

Atomic layer deposition of HfO₂ investigated in situ by means of a noncontact atomic force microscopy

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An ultra high vacuum atomic force microscope operating in a noncontact mode has been employed to investigate *in situ* atomic layer deposition (ALD) of HfO₂. Tetrakis-di-methyl-amido-Hf and H₂O were used as precursors and the deposition process was performed on Si(001)/SiO₂ substrate maintained at 230 °C. The relation between the film growth and the root mean square surface roughness was studied after each ALD cycle. The histograms of the initial stages of the ALD process have been compared in terms of the surface height data as a way of characterizing the growth process. Parameter values corresponding to HfO₂ layer thickness and coverage were calculated. A detailed analysis of the surface height histograms allowed one to construct a simplified growth model and confirm the completion of the first HfO₂ layer after four ALD cycles.

Keywords: *atomic layer deposition; high-k dielectric thin films; atomic force microscopy*

1. Introduction

High-*k* hafnium based gate dielectric materials are the main components allowing improvement in the miniaturization of advanced integrated circuits, particularly complementary metal oxide semiconductor devices [1–3]. Fabrication of high-*k* layers with thicknesses that measure just a fraction of a monolayer can be achieved by the atomic layer deposition (ALD) technique [4, 5]. ALD is a repeated deposition and oxidation process allowing conformal, homogeneous, controlled growth of ultrathin films [6]. The evolution of surface texture occurring in the initial stages of the ALD process is still not known, although several growth models exist [7–9].

In most cases, experimental data obtained *ex situ*, may suffer from sample contamination that may significantly distort properties of materials. We recently proposed An *in situ* technique has been proposed for measuring the early stages of ALD growth by means of synchrotron radiation photoelectron spectroscopy [10]. For the study

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demonstrated in this paper, the ALD reactor was attached to an ultra high vacuum (UHV) atomic force microscope (AFM). By means of this setup, the substrate was transferred into an AFM measurement chamber without breaking the vacuum and the surface topography was measured in the cycle by a cycle routine.

Outstanding resolution in real space is routinely achieved by a powerful technique of frequency-modulation (FM) AFM [11–14]. In this paper, the application of FM-AFM has been applied to topography measurements of the initial stages of ALD growth. The deposition process was started on SiO₂/Si(100) substrate and 4 ALD cycles were completed. Both the root mean square (RMS) surface roughness and surface height histograms were used to analyze the growth process. Based on the surface height histogram data fitted with Gaussian functions, it was shown that RMS surface roughness is closely related to the standard deviation of the surface height. The RMS surface roughness measured in early stages of the ALD process can be correlated with existing models [15, 16]. Upon undertaking a detailed analysis of the surface height histograms, it was possible to develop a simplified model of the HfO₂ growth.

2. Experimental

Sample preparation. Chemically oxidized Si(001) p-type substrate with a 2.2 nm SiO₂ layer was used for sample preparation. The sample was sonicated in spectrophotometric grade water for 120 s and dried with pure nitrogen. Then it was immersed in commercially available diluted 0.1 M HF solution for 120 s, again cleaned in spectrophotometric grade water for 20 s and dried in nitrogen. Subsequently, within one minute, the substrate was placed in the UHV chamber, via the fast-entry loadlock. Synchrotron radiation photoelectron spectroscopy tests of the samples revealed that after etching the mean thickness of the SiO₂ layer was reduced to ca. 0.5 nm (not shown).

The ALD reactor was equipped with valves for introducing the Hf-precursor and the oxygen source, with a current feed-through for the direct heating of the sample, and a manipulator for transferring the sample into the AFM measurement chamber. During the growth process, the substrate temperature was maintained at 230 °C and the whole ALD reactor was heated to 60 °C. The pulse duration for tetrakis-di-methyl-amido-Hf (TDMAHf) was 1 s, under the pressure of 1×10^{-3} mbar, and for H₂O 2 s, at 1×10^{-2} mbar. During the process, TDMAHf was heated to 60 °C. After each exposure to TDMAHf and H₂O, the chamber was purged for 1 s with N₂ under the pressure of 1×10^{-2} mbar. The duration of one complete cycle was 45 s.

Noncontact AFM measurements and topography analysis. Omicron large sample beam deflection UHV/AFM operated in a FM mode was used for topography measurements at ambient temperature. Silicon cantilevers, with typical tip radius-of-curvatures of less than 7 nm, were utilized. The average spring constant and resonance frequency were about 42 N/m and 320 kHz, respectively. The images were recorded

under the scan frequency of 1 Hz with the resolution of 256×256 pixels. For each ALD cycle, we measured 3 AFM images at various positions, and also with various scan areas. The scanning probe image processor (SPIP, Image Metrology, Denmark) was used for the AFM data analysis.

For AFM data analysis, the most commonly applied parameter is the RMS surface roughness S_q , which equals the standard deviation of the surface height, and thus it describes the spread of the surface height histogram, also called the height distribution (HD), around the mean value. A Gaussian or near-Gaussian surface HD is expected to result from an entirely random ALD process. An analysis of the HD can be applied to extract additional information about ultrathin film growth in ALD process. This is especially valid in the early stages of ALD growth before the completion of the first HfO_2 layer.

A multi-normal probability procedure that finds the parameter values of the Gaussian peaks in the surface topography was proposed by Cogdell [17]. The procedure can be used for surface characterization, once it has completed the task of HD data-fitting Gaussian functions. For instance, in the so called dual process, one can distinguish between two surface textures even when one surface lies on top of the other. Nevertheless, there is no established method of HD data fitting in the case of ALD processes. The authors propose a data-fitting strategy based on the Levenberg–Marquardt least square algorithm using Gauss functions. It is a well known fact that ALD does not produce a complete layer after one cycle, due to steric hindrance [18]. Consequently, in the surface height histogram, two contributions are observable before the completion of the first layer; one is attributed to the substrate and the other to the deposited material. A dual process is relevant for the data study, because a layer of HfO_2 on a SiO_2 substrate is deposited, resulting in two distinguishable Gaussian peaks in the HD data.

3. Results and discussion

Figure 1 shows the surface topography, obtained by NC-AFM measurement, before the ALD process cycle (0) and after each subsequent ALD cycle (1–4). From the topography, RMS surface roughness was calculated, and surface height histograms were obtained (Fig. 2, left column).

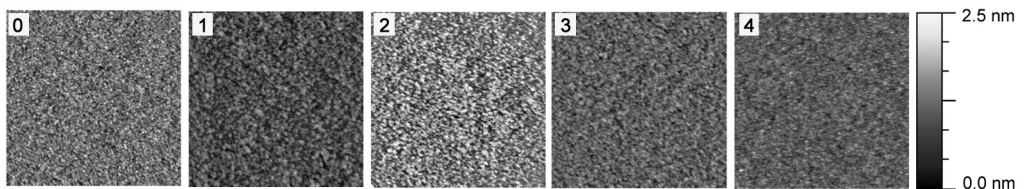


Fig. 1. Results of NC-AFM investigations in the first four ALD cycles performed with TDMAHf and H_2O as precursors. Each number corresponds to a completed ALD cycle. Cycle (0) depicts SiO_2 substrate before deposition. Image size: 400×400 nm

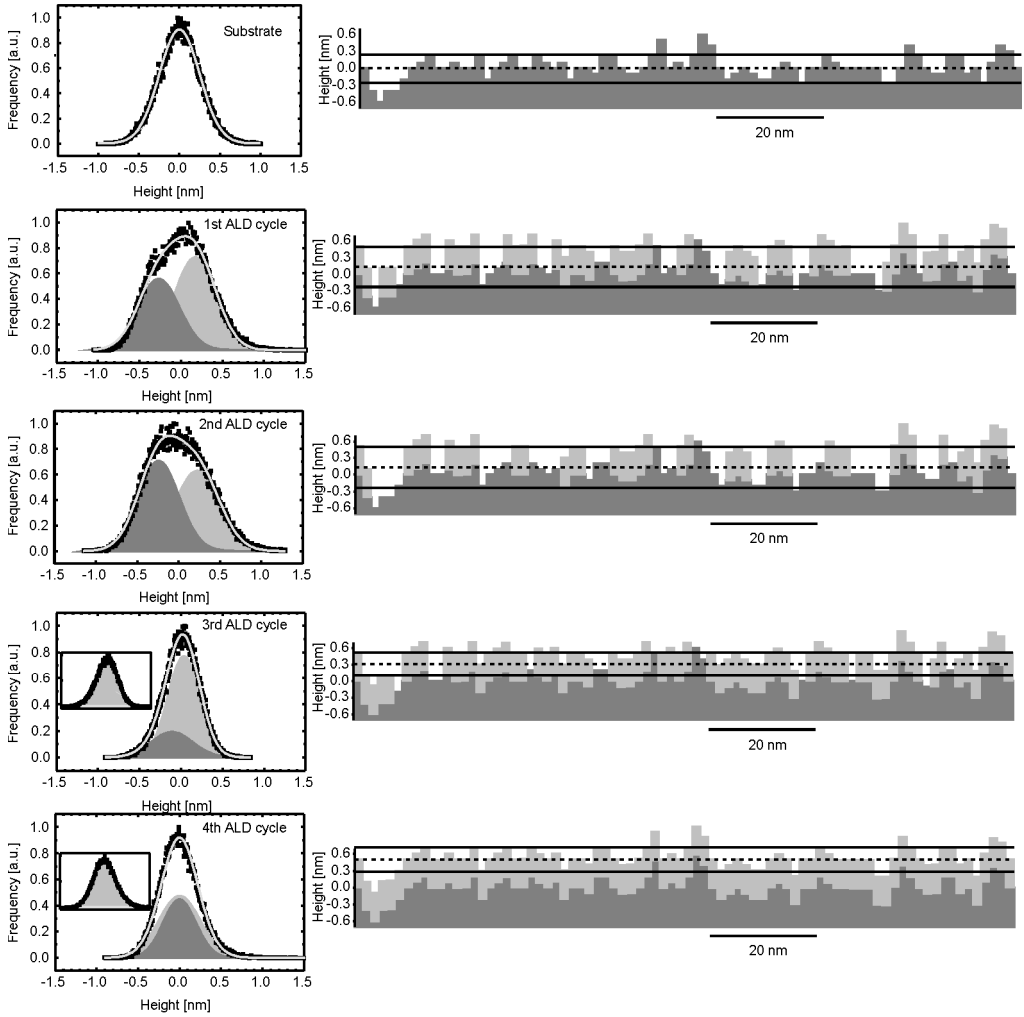


Fig. 2. Left column: surface height histograms calculated from topography images. For each ALD cycle the raw height data is leveled using the plane correction in order to set the arithmetic mean value μ of the image to zero. The curves are normalized to the same maximum level. Fit performed with a fixed width of the substrate peak taken from cycle 0. Dark grey peaks represent SiO_2 substrate, and light grey – deposited HfO_2 . Right column: proposed model of the ALD growth. For each cycle HfO_2 coverage was calculated from the area ratio of the peaks present in the height histograms

In general, AFM measurement produces a model of the surface as a discrete two dimensional function $z(x,y)$ with $M \times N$ elements. However, in most cases, AFM images are square matrices with $M = N$ and 256×256 or 512×512 elements. For calculating the RMS surface roughness, we applied the equation

$$S_q = \left(\frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} (z(x_k, y_l) - \mu) \right)^{1/2} \quad (1)$$

where $z(x_k, y_l)$ is the height of the surface model at the point with coordinates k and l with μ being the arithmetic mean of the height of the surface model. We set the μ value of the surface to zero by applying the plane correction in the SPIP software. Equation (1) is identical with the definition of standard deviation, thus the S_q parameter can also be considered as the standard deviation of the surface height.

In principle, it is possible to calculate RMS surface roughness from the surface height histograms. For such calculations, we fit the surface height histogram with one Gaussian peak, and RMS surface roughness is then equal to the half of the width of the peak. We use the Gaussian function of the form:

$$h(x) = h_0 + \frac{A}{w \left(\frac{\pi}{2}\right)^{1/2}} e^{-\frac{2(x-\mu)^2}{w^2}} \quad (2)$$

where h_0 and A are the values of the baseline and peak area, respectively, w is the width of the peak, $\sigma = w/2$ is the standard deviation of the surface height. With the μ parameter set to zero, we can directly compare the surface height histograms, as in general the arithmetic mean is different for each ALD cycle and this causes the Gaussian peaks to shift. As all the surface histograms have Gaussian or near-Gaussian distributions, the RMS surface roughness S_q and the standard deviation σ of the surface height should be closely related, and this fact is evident in Table 1, as well as the associated data plot shown in Fig. 3. Throughout this paper the standard deviation of the surface height will be used as calculated from Eq. (1), as an RMS surface roughness parameter.

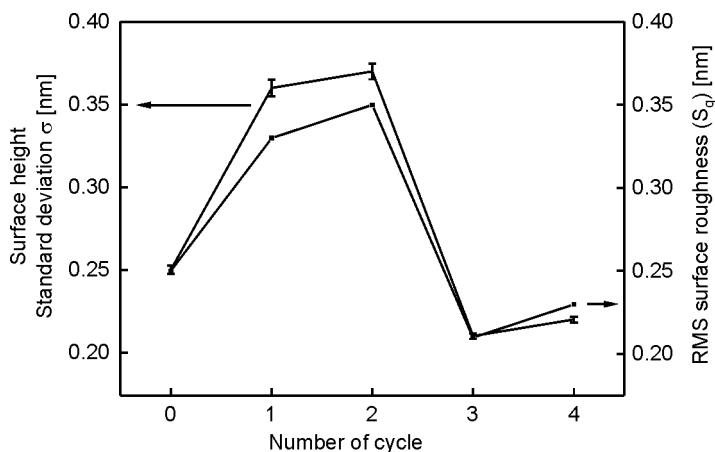


Fig. 3. Evolution of the RMS surface roughness during the ALD growth. The error bars for the plot of the standard deviation of the surface height σ are derived from the fit error of the Gaussian peak width

From the calculated data, we see that, after the first ALD cycle, S_q increases from 0.25 nm to about 0.33 nm and reaches a maximum value of 0.35 nm in the second

cycle. In the third and fourth cycle S_q equals 0.21 nm and 0.23 nm, respectively. As a result of HfO₂ deposition, starting from the third cycle, S_q decreases. After the fourth ALD cycle, S_q is close to the surface roughness observed before the start of the ALD process (cycle 0). The RMS surface roughness behaviour is in agreement with the ALD growth model developed by Nilsen et al. [16, 18]. The model predicts that at the beginning of the ALD process, the surface roughness initially increases, reaches a maximum value, and then subsequently decreases as a result of amorphous material deposition.

Table 1. Evolution of the RMS surface roughness during the ALD growth.
For not perfectly Gaussian surface the S_q and σ parameters differ.

Cycle number	RMS surface roughness (S_q) [nm]	Surface height standard deviation (σ) [nm]	σ error [nm]
0	0.25	0.249	0.003
1	0.33	0.360	0.005
2	0.35	0.374	0.005
3	0.21	0.208	0.002
4	0.23	0.223	0.002

Surface height histograms (Fig. 2, left column) can be used to calculate how the HfO₂ coverage changes dynamically with the deposition cycle, i.e. during the ALD growth. Clear evolution of the surface height histograms from a single Gaussian (substrate) to a near-Gaussian, especially evident in the first and second cycle is observed. The height histogram turns again into a Gaussian, for the third and fourth ALD cycles, which was also confirmed by a single Gaussian fit (Fig. 2, left column insets). For the calculations of the surface coverage, the surface height histograms are fitted with two Gaussian peaks of the form stated in Eq. (2): the first Gaussian peak is attributed to the SiO₂ surface, whereas the second is attributed to the HfO₂ deposited material. In the data-fit, we used fixed width of the SiO₂ peak assuring that we deal with conformal, efficient ALD growth that is not modifying the RMS surface roughness of the substrate. However, we do see alerting of the substrate already from the first ALD cycle as the SiO₂ Gaussian distribution is not perfectly fitted to the left tail of the surface height histogram. There are two explanations for this. Firstly, it is not possible to measure exactly the same area with an AFM tip after each ALD cycle and, secondly, the substrate surface is somehow modified during the ALD growth. Table 2 presents the relevant data describing the evolution of the HfO₂ coverage during the initial deposition cycles.

The presented results allowed us to construct a mathematical model of the HfO₂ growth in the early stages of the ALD process (Fig. 2, right column). The model shows only the SiO₂/HfO₂ interface profile. The profile roughness R_q is derived from the S_q parameter and, for the purpose of simplification, we assumed $R_q = S_q$. The initial roughness of the SiO₂ surface is connected with the Si roughness. Much research was

performed in the field of very thin SiO_2 layers and it is now established that the roughness of the SiO_2 is duplicating the roughness of the Si substrate [19, 20], although this may not necessarily be true for a native oxide [21].

Table 2. HfO_2 coverage calculations

Cycle number	SiO_2 peak area	HfO_2 peak area	$\text{SiO}_2/\text{HfO}_2$ ratio	$\text{HfO}_2/\text{SiO}_2$ ratio	HfO_2 coverage [%]
0	—	—	—	—	0
1	0.35	0.46	0.76	1.32	62
2	0.44	0.47	1.02	0.98	49
3	0.12	0.37	0.32	3.08	84
4	0.30	0.22	1.36	0.73	100

The mathematical model of the SiO_2 surface is based on real measurement data. The numerical values of the raw data for the cross-section were rounded off and recompiled to form a discrete grid of height values. The mesh spacing of the grid corresponded to a sampling distance of 0.1 nm. The entire substrate is represented as a discrete collection of 80 vertical columns lying in a grid. Based on the number of grids, the $\text{HfO}_2/\text{SiO}_2$ coverage ratio was estimated from the height histograms. In the calculations, we assumed that the area ratio equal to 1 reflects 50% of the surface coverage. Height of each element of HfO_2 grid was 0.5 nm as this value is in agreement with the literature [22–24].

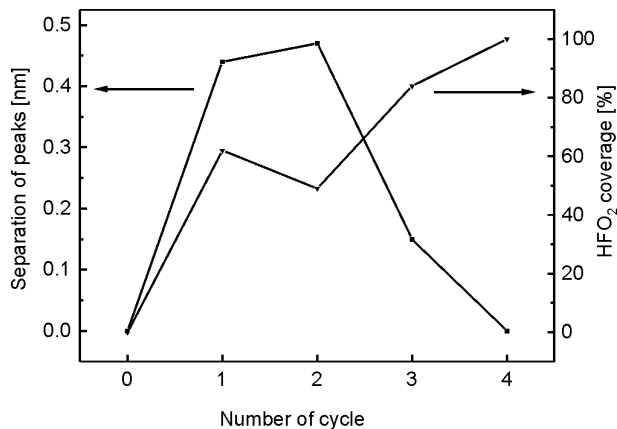


Fig. 4. Separation of peaks and HfO_2 coverage in the initial stages of the ALD growth. For the coverage around 50%, the separation of peaks reflects the height of the incomplete HfO_2 layer

With some assumptions, the peak separation presented in Fig. 4 can be interpreted in terms of an incomplete HfO_2 layer, having non-uniform thickness. Three different fitting procedures were used and up to the second cycle the peak separation equal to (0.46 ± 0.02) nm was obtained (average value taken from 6 data fits) [25]. For the sur-

face coverage of approximately 50%, where the AFM tip refers to both the SiO₂ and HfO₂ surfaces in approximately equal amount, the peak separation faithfully reflects the true height of deposited HfO₂ material. For the HfO₂ surface coverage exceeding 84%, the SiO₂ surface no more can serve as a height reference. In that case, the AFM tip detects more HfO₂ surface, and due to observed conformal growth, the deposited high-*k* surface roughness duplicates the SiO₂ substrate roughness, thus as a result the mean peak separation is reduced. In consequence, after completion of the first HfO₂ layer, the separation of the peaks equals zero.

Black horizontal lines reflect the standard deviation of the surface height and may be directly connected to RMS surface roughness. The middle dashed line is the arithmetic mean value of the height data and shifts (approximation) to positive values of the height vs. ALD cycles.

The presented model is more accurate in terms of the height than in horizontal direction as the correlation length was not taken into account. In a rough estimation, the model reflects the behaviour of the surface skewness correctly. Due to the fixed substrate roughness, the obtained model is an approximation. From the height histogram data, clearly substrate changes vs. the ALD cycles can be seen. This is most evident in the second ALD cycle in which the HfO₂ coverage is smaller than in the first ALD cycle and the peak separation slightly increases. The first possible explanation for substrate modification might be the interfacial layer growth between the deposited HfO₂ and the SiO₂ substrate [26–29]. A small increase in peaks separation between the first and second cycle may indicate that underneath the deposited HfO₂ (and only there) the HfO₂/SiO₂ interface increases. However a very small difference equal to 0.03 nm, being at the limits of AFM sensitivity, cannot be reflected on the model picture. In another explanation we may state that, the SiO₂ substrate is so rearranged in the second cycle that the SiO₂ surface is larger. Third possibility may be connected with slightly different measurement positions between first and second ALD cycle. As the presented possibilities are hard to reflect in the model, the HfO₂ coverage was simply lowered in the model picture. In the third ALD cycle, the HfO₂ coverage reaches 84% and finally in the fourth cycle the layer is complete when the peak separation equals zero.

In the first four cycles, the ALD process follows substrate morphology, meaning that the starting SiO₂ surface influences HfO₂ growth in the initial phase of the deposition [30]. High quality surface fabricated by properly chosen etching procedures might be desirable when performing the ALD process [31].

As a general rule, AFM measurements suffer from the tip sample convolution effect, due to the tip shape and mainly to finite tip radius [32–34]. Most particularly, this effect strongly depends on the height and aspect ratio of the features present on the surface and the tip radius. Nevertheless, in the presented measurements, this effect is lowered due to the small surface roughness and low aspect ratio of the observed features.

4. Conclusions

We showed that the FM-AFM technique is sensitive to surface changes induced by the ALD process from the very beginning of the deposition. RMS surface roughness increases during the first two ALD cycles. From the third ALD cycle and onwards, the surface becomes smoother as a result of amorphous HfO₂ deposition. We have illustrated that the study of surface height histograms is very helpful to gain additional information about the ALD growth. By detailed analysis of the peaks appearing in the surface height histograms, it was possible to calculate the HfO₂ coverage in the early stages of the ALD process, and confirm that the first high-k layer was complete after four ALD cycles. The completion of the first HfO₂ layer after four ALD cycles was also confirmed by synchrotron radiation photoelectron spectroscopy (not shown). The surface coverage calculations were helpful for developing a simplified model of the HfO₂ growth in the initial phase of the ALD process. Forthcoming experiments with more ALD cycles will reveal additional details about HfO₂ the nanoscale dynamics of HfO₂ deposition on SiO₂/Si(001) substrate.

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