to a base oxide reoxidation caused by residual Oxygen in the Ar process gas during the annealing process. The annealing impact on the HfZrO₄ thickness and the band gap has been investigated by VASE. According to the TEM pictures and optical inline measurements the thickness of the SiON base oxide layer was held constant at 8Å for as deposited and 16Å for annealed
samples. The results are sown in figure 7. There is just a small HK thickness increase caused by the annealing itself visible. This supports the TEM results.

Figure 6. Brightfield-HRTEM pictures of 20Å MOCVD (left) and ALD deposited HfZrO$_4$ samples after an annealing process. After the annealing the films are crystalline in both cases. In relation to the as deposited condition the SiON base oxide thickness has doubled during the annealing for both deposition techniques.

Figure 7. Annealing thickness and band gap changes of MOCVD and ALD deposited HfZrO$_4$ layers obtained with VASE. The annealing causes slightly increased thickness and band gaps. There are just marginal differences between MOCVD and ALD visible. The general behavior is comparable.
In terms of thickness the annealing causes a base oxide reoxidation rather than attacking the HK film. In addition the band gap is slightly increased by the annealing for both samples to a similar degree. Further characterization with 20Å HfZrO$_4$ films has been accomplished via AFM shown in TABLE II.

**TABLE II.** AFM results for as deposited and annealed 20Å HfZrO$_4$ films. No remarkable difference between MOVCD and ALD has been found.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AFM rms [nm] as deposited</th>
<th>AFM rms [nm] annealed</th>
<th>Mean grain size [nm] annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCVD HfZrO$_4$</td>
<td>0.13</td>
<td>0.24</td>
<td>20.5</td>
</tr>
<tr>
<td>ALD HfZrO$_4$</td>
<td>0.12</td>
<td>0.22</td>
<td>21.2</td>
</tr>
</tbody>
</table>

Again similar properties for ALD and MOCVD have been observed. The AFM roughness mean square (rms) values for the MOCVD and ALD sample as well are doubled after the annealing compared to values after the deposition, providing another hint at the crystallization during the annealing step. The mean grain size values of the annealed, crystallized samples are comparable and determined to be 20.5 nm for MOCVD and 21.2 nm for ALD, respectively.

**Electrical Results**

We have recently reported the electrical results of 32nm CMOS high performance logic transistors on SOI substrates having 18Å, 21Å, 25Å and 29Å thick HfZrO$_4$ gate dielectrics deposited with MOCVD and ALD (Hf/Zr ratio 1:1) [12]. HfZrO$_4$ dielectrics are demonstrated to be equivalent in terms of gate leakage current, capacitance equivalent thickness, threshold voltage, and performance as well as reliability behavior (Bias Temperature Instability and Hot Carrier Injection). In this work we evaluate the interface trap density $D_{it}$ of MOCVD and ALD deposited HfZrO$_4$ dielectrics integrated in transistors with gate length of 200nm on SOI substrates. The interface trap density between the gate oxide and substrate has been measured with the charge pumping method at 2 MHz. In figure 8 the charge pumping currents for NMOS SOI transistors with 21Å, 24Å and 29Å thick HfZrO$_4$ gate dielectrics are shown. Each curve represents the median obtained from CP measurements of 9 devices. The charge pumping currents decrease with increasing high-k thickness resulting in lower $D_{it}$ values. Besides ALD deposited HfZrO$_4$ exhibits by trend lower charge pumping currents at same thickness compared to the MOCVD deposited one. $D_{it}$ values are obtained from the charge pumping current maxima as described in [16]. In figure 9 the long channel mobility $\mu$, calculated with the following formula taken from [17]

$$\mu = \frac{L g_m}{W C_{ox} V_{DS}}$$

is plotted against the $D_{it}$ values. Here $W$ and $L$ stand for the gate length and width of the gate, $C_{ox}$ for the gate oxide capacitance, $V_{DS}$ for the source drain voltage and $g_m$ expresses the transconductance. Besides the x and y error bars are included as well. Corresponding to lower charge pumping currents the interface trap density decreases with the HK-layer thickness for all samples. For the comparison of the deposition method there are no significant differences between ALD and MOCVD, even though samples with ALD deposited high-k oxide exhibit slightly lower $D_{it}$ values. But the differences are in the within wafer variation indicated by the error bars. Overall a linear correlation between mobility and $D_{it}$ is observed for MOCVD and ALD as well.
Figure 8. Charge pumping current for NMOS SOI transistors with 21Å, 25Å, and 29Å thick HfZrO₄ gate dielectrics. The current becomes lower as the oxide thickness increases. Additionally, ALD deposited HfZrO₄ exhibits a slightly lower charge pumping current compared to MOCVD.

Figure 9. NMOS long channel mobility plotted against $D_{it}$. The error bars represent the upper and lower quartile of the $D_{it}$ distribution in the x direction and mobility distribution in the y direction over all measured devices on a wafer. The interface trap density decreases with the HK-layer thickness. Interface trap density is slightly lower for samples with ALD deposited high-k oxide. The differences are in the usual within wafer variation indicated by error bars.
As an example for reliability data the results of fast wafer level Time Dependent Dielectric Breakdown (TDDB) measurements for NMOS transistors with MOCVD and ALD deposited HfZrO$_4$ and two different thicknesses is shown in figure 10. The breakdown voltage is plotted against the initial gate leakage current determined prior to the breakdown test. As expected a linear correlation between current and breakdown voltage is observed for MOCVD and ALD. Besides the data are in line for both deposition methods what results in equivalent product lifetimes.

![NMOS Breakdown Voltage](image)

Figure 10. TDDB breakdown voltage plotted against the initial gate leakage current measured prior to the breakdown test. The breakdown voltage correlates with the current for ALD and MOCVD. For both deposition techniques the data are inline.

**Conclusion**

MOCVD and ALD deposited HfZrO$_4$ dielectrics for 32nm high performance logic technology applications have been investigated with respect to their physical properties in detail. All parameters indicate a comparable behavior for MOCVD and ALD. But particularly with regard to manufacturability and cost of ownership MOCVD has clearly an advantage. This work further supports the statement that MOCVD is a promising alternative to ALD in high volume manufacturing.
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