**I. INTRODUCTION**

Atomic layer deposition (ALD) is extremely important in materials science as it is capable of producing a variety of materials, including oxides and nitrides, and metals. The conformal growth guaranteed by ALD enables a superior uniformity on large area substrates, and also an accurate coverage of nonplanar substrates and nanostructures.\(^1\) The low temperature of ALD is also vital for coating organic substrates and nonplanar biological matter.\(^2\) With a cycle-by-cycle analysis of the initial stages of ALD, it is possible to study the nucleation phenomena as well as the interface reactions and thickness dependent properties of the deposited thin film. The latter can be ideally tailored by varying growth parameters, e.g., substrate temperature,\(^3\) substrate chemical composition,\(^4\) surface pretreatment,\(^5\) precursor type,\(^6\) and pulse duration.\(^7\)

ALD grown HfO\(_2\) is actually replacing SiO\(_2\) in CMOS technology for the volume production of high-performance microprocessors.\(^8,9\) The use of halides, amidinate, alkylamide, and cyclopentadienyl precursors for HfO\(_2\) deposition has been reported mostly with either O\(_3\), O\(_2\), or H\(_2\)O as oxygen sources.\(^10-12\) In this work, we used an alkylamide Hf precursor, Hf(N(CH\(_3\))\(_2\))\(_2\), and water.

The initial nucleation stage of ALD is extremely important for obtaining continuous and pinhole-free ultrathin films as the lack of uniform nucleation can induce the island growth, with islands eventually coalescing and forming a continuous film only after a large number of cycles. For ultrathin films, an insufficient nucleation induces a rough and not conformal growth. Thus, in cases where the scarce nucleation depends on surface preconditioning, great care should be taken to perform the adequate surface preparation before ALD. In previous studies we observed that a thin oxide coating is required for the efficient nucleation of HfO\(_2\) on Si(100).\(^13\) However, for microelectronic purposes, SiO\(_2\) interface should be kept as thin as possible to avoid the deleterious effects of the lower SiO\(_2\) dielectric constant on the gate stack. We also demonstrated that in situ investigations with synchrotron radiation photoemission spectroscopy (SR-PES),\(^14\) x-ray absorption spectroscopy,\(^15\) and AFM (Ref. 16) offer the possibility of studying the initial stages of HfO\(_2\) ALD with great accuracy. Here, we show how the unique combination of several surface sensitive techniques like AFM, SR-PES, ultraviolet photoemission spectroscopy (UPS), and electron energy loss spectroscopy (EELS) can give detailed information about morphological, chemical, and electronic properties of the very initial stages of HfO\(_2\) growth, and, by the accurate analysis of all experimental results, a growth model for ALD can be proposed.

The paper is organized as follows. In Sec. II we give some experimental details; in Sec. III we show the results of all measurements; in Sec. IV we give a full discussion of all results and introduce the ALD model. Finally, conclusions are drawn in Sec. V.
II. EXPERIMENT
A. Sample preparation

Samples were cut from a $p$-type Si wafer and were etched by dipping in a diluted HF solution for 120 s. The use of a diluted solution assures that the native Si-oxide is not completely removed after 120 s, as observed by the small oxide peak in the photoemission spectra of Si 2p. After etching, the sample was mounted on the sample holder and introduced into the ALD reactor through a load lock. Before starting the ALD the sample received a further cleaning cycle in vacuum in order to remove the hydrocarbon contamination represented by adsorbed C–H species. The cleaning step consisted of heating the sample to about 450 °C to let desorb the C–H species. However, as the heating in high vacuum conditions would cause the diffusion of carbon into the open structure of the Si(001) surface and Si–C bond formation, the heating was accompanied by water pulses. Water is used to hydrolyze the C–H species and to produce more volatile products that desorb more easily than the long C–H chain typical of hydrocarbon contamination. We want to point out that the use of water at low temperatures (below 500 °C) does not produce any detectable Si-oxidation; but, on the contrary, could increase the hydrolysis of the substrate supporting the typical ALD reactions, terminating the SiO$_2$ surface with –OH species.

B. ALD reactor setup and operation

A stainless-steel UHV-compatible vessel is adapted as an ALD reactor by connecting a gas delivery system (GDS) using a UHV-sealed feedthrough. The GDS and the ALD reactor are described elsewhere. The tetrakis-dimethylamino-Hf (TDMAhf) precursor was maintained at room temperature as in previous experiments it was observed that repeated heating–cooling cycles lead to degradation of the precursor. The base pressure of the ALD reactor was 10$^{-7}$ mbar before starting the experiment. In order to assure saturation of the surface during the precursor pulse, we exposed the sample to two subsequent TDMAhf pulse. Each pulse was 2 s long and between two pulses we waited 5 s. Between each two pulses the chamber was not purged. During the TDMAhf pulses the pressure in the ALD reactor reached 2 × 10$^{-5}$ mbar. After the introduction of TDMAhf, the reactor was purged by two N$_2$ pulses. A second line was used for delivering the oxygen source (H$_2$O), also maintained at room temperature. The water pulse was 1 s long. The ALD reactor was maintained at about 80 °C to decrease the adsorption of water on the reactor walls. The sample was heated to 280 °C during ALD. After both TDMAhf and H$_2$O pulses the chamber was purged with two subsequent N$_2$ pulses (0.5 s each pulse) separated by 5 s. After each preparation step the sample was transferred into the measurement chamber, separated by the ALD reactor with a valve. The measurement chamber had a usual base pressure of about 2 × 10$^{-10}$ mbar. The pressure increased during the transfer, but it decreased again within 5 e min to the 10$^{-10}$ mbar range, showing that the pressure increase was mostly due to inert gas present in the ALD reactor.

C. Measurement setups

1. Noncontact-atomic force microscopy setup

Topography measurements were acquired at room temperature using an Omicron large sample beam deflection UHV/AFM operated in frequency modulation noncontact mode based on a design of Howald et al. The setup is based on detecting the cantilever oscillation by the optical beam deflection technique. Silicon cantilevers with typical tip radius of curvature of less than 7 nm, resonant frequency of 320 kHz, and spring constant of 42 N/m were used. Images were recorded at scan frequency of 1 Hz with a resolution of 256 × 256 pixels. For each ALD cycle we measured three AFM images at different spots also with different scan areas. The Scanning Probe Image Processor 4.4.6.0 (SPIP, Image Metrology, Denmark), WSXM 5.0 (Ref. 21), and Gwyddion 2.19 were used for the AFM data analysis.

2. Synchrotron radiation-photoemission spectroscopy

Synchrotron radiation (SR), from the U49-2/PGM2 beam line in BESSY-II, Berlin, Germany, was used to collect photoemission spectra. The beam line operates in the soft x-ray energy range (85–1800 eV). Electrons were collected with a hemispherical analyzer PHOIBOS-150 (SPECS Surface Nano Analysis GmbH) equipped with a high-resolution CCD camera. The analyzer was operated in angle-integrated mode (acceptance angle was 8°); pass energy was set to 5 eV for Si 2p spectra and 10 eV for O 1s, Hf 4f, and VB spectra. The total resolution at 640 eV was between 35 and 50 meV, depending on core level measured. Both (light incidence and electron emission) angles were fixed at 45° to further increase the surface sensitivity of photoemission. Both photon flux and sample’s drift current were measured parallel to photoemission spectra in order to normalize the photoemission intensity.

3. Electron energy loss spectroscopy and ultraviolet photoemission spectroscopy

EELS was measured using an electron monochromator to produce an electron beam with energy of 50 eV and resolution of 50 meV. The loss spectra were measured in reflection mode with fixed incident and emission angles of about 45°. Electrons were collected with a hemispherical analyzer R150 equipped with 5 channeltrons. The analyzer was operated in angle-integrated mode and the pass energy was set to 1 eV, resulting in a good signal to noise ratio. The elastic peak was measured with an energy step of 50 meV, while the inelastic part of the spectra was measured with 100 meV energy step.

The same measurement setup was used in combination with a helium discharge lamp to collect the ultraviolet photoemission spectra. He I (20.212 eV) was used to determine the
secondary electron cutoff (SEC) and the valance band maximum (VBM) for the substrate before and after each ALD cycle. Photoemission spectra were collected in normal emission.

D. AFM data evaluation

Film growth occurs in out of equilibrium conditions and the formation of a growth front is usually a complex phenomenon; for example, the random fluctuation of molecules arriving at the surface creates growth front roughness. Adsorption events may be treated as noise because molecules do not reach the surface uniformly at the same time. Despite the existence of random events usually producing roughness, the properties of a deposited film can be properly described by the competition between interface roughening and smoothening effects, where the latter may be due to surface diffusion or reemission processes. Although the concept of growth front roughness was mainly applied to describe growth of physical vapor deposition (PVD) films, we can consider some analogy with ALD when the (continuous) time used for the description of PVD is substituted by the (discrete) number of ALD cycles. In ALD, precursors adsorb on the surface until saturation is reached; however, after one complete cycle the coverage of the surface is smaller than unity because of steric hindrance of precursors. However, the ALD reactions between the adsorbed species and the second precursor change the size of the adsorbed species on each adsorption site, leaving the surface only partially covered. In this context, the analogy between a continuous growth mechanism after a time \( t_0 \) and ALD after the \( n \)th cycle can be formalized, included the concept of growth front roughness.

Recently, it was verified that fractal features, related to scaling theories, provided new ways of quantitatively describing the surface roughness and the growth kinetics in a simple way. The dynamic scaling hypothesis is a theoretical approach that employs the fractal self-affine scaling model for the description of the morphological evolution of a growth front by scaling exponents and AFM can be used to experimentally determine the morphology of surfaces during the growth process, as the height–height correlation function (HHCF) of AFM images is closely related to some of these scaling exponents. For a surface height profile \( h(x,t) \) the HHCF is defined as

\[
H(r,t) = \left\langle |h(x+r,t) - h(x,t)|^2 \right\rangle, \tag{1}
\]

where the angular brackets symbolize averaging over the whole profile, \( h \) indicates the surface height with respect to the substrate at a position \( x \) at (growth) time \( t \), and \( r \) is the lateral separation length between the two surface heights. For an isotropic surface the HHCF is not dependent on the specific orientation and a new variable \( r = |r| \) can be introduced to finally express the correlation function as \( H(r,t) \). The dynamic scaling hypothesis requires HHCF to behave as

\[
H(r,t) \approx (mr)^{\alpha} \quad \text{for } r < \xi \quad \text{and} \quad H(r,t) \approx 2w^2 \quad \text{for } r \gg \xi,
\]

where \( w \) is the surface width, \( \xi \) is the lateral correlation length, \( \alpha \) is the roughness exponent, and \( m \) is the local slope. The surface width is the most common parameter used in AFM data analysis to describe surface roughness and corresponds to the standard deviation of the surface heights, also called rms surface roughness (\( S_q \)). The lateral correlation length is related to the length beyond which the surface heights are not significantly correlated. For a surface covered by similar islands, the lateral correlation length is the measure of islands’ size (Fig. 1). The roughness exponent depicts the irregularity of the surface texture: smaller values of \( \alpha \) imply a rougher local surface, \( \alpha \) lies between 0 and 1. The roughness exponent is directly connected to fractal dimension as \( d = 2 - \alpha \) (for \( 1 + 1 \) dimension), which describes the complexity of the analyzed profile. The local slope, defined as

\[
m = \left( \frac{\sqrt{2} w}{\xi} \right)^{1/2}, \tag{2}
\]
delivers information about two possible growth modes: stationary (normal) or nonstationary (anomalous).

The surface width \( w \) and the correlation length \( \xi \) grow as a power law with growth time, \( w \approx t^\beta \) and \( \xi \approx t^{1/\gamma} \), and the exponents \( \beta \) and \( 1/\gamma \) are defined as growth exponent and dynamic exponent, respectively.

It is assumed that the three scaling exponents \( (\alpha, \xi, 1/\gamma) \) accurately describe the surface growth process. In contrast to fractals, which are self-similar, a surface following dynamic scaling theory is self-affine because the vertical direction does not scale in the same manner as the lateral direction. An essential feature of a self-affine surface is that the HHCF reaches a constant value equal to \( 2w^2 \) at a distance larger than correlation length, meaning that the surface height variation is random beyond that length. This postulation is valid for a number of surface growth models where local smoothing effects, such as surface diffusion, compete with noise. An analytical expression for the correlation function is hardly available and simplifications are necessary. For an isotropic surface, it is possible to derive the HHCF function of the following form
during a complete cycle the coverage of the surface is smaller than

\[
\text{01A143-3 Kolanek et al.: In situ study of atomic layer deposition of HfO}_2 \text{ on Si}
\]
By fitting the HHCF, calculated from the AFM profile, with Eq. (3) it is possible to extract all three parameters \((a, \xi, w)\). Finally, it is possible to derive the other scaling exponents \((\beta\) and \(1/z)\) from the time evolutions of surface width \(w\) and lateral correlation length \(\xi\), respectively.

### III. RESULTS

#### A. Noncontact-AFM investigations of the surface morphology

Figures 2(a)–2(d) show the surface topography of the starting SiO2 surface and after the 1st, 4th, and 34th ALD cycle, respectively. The rms surface roughness variation during ALD is shown in Fig. 3(a). At least three images in each cycle were recorded and fluctuations of \(S_q\) values of less than \(\pm 5\%\) were observed. The value of \(S_q\) for the starting surface is 0.18 nm. After the first ALD cycle \(S_q\) increases and reaches a value of 0.23 nm. With the second cycle, \(S_q\) decreases, indicating that the surface is becoming smoother as a result of HfO2 deposition. In the fourth cycle \(S_q\) equals 0.19 nm, very close to the value before ALD, and is the smallest value measured on deposited material. From the fourth cycle on, the \(S_q\) parameter starts to increase linearly with material deposition, reaching the value of 0.25 nm in the 34th cycle and 0.42 nm after the 100th cycle [inset in Fig. 3(a)]. Figure 3(b) shows also the behavior of the surface width variations, calculated from HHFC analysis, in the initial stages of deposition. As expected, both surface parameters \(S_q\) and \(w\) are comparable.

#### B. Valence band investigations

In Fig. 4 we show a reference valence band spectrum obtained in the fifth ALD cycle with the photon energy of 150 eV. The spectrum shows typical features for the Si/SiO2/
HfO₂ interface. The most prominent features are the strong Hf 4f peak occurring in the range 17–20 eV and the O 2p derived valence band states in the range 7–13 eV.

The cycle-by-cycle evolution of the valence band region is shown in a more detailed way in Fig. 5, where the spectra are measured at 640 eV. The first and the last spectra, corresponding to the substrate before ALD and after 12 ALD cycles, respectively, are indicated by arrows. In the first spectrum the O 2p states of SiO₂, starting at 5.6 eV, are visible together with the Si-related states from the Si substrate near the valence band maximum. The deposition of HfO₂ results in a broadening of the O 2p-related states, with a shift of the onset from 5.6 to 4.5 eV. The feature between 1 eV and the O 2p offset is attenuated by the HfO₂ growth. The O 2p broadening and its onset shift saturate within the tenth cycle.

The broadening observed in the SR-PES spectra can be further followed in the UPS data, where Si states are suppressed by the photon energy used (Fig. 6).

C. Core level investigations

Core level spectra show the growth of HfO₂ through the attenuation of the Si 2p signal, the change of O 1s peak shape, and the increase of Hf 4f. In Fig. 7 we show the Si 2p spectra measured with 640 eV of the clean substrate and after cycle-by-cycle ALD up to the 12th cycle. Arrows indicate the substrate and the 12th cycle, with every second cycle skipped. The resolution was set to about 35 meV, giving the possibility to observe the spin-orbit splitting of the bulk component at 99.7 eV with 0.6 eV energy separation and the statistical 1:2 branching ratio. The intermediate oxidized components can be observed at binding energies between 100 and 103 eV. The emission from SiO₂ at 103.5 eV results in a strong contribution. After the deposition of HfO₂ a clear decrease of the Si 2p spectrum is observed, together with a remarkable shift of 1.1 eV of the emission from the SiO₂ to lower binding energies, and a smaller shift of 0.2 eV of the Si bulk emission.

The line shape changes of the O 1s spectra are reported in Fig. 8. For clarity, we show only the most prominent features out of the measured series. All spectra were taken at 640 eV. The SiO₂ and HfO₂ components are well separated and are located at 533.3 and 531.4 eV, respectively. The variation of the O 1s line shape shows first a decrease of intensity due to the attenuation of the SiO₂ component, followed by a shift to lower binding energies, and, after the fourth cycle, by the emission at 531.4 eV.

Finally, in Fig. 9 we show the spectra of Hf 4f. The spin-orbit splitting of 1.65 eV as well as the expected branching ratio of 3:4 clearly shows the presence of only one
component. Below the tenth cycle a small shift of about 0.55 eV to lower binding energy is observed, but above the tenth cycle the main emission is backshifted by a value of about 0.25 eV.

D. EELS measurements

In Fig. 10 we show the most prominent EELS features measured cycle by cycle. Using a primary energy of only 50 eV we suppress the plasmon losses, while they are enhanced in experiments with high kinetic energy electrons, i.e., transmission energy loss spectroscopy and in the ELS mode of a transmission electron microscope (TEM). Moreover, at low kinetic energy the probability of multiple scattering (typically present in TEM measurements) is negligible, and spectra are dominated by the loss function onset only. Finally, the low excitation energy results in an enhanced surface sensitivity, essential for studying the initial growth of HfO2 ALD layers. To better compare the spectra, they are scaled by a factor of 45 and normalized to the intensity of the SiO2 substrate at 14 eV loss energy. The most evident feature of the loss function is the loss function onset between 8.6 eV (before ALD) and 6.1 eV (after the last ALD cycle). Remarkably, the onset has a large shift already after the first ALD cycle. Afterwards, the onset decreases smoothly, and spectra are dominated by line shape change only. Within the gap one can observe some localized features around 5 and 6.5 eV, which stem from the SiO2 substrate and decrease upon ALD growth. These localized gap states are tentatively attributed to the existence of residual carbon after the cleaning process or to oxygen vacancies localized near and/or at the surface region of the sample.

IV. DISCUSSION

A. Discussion of the AFM results

As mentioned earlier, for each ALD cycle we measured three images at random positions on the sample and from each 3D image we extracted three profiles at different positions in the fast scanning direction. As a result, nine profiles for each ALD cycle are obtained, allowing the statistical analysis. The HHCF of each ALD cycle is obtained by averaging the nine curves [Fig. 11(a)]. The HHCF evolution reflects the complex behavior of the surface morphology during ALD growth. An example is shown in Fig. 11(b), where HHCF curves obtained before ALD and after the 1st, 4th, and 34th cycles are depicted. The shape of the HHCF curves reveals a typical behavior for self-affine fractal surface as described earlier: the HHFC increases linearly with distance and reaches a plateau at distances larger than the correlation length. The values of $2a$ (slope of the curve) are similar for all curves as well as the correlation length ($2w$), which is about 8 nm. Despite these similarities, we also observe that the value of the plateau depends on the ALD cycle, being smaller for the 0th and 4th cycles compared to the 1st and the 34th cycles. Further, the HHCF function has only weak oscillations above the plateau.

The three parameters ($w$, $\xi$, $\alpha$) were obtained by fitting the HHCF of each ALD cycle with Eq. (2). The small statistical error for each parameter indicates that the surface
topography is homogeneous within the investigated image area. Additionally, the HHCF analysis performed in the slow scan direction (not shown) gives similar parameters to those extracted from the fast scan direction, demonstrating that the surface is isotropic, and assuring that the analysis based on HHCF in the fast scanning direction is meaningful for the entire topographic image. Obtained parameters are shown in Fig. 12 and are reported in Table I. They change clearly during the initial stages of ALD (from the first to the eighth cycle). The vertical resolution of AFM is higher than the horizontal, explaining why the nonplanar parameters ($S_q$ and $w$) are more sensitive for the layer closure compared to the planar parameters ($S_{cl}$, $S_{fd}$). Consequently, we will focus on the surface width variations in the next paragraph. We will further discuss the behavior of all other parameters in the following. In order to guide the attention of the reader to the important features of our analysis we introduced in Fig. 12 dashed vertical lines that indicate the ALD cycles for which the first and the second monolayer of HfO$_2$ are completed. Inset shows the variation of the surface width including the 100th ALD cycle.

1. Surface width $w$

The surface width $w$ behavior [Fig. 12(a)] is consistent with the rms surface roughness measured directly from 3D

![Fig. 11. Log–log plots of the HHCF evolution during ALD. (a) Waterfall representation of all HHCF curves. Arrows indicate the general variation of the surface width. (b) HHCF of the substrate before ALD and after the 1st, 4th, and 34th cycles, respectively. Black arrows indicate approximate positions where surface characteristics are acquired.](image)

![Fig. 12. Evolution of growth parameters and surface characteristics calculated from HHCF and from image analysis during ALD: (a) surface width, (b) correlation length, (c) roughness exponent, (d) local slope, and (e) surface fractal dimension. Vertical dashed lines indicate the ALD cycles for which the first and the second monolayer of HfO$_2$ are completed. Inset shows the variation of the surface width including the 100th ALD cycle.](image)

<table>
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<th>Cycle</th>
<th>$S_q$ (nm)</th>
<th>$w$ (nm)</th>
<th>$S_{cl}$ (nm)</th>
<th>$S_{fd}$</th>
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AFM images (Fig. 2). The close relation between the two characteristics confirms the isotropic nature of the surface and the validity of the HHCF analysis. The first region is characterized by the strong variation in the first and second ALD cycle, resulting in a peak. It is important to mention that an rms surface roughness peak was predicted for the ALD growth in the model proposed by Nilsen et al.32 According to that model, ALD induces an initial increase of surface roughness reaching a maximum value and then decreases as a result of amorphous material deposition. In that model the peak position depends on the so-called “number of nuclei” and for a large value it is shifted toward smaller ALD cycles.32 From this observation we may affirm that the observed peak of surface width after the first ALD cycle corresponds to a very large number of nucleation sites. The nucleation sites are directly connected with the coverage of the –OH species, which amount may decreases as a result of amorphous material deposition. In that model the peak position depends on the so-called “number of nuclei” and for a large value it is shifted toward smaller ALD cycles.32

The broad peak of roughness exponent connects the first and second regimes. After deposition of two layers of HfO2 the roughness exponent is close to the value obtained for the starting SiO2 surface. This state is maintained in the third regime.

2. Correlation length \( \xi \)

Similar to the surface width, the correlation length \( \xi \) [Fig. 12(b)] has a maximum in the first regime after the first ALD cycle, while in the next three cycles the parameter decreases to reach a value close to the initial surface. This behavior may be interpreted as an indication of the closure of the first HfO2 layer. Similar surface width and correlation length \( \xi \) after the fourth cycle indicate that the HfO2 surface is a replica of the starting SiO2 substrate as is expected from properly performed ALD process, where conformal growth is obtained. In the second regime, the second peak is observed at the seventh ALD cycle, while in the third regime the correlation length slowly decreases to a value found for the starting substrate.

3. Roughness exponent

The behavior of the roughness exponent is exactly specular to that of the correlation function [Fig. 12(c)]. This is understandable by considering that the roughness exponent describes a rougher surface for smaller values. The broad peak of roughness exponent connects the first and second regimes. After deposition of two layers of HfO2 the roughness exponent is close to the value obtained for the starting SiO2 surface. This state is maintained in the third regime.
4. Local slope m

The local slope $m$ shown in Fig. 12(d) is calculated from Eq.(2). The error bar is obtained by applying the error propagation procedure to Eq.(2). In regimes I and II the behavior of $m$ is similar to that of the roughness exponent, but weaker. In regime III the local slope $m$ increases stronger than the roughness exponent. The variations of local slope during ALD mean that the deposition of HfO$_2$ happens in a nonstationary mode. The growth is dominated by surface diffusion when the local slope increases as $\sqrt{\ln(t)}$ (where $t$ is thickness) and the scaling exponents $z$ and $\beta$ are equal to 1 and 0.25, respectively. Actually in regime III we indeed observe a $\sqrt{\ln(t)}$ variation of the local slope [dotted line in Fig. 12(d)] but with the scaling exponents $z$ and $\beta$ equal to 0.55 and 0.02, respectively. Thus, a simple surface diffusion should be excluded for the ALD growth, although some surface relaxation is present.

5. Surface fractal dimension $S_{fd}$

The surface fractal dimension $S_{fd}$ shown in Fig. 12(e) is calculated from 3D AFM images by applying the power spectrum density method. The surface fractal dimension has a minimum where the roughness exponent has a maximum, as expected because the two parameters are related. The surface complexity is at its minimum in regimes I and II and in regime III is close to the complexity observed for the starting surface. It has been reported in literature that the surface fractal dimension measured by AFM needs to be corrected for the tip sample convolution effects. The performed analysis reveals that the surface fractal dimension is always underestimated and because $S_{fd}$ is related to the $z$ exponent by $d = 3 - z$ (for 2+1 interface), $z$ is always overestimated.

B. Scaling exponents

The dynamic scaling approach is an effective method for understanding the temporal evolution of surface growth. However, before determining scaling exponents, some general issues connected with the application of the scaling theory to ALD growth need be clarified. In most cases, the variation of surface width and correlation length as a function of deposition time is used for the determination of growth and dynamic exponent ($\beta$ and $1/z$). As ALD has a discrete character, it differs from continuous deposition processes, and the film thickness needs to be used instead of deposition time for the determination of scaling exponents. For continuous deposition processes the amount of deposited material is controlled by mass transport or rates of surface reactions. The cyclic and discrete properties of ALD mean that the deposited material is controlled by growth rate per cycle (GPC), steric hindrance effects, and surface termination. If we try to neglect steric hindrance and surface termination effects, a linear relationship between GPC and ALD cycles can be assumed and the variation of AFM characteristics as a function of thickness may lead to the determination of scaling exponents.

As GPC we may use 0.1 nm/cycle as this value is often reported in the literature for TDMAHf precursor and is also confirmed by our SR-XPS investigations. From noncontact AFM and SR-XPS investigations we assume that 1 ML of HfO$_2$ is completed after 4 ALD cycles. Thus, in the scaling analysis we expect that 1 ML of HfO$_2$ material has thickness of $(0.4 \pm 0.1)$ nm. Our measurements and other experimental results demonstrate that for SiO$_2$ substrates with dense –OH terminations the thickness increases linearly with number of ALD cycles.

The scaling parameters vary considerably before the closure of two HfO$_2$ layers; therefore we introduced seven regions [Fig. 3(b), Table II] where those values change strongly. The seven regions are mostly formed by one single ALD cycle, meaning that the scaling parameters change at almost each cycle. Only the fourth and seventh regions are formed by more than two ALD cycles. The fourth region comprehends cycles 3 to 6, corresponding to the formation of the first layer and starting of the second layer. The seventh region is instead formed by cycle 8 up to 34. To calculate the scaling exponents we used least square linear fit to the data in between the regions. The roughness exponent is given directly in Fig. 12(c). Results are shown in Fig. 13 and are listed in Table II.

From the analysis of the dynamical scaling exponents in our ALD experiment we show that the fractal theory indeed can be applied for the analysis of ALD growth on Si/SiO$_2$ substrates if a careful analysis is done. Moreover, the dynamical scaling theory shows that the initial ALD growth process is rather complex as the three parameters vary significantly within the first 10 cycles, although in different ways: almost no variation of $z$, while $\beta$ varies only within the first...
four cycles, and $1/z$ shows two maxima when completing the first and second layer, respectively.

By taking only $b$ into account it is interesting to note that in the first ALD cycle its value reaches 0.44, close to the theoretical value of the continuous growth equation in RD regime (0.5). Values of the $b$ parameter close to 0.5 are often observed at the very early stages of growth on a flat substrate when noise is the most dominant growth. Between the 34th and 100th ALD cycles the $a$, $b$, and $1/z$ exponents are equal to 0.59, 0.03, and 0.02, respectively. The small value of $1/z$ indicates a very slow island coalescence.

C. Discussion of EELS results

The energy loss signal gives an estimate of the bandgap of the dielectric film by linearly extrapolating the onset [Fig. 14(a)]. For SiO₂ a value of about 8.6 eV is found, while after ten ALD cycles the value is around 6.1 eV. The difference in the value for SiO₂ with respect to the literature (9 eV) is probably due to the dipole moment of the existing –OH groups on the surface, which are necessary for ALD and are due to the surface preparation. The dipole moment influences the electrons when they interact with the surface and reduces the energy of the inelastic scattered electrons, resulting in a decrease of the loss function onset of about 0.4 eV. The onset value after the first cycle is already 6.9 eV, with a shift of 1.7 eV with respect to the initial value. This large shift is a result of the superposition of the loss spectra of SiO₂ and HfO₂. Because of our high surface sensitivity the contribution of the deposited HfO₂ (about half layer) on the surface gives a strong change of the spectra. After three cycles, with a surface coverage of about 3/4, the value already approaches the bulk value of HfO₂. Afterwards, the change of bandgap becomes smaller and starts to saturate at around the tenth cycle, although the value reported in literature for “bulk” HfO₂ is not reached. This could again be due
to the formation of the interface dipole (at the SiO₂/HfO₂ interface), which influences the inelastic scattered electrons in the opposite way compared to the case of –OH dipoles on the SiO₂ surface. The dipole layer would be due to charge transfer from HfO₂ to silicon, which leaves positive charge on the dielectric side of the interface, with opposite charge appearing in silicon to screen it.

Besides the loss function onset, the area delimited by the loss spectrum and the background line [hatched area in the inset of Fig. 14(b)] indicates the growth of HfO₂, because it is connected to the intensity of the loss function coming from HfO₂. The area increases up to the third cycle and has a plateau between the third and the fourth cycle. The plateau around the fourth cycle is an indication of the layer closing, as confirmed by AFM and synchrotron radiation photoemission measurements. The same behavior is also observed for the next four cycles, resulting in a second saturation around the eighth cycle. This corresponds well with the closing of the second deposited layer of HfO₂. Afterward, no further increase of the area under the loss function is observed, because of the limited detection depth of low energy EELS.

D. Discussion of UPS results

From the UPS measurements shown in Fig. 6, the VBM and the SEC can be obtained for the SiO₂ substrate and after each ALD cycle using a linear fit with most negative and positive slopes at the VBM and SEC, respectively. The intersection with the baseline determined the value for the VBM and the SEC. Then, we calculated the difference of VBM and SEC after each cycle with respect to the values of the

FIG. 13. (Color online) Variations of scaling exponents $a$, $b$, and $1/z$ during the initial ALD process. Gray bars represent the range of changes of the scaling exponents from the 0th to the 34th ALD cycles. Solid stars show values of the scaling exponents for the range from the 34th to the 100th ALD cycles. $1/z$ values are negative because the lateral dimension of the islands on the surface is decreasing in the region of interest. Although we could not find any evidence of such a behavior in the literature, there has been evidence of $1/z = 0$.

FIG. 14. Variation of bandgap after cycle-by-cycle EELS measurements (a) and of the area under the EELS spectra calculated in a cycle-by-cycle routine (b). The inset explains the evaluation of the area in the EELS data.
clean SiO₂ substrate. The results are presented in Fig. 15 as a function of cycle numbers. A decrease of both values is clearly observed, but, while the VBM is saturating after around the eighth cycle (corresponding to the closure of the second HfO₂ layer), the SEC is further decreasing up to the tenth cycle. The saturation of VBM is possibly due to the low detection depth of UPS, in the order of 1 nm. The observed shift is about 0.75 eV, which is close to the value observed in SR-PES. The further decrease of SEC could be due to the interface dipole formation as observed also in EELS measurements.

E. SR-PES discussion

In Fig. 16 we show the thickness of deposited HfO₂ films from various experiments. With the exception of experiments 4 and 7, all ALD films showed a thickness compatible with a growth rate per cycle of 0.1 nm/cycle. Experiments 4 and 7 were performed just after the water cleaning procedure. Our cleaning procedure, described in Ref. 13, is performed in order to remove surface contamination of hydrocarbon and to increase the density of –OH termination. In experiments 4 and 7 the growth rate is too large because of the presence of CVD growth produced by the presence of water adsorbed on the reactor walls. The difference between experiments 4 and 7 and all other experiments consists in performing ALD just after the water cleaning. In all other experiments, the sample was transferred into the measurement chamber after the water cleaning for characterizing the substrate before ALD. The first ALD cycle was then performed after about 10 min. This time was sufficient to evacuate the ALD reactor of water, adsorbed on the chamber walls, upon heating the reactor at 80 °C.

The cycle-by-cycle experiments show the decrease of Si 2p (and the corresponding increase of Hf 4f) intensity because of HfO₂ growth on top of SiO₂. This can be observed in Fig. 17, where the intensity of the two peaks, calculated as the peak area, is shown as a function of ALD cycle. This evidence is discussed in the following, where a growth model for ALD is obtained from the SR-PES data in conjunction with the statistical analysis of AFM images reported previously.

F. Growth model from SR-PES

We use the general approach to calculate the layer thickness of an adsorbate by the weakening of the substrate’s intensity. The intensity attenuation of the Si 2p is given by

\[ I_{Si} = (1 - f)I_{Si0}^0 + f \cdot I_{Si0}^0 \cdot \exp \left( -\frac{d}{\lambda \cos \theta} \right), \]  

(4)

where we introduced the condition that islands with a constant height \( d \) cover a fraction \( f \) of the surface, while the \( (1 - f) \) fraction of the surface is not covered and the signal of the Si 2p level is not attenuated. In the same way we define the intensity of the Hf 4f level as
calculate the growth of islands with a constant height in the order of 0.4 nm would effectively deliver a roughness of the same order as that observed in the AFM experiments. Accounting for this extra growth would decrease the height of the islands to about 0.4 nm. It should also be noted that the growth of islands with a constant height in the order of 0.4 nm would effectively deliver a roughness of the same order as that observed in the AFM experiments.

Finally, we can conclude the presence of island growth within the first layer: the height of the islands amounts to about 0.4 \((\pm 0.1)\) nm; the height distribution is uniform as higher islands can be excluded. The island height can be considered to resemble an O–Hf–O unit as the smallest ALD building block or the smallest possible HfO2 cluster.

The modeling also enables one to estimate the lateral dimensions of the ALD islands. In fact, the value of \(f\) can be determined for each cycle and the surface fraction after the first ALD cycle is in the order of 0.4. This value determines the closest Hf–Hf distance in a closed packed layer of adsorbed TDMAHf precursor molecules. If we take a van der Waals radius of 0.5 nm for the TDMAHf molecule the Hf–Hf distance would be around 1 nm. After the oxidation process then the lateral distance between O–Hf–O clusters would be 0.6 nm, which results in a surface filling of 0.4—in remarkable agreement with our results from the Hf 4f and Si 2p core levels. It could be understood that the self-limiting step is the van der Waals dimension of the precursor, which just determines the Hf–Hf distances. The oxidation then causes the formation of separated HfO2 islands with the same Hf–Hf distance. These results from the model are in agreement with both photon energies. This value corresponds to about twice the Hf–O bond length. For the case of 150 eV and an island height of 0.5 nm the complete layer coverage \(f = 1\) is reached after five cycles, while for 640 eV it is reached after four cycles. If instead, an island height of 1.2 nm were used, the coverage \(f = 1\) would be reached after more than 12 cycles in the case of 150 eV, while only after 9 cycles with 640 eV. The latter eventuality appears, therefore, to be highly unrealistic and can be excluded. Higher islands would give even worse agreement, while smaller islands could still be possible. In these calculations the growth of an interfacial SiO2 layer is not considered.

The ratio between the two intensities is given by \(R = I_{\text{Hf}} / I_{\text{Si}}\).

This data analysis is sensitive to the choice of the corresponding values of \(\lambda\) and \(I_0\). We have determined these parameters within our numerous experiments in which the linear dependence of the growth rate versus cycle number allows an accurate calibration. By calculating the ratio \(R\) for discrete values of \(f\) between 0 and 1 as a function of island height \(d\), we can determine the fraction \(f\) of surface coverage by the HfO2 islands. The results can be seen in Figs. 18 and 19 for two different photon energies. By changing the photon energy, the ratio \(R\) changes, because both \(\lambda\) change. To calculate \(I_0\) and \(I_{\text{Hf}}\) values, we used the intensities of the Si 2p and Hf 4f spectra before starting ALD and after the Hf 4f saturation, respectively. In this way, we obtained \(I_{\text{Hf}}^0/I_{\text{Si}}^0 = 10\) for 640 eV and \(I_{\text{Hf}}^0/I_{\text{Si}}^0 = 2.1\) for 150 eV excitation energy, respectively. The comparison of the calculated ratios \(R\) with the measured values are plotted for both photon energies in Figs. 18 and 19, where the measured data are represented by black dots.

By taking only one photon energy it would not be possible to have a univocal solution, because there is an infinite number of coverage fraction combinations that would determine a certain measured intensity ratio. Only by comparing the results at different photon energies is it possible to reduce the multiplicity of the results. So, comparing the results obtained at 150 and 640 eV, we may determine the average height of the islands and the coverage after each ALD cycle. It is important to note that these determinations are only possible by using synchrotron radiation, as the photon energy may be changed over a wide range. We tried to fit the data for several island heights, but only for a value of the island height between 0.4 and 0.6 nm could we get reasonable agreement with both photon energies. This value corresponds to about twice the Hf–O bond length. For the case of 150 eV and an island height of 0.5 nm the complete layer coverage \(f = 1\) is reached after five cycles, while for 640 eV it is reached after four cycles. If instead, an island height of 1.2 nm were used, the coverage \(f = 1\) would be reached after more than 12 cycles in the case of 150 eV, while only after 9 cycles with 640 eV. The latter eventuality appears, therefore, to be highly unrealistic and can be excluded. Higher islands would give even worse agreement, while smaller islands could still be possible. In these calculations the growth of an interfacial SiO2 layer is not considered. Accounting for this extra growth would decrease the height of the islands to about 0.4 nm. It should also be noted that the growth of islands with a constant height in the order of 0.4 nm would effectively deliver a roughness of the same order as that observed in the AFM experiments.

Finally, we can conclude the presence of island growth within the first layer: the height of the islands amounts to about 0.4 \((\pm 0.1)\) nm; the height distribution is uniform as higher islands can be excluded. The island height can be considered to resemble an O–Hf–O unit as the smallest ALD building block or the smallest possible HfO2 cluster.

The modeling also enables one to estimate the lateral dimensions of the ALD islands. In fact, the value of \(f\) can be determined for each cycle and the surface fraction after the first ALD cycle is in the order of 0.4. This value determines the closest Hf–Hf distance in a closed packed layer of adsorbed TDMAHf precursor molecules. If we take a van der Waals radius of 0.5 nm for the TDMAHf molecule the Hf–Hf distance would be around 1 nm. After the oxidation process then the lateral distance between O–Hf–O clusters would be 0.6 nm, which results in a surface filling of 0.4—in remarkable agreement with our results from the Hf 4f and Si 2p core levels. It could be understood that the self-limiting step is the van der Waals dimension of the precursor, which just determines the Hf–Hf distances. The oxidation then causes the formation of separated HfO2 islands with the same Hf–Hf distance. These results from the model are in
good agreement with the results from the EELS and from AFM, where we also found the formation of 1 ML of HfO$_2$ around the fourth cycle. We can conclude that the ratio of Hf/Si from synchrotron radiation measurements can be used to define the growth mode in ALD of HfO$_2$.

Next, we discuss the growth after the first layer is completed. Our data points can be modeled if we assume an homogeneous growth with $f = 1$ on top of the first completed layer. To do so, we included in our model the curves for homogeneous film growth ($f = 1$ with increasing film thickness $d$, dashed curve in Figs. 18 and 19). The general behavior of our data is very well described by that simple model. It should be mentioned that at higher film thickness the accuracy decreases as the intensity from the substrate is weakened exponentially.

G. Discussion: Combination of techniques

In general, all the measurement techniques used in this study are extremely surface sensitive. Nevertheless, each of them reflects different materials properties or reports to a different physical mechanism. However, all of them have been shown to be sensitive to describe the changes of the material properties induced by the ALD process. Here, we want to compare all the above-reported results. In Fig. 20 are plotted the most important results as a function of the number of ALD cycles [Figs. 20(a)–20(f)]. Results are arranged from the most surface sensitive [Figs. 20(a) and 20(b)] to the least surface sensitive [Fig. 20(f)] technique.

We can discuss whether the observed experimental differences arise from differences in the surface sensitivity of each method or whether these curves can be arranged to give a common picture on the growth properties of ALD layers within the first cycles. The behavior within the first two regions is very different for the various parameters and properties measured or calculated from the various experimental techniques.

In regime I we have already established the island growth. In regime II we attribute the changes observed in the AFM data up to the eighth cycle to the two-dimensional growth of the second layer. The noncontact-AFM results reveal the most complex variations within the initial ALD cycles (regime I) and are indicative of the deposition progress unfolding in a complex manner [Figs. 20(a)–20(c)]. Both $w$ and $\zeta$ parameters have an initial maximum, which is not found in any of the other techniques. Hence, it must be associated with structural properties. At the end of regime II the surface is a kind of replica of the substrate, as the parameters are close to those observed on the starting surface. The point separating the second and the third regimes is identified as the eighth ALD cycle. In regime III, saturation or linear increase/decrease of the investigated parameters is evidenced. Although EELS is a technique sensitive to the long range Coulomb electrostatic interactions of the incident electrons with the core potentials of atoms within the surface layer, the position of the loss function onset has the strongest variation within the first ALD cycle [Fig. 20(c)], indicating that the small clusters at the surface behave as HfO$_2$. For increasing number of cycles, the area under the EELS spectra shows just very smooth variations and only weak but distinctive steps near the fourth and eighth ALD cycles, which may be connected with the completion of the first and the second HfO$_2$ layers, respectively. The rather slow and smooth changes after the eighth cycle can be explained by local dipole moments associated with the small islands and their almost three-dimensional distributions.

The UPS data are commonly considered to be very sensitive against changes of surface potentials. Results obtained by UPS show a linear decrease of both SEC [Fig. 20(e)] and VBM [Fig. 20(f)] with the latter saturating around the eighth cycle. The behavior of SEC follows nicely the long range variation of the EELS data and might be accordingly assigned to a change of the interface dipole. In the valence band regime, UPS data record the changes of the width of the O 2$p$ derived valence band states, which are sharper for the SiO$_2$ covered substrate than for the bulk HfO$_2$. Here we find that the bulk values are reached after ten cycles (Figs. 5 and 6).

The SR-based core level data results obtained by SR-PES for the Hf 4$f$ and Si 2$p$ core levels provide high surface sensitivity. Because of the direct relation of surface sensitivity and mean free path of emitted electrons this technique allows...
for quantitative modeling of growth layer as demonstrated previously.

At the end we shall summarize that, first, all the applied techniques are sensitive enough to record the subtle changes caused by the individual ALD cycles. Second, the different information obtained by this unique combination of techniques enables a consistent picture of the initial growth mechanisms. Third, all data agree that the intrinsic properties of HfO₂ are fully developed within the first two layers (eight ALD cycles). Below that coverage we find island growth, which gives different results for the different techniques.

Our analysis shows also that there is not a single mechanism responsible for the ALD, but a combination of different mechanisms in three main growth regimes.

An interesting question arises whether surface diffusion could possibly be present in regimes I and II, as the low surface roughness could suggest. It would be very interesting to learn about these physical phenomena and their relevance in the ALD growth process.

Finally, we compare the critical exponents of our cycle-by-cycle analysis with those derived and established for other film deposition methods like MBE, CVD, or sputtering. In Fig. 13 we have plotted the derived critical exponents against cycle numbers up to the eighth cycle. We do not observe further changes of these exponents in the third regime. As described earlier, we find that α is constant, β has some variations within the first 4 cycles, while only 1/β shows significant oscillations which become stronger toward the eighth cycle. The growth mechanisms in ALD are clearly different from those observed in other deposition methods as demonstrated for the β parameter in Fig. 21. Differences are due to quite unusual experimental parameters like the low deposition temperature and the low gas flux rates as well as the time separation between the adsorptions of the two precursors. This difference shows up in the β value, which is zero for the ALD process after the initial eight cycles. In contrast, for thermal evaporation (0.2), sputtering (0.4), and CVD (0.1–0.6) it is nonzero.

V. CONCLUSIONS

In summary, based on a comparative in situ study employing simultaneous investigation by UHV-AFM, EELS, SR-XPS, and UPS we conclude that island growth is the dominant mechanism during the initial growth of HfO₂ ALD layers on Si substrates. Islands are very small with a height of 0.4 nm and lateral dimension of 0.5 nm. We distinguish three regimes. Initially, islands enhance surface roughness; with increasing ALD cycles, the film forms a replica of the initial surface roughness as the 2D film growth is completed within the first 8 cycles; finally, a statistical growth follows and surface roughness increases linearly with increasing cycle number. An interfacial dipole can be deduced by the comparison of EELS and UPS data, while synchrotron radiation photoemission can be used to determine the island formation when at least two photon energies are used.

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