

# Nucleation of HfO<sub>2</sub> atomic layer deposition films on chemical oxide and H-terminated Si

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HfO<sub>2</sub> thin films have been deposited by an atomic layer deposition (ALD) process using alternating pulses of tetrakis-ethylmethylamino hafnium and H<sub>2</sub>O precursors at 250 °C. The as-deposited films are mainly amorphous and nearly stoichiometric HfO<sub>2</sub> (O/Hf ratio ~1.9) with low bonded carbon content (~3 at. %). A comparison of the nucleation stage of the films on OH- and H-terminated Si(100) surfaces has been performed using Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry (SE). We find for the initial 5–7 process cycles that the film nucleates more efficiently on the OH-terminated surface. However, after the 7th cycle both surfaces exhibit similar surface coverage, which takes about 40 cycles to reach a steady growth rate per cycle. Angle resolved XPS measurements reveal the formation of a ~6 Å interfacial layer after four ALD cycles on the H-terminated surface and the thickness of the interfacial layer does not change substantially between the 4th and the 50th process cycles as shown by transmission electron microscopy. Although the surface coverage is comparable for both starting surfaces, film measurements performed by SE suggest that thick films deposited on H-terminated Si are ~5% thicker than similar films on the chemical oxide surface. Atomic force microscopy (AFM) measurements reveal higher surface roughness for the films deposited in the H-terminated surface. The SE and the AFM data are consistent with higher porosity for the films on H-terminated surfaces. © 2007 American Institute of Physics. [DOI: [10.1063/1.2764223](https://doi.org/10.1063/1.2764223)]

## I. INTRODUCTION

Hf-containing oxides such as HfO<sub>2</sub>, HfSiO, and HfSiON, are among the leading candidates for the replacement of SiO<sub>2</sub> as a gate dielectric in metal–oxide–semiconductor field effect transistors.<sup>1</sup> Among the desirable properties for gate dielectrics that Hf-based oxides seem to possess are high dielectric constant ( $k \sim 25$ ), good electrical properties,<sup>2</sup> good thermal stability for the nitrided oxides,<sup>3</sup> and stability toward reactions with atmospheric CO<sub>2</sub> and moisture.<sup>4</sup> For many applications, uniform very thin films are required, and atomic layer deposition (ALD) has proven to be an excellent technique to provide such films, displaying monolayer growth control even on surfaces with uneven topography.<sup>5,6</sup> One of the main problems plaguing most thin film deposition approaches for HfO<sub>2</sub> is the formation of SiO<sub>2</sub> at the interface between the deposited film and the silicon substrate.<sup>7</sup> The formation of such an interfacial layer is undesirable because it increases the equivalent oxide thickness of the gate stack.

ALD is based on favorable self-limiting surface reactions and until very recently it was believed that OH termination of the starting Si surface was required for the nucleation of metal oxide thin films, such as the reaction process outlined by Hausmann *et al.*<sup>8</sup> Therefore, it would seem that depositing a high- $k$  material on a Si-H surface would prove very difficult since the ALD chemistry is not optimized for

growth on such a surface and a SiO<sub>2</sub> layer should be grown first to provide favorable high- $k$  nucleation conditions. In support of this theory, there are reports of very long incubation periods for ALD growth on Si-H such as the deposition of HfO<sub>2</sub> from HfCl<sub>4</sub> and H<sub>2</sub>O by Green *et al.*<sup>9</sup> However, a recent report by Ho *et al.*<sup>10</sup> shows that the deposition of HfO<sub>2</sub> from tetrakis-ethylmethylamino hafnium (TEMAH) and D<sub>2</sub>O proceeds though reaction of the metalorganic precursor with the Si-H surface and no substantial nucleation barrier nor formation of interfacial SiO<sub>2</sub> was observed.

In this work we study the nucleation and interface morphology of HfO<sub>2</sub> ALD films from TEMAH and H<sub>2</sub>O under regular process conditions on chemical oxide and H-terminated Si surfaces. We find that initially there is a nucleation barrier on the H-terminated (HF-last) surface that is overcome by the 7th ALD cycle, and the growth rates on both starting surfaces are then similar. A 6 Å interfacial layer consisting of a SiO<sub>x</sub>/Hf-silicate is detected with angle resolved x-ray photoelectron spectroscopy (ARXPS) and transmission electron microscopy (TEM), for films deposited on a HF-last surface and the thickness does not change from 4 to 50 ALD cycles, implying a stable interface.

## II. EXPERIMENT

HfO<sub>2</sub> films were deposited in a homemade, hot wall stainless steel flow tube ALD reactor equipped with a quartz crystal microbalance and computer controlled by a LAB-VIEW® routine. The fixed volume approach described by

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Hausmann *et al.*<sup>11</sup> was used for the delivery of both reagents. The TEMAH precursor vessel, fixed volume, vacuum valves, and associated hardware were placed in an oven for easy and uniform temperature control. For the specific experiment, the TEMAH vessel was kept at 106 °C to assure that the vapor pressure of the precursor was higher than the flow tube pressure. De-ionized (DI) water was stored in a stainless steel cylinder and the air was removed through several freeze, pump, and thaw cycles. The H<sub>2</sub>O vessel was maintained at room temperature throughout deposition, ~24 °C. A constant flow of ultrahigh purity N<sub>2</sub> gas (15 sccm) was used to maintain a flow tube process pressure of ~180 mTorr during deposition. The reactor is equipped with a 60 l/s turbo pump to maintain a clean environment when the system is idle and to assist in the quick evacuation of the flow tube after a sample is loaded; the reactor was exposed to the ambient only when samples were loaded, while subjected to a continuous purge of ultrahigh purity N<sub>2</sub> to minimize contamination. Particularly for the experiments on H-terminated Si surfaces it was found that a delicate balance exists between obtaining a clean starting reactor environment and maintaining integrity of the starting surface. Initially, the reactor was purged for over 2 h between sample loading and deposition commencement. However, when H-terminated Si substrates were used we observed predeposition surface oxidation. To maintain the H-terminated Si surface intact, the reactor purge time was decreased to ~30 min after the sample was loaded. Sample surfaces that were removed from the reactor after 30 min and examined promptly with spectroscopic ellipsometry (SE) showed that the H termination protected the surface from oxidation under these conditions. The depositions on the OH- and H-terminated surfaces were performed simultaneously to ensure a valid comparison of the two films.

Film thickness was measured by a spectroscopic ellipsometer with a spectral range of 380–900 nm (180 wavelengths). The optical constants for HfO<sub>2</sub> were obtained by the library provided by the vendor. In most cases a two layer model of SiO<sub>2</sub> and HfO<sub>2</sub> on Si was assumed. Compositional analysis of the samples was performed *ex situ* by a Kratos AXIS Ultra x-ray photoelectron spectrometer (Al source  $h\nu = 1486.6$  eV) at 0° takeoff angle with 0.5 eV step size for survey scans and 0.1 eV step size for high-resolution scans. All takeoff angles were measured with respect to the surface normal. Sample charging effects were compensated for by using the system's electron flood gun neutralizer and by setting the Si substrate peak at a binding energy of 99.3 eV. The peaks were integrated and background corrected using the Vision II software package available with the instrument. Rutherford backscattering spectrometry (RBS) measurements were made using a 1.2 MeV He<sup>+</sup> beam obtained from a National Electrostatics 5SDH-2 positive ion accelerator. The backscattering angle was 170 deg and the spectra were collected using a surface barrier detector subtending approximately 5 msr. All RBS data were interpreted using the simulation program RUMP.<sup>12</sup> Atomic force microscopy (AFM) measurements were performed with a Digital Instruments 3100 in the tapping mode.

Sample preparation included cleaning pieces of highly

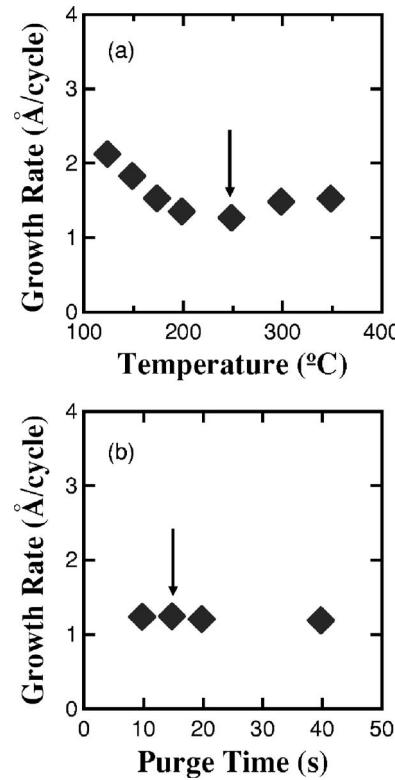


FIG. 1. (a) Effect of the deposition temperature on the growth rate. A minimum growth rate of 1.2 Å/cycle was achieved at 250 °C. (b). Effect of the purge time on the growth rate at 250 °C. The selected 15 s purge is sufficiently long to remove any unreacted precursor from the deposition zone.

doped (0.001–0.005 Ω/cm) *p*-type Si(100) wafers in JT Baker clean for 5 min and a 5 min DI water rinse. For the H-terminated substrates preparation included an additional 20–30 s buffered oxide etch dip and N<sub>2</sub> drying. The SC1 chemical oxide was grown on H-terminated substrates using the recipe described by Green *et al.*<sup>9</sup> SE measurements showed that a reproducible 15 Å SiO<sub>2</sub> layer was formed on the cleaned Si surface. High-resolution TEM (HRTEM) data were provided by Evans Analytical Group.

### III. RESULTS

In Fig. 1 we show the effect of the temperature (a) and purge time (b) on the film growth rate on native oxide as measured by SE. Each point represents the average of several measurements across each sample. The error in the film thickness, which is represented by a combination of the standard deviation of the SE measurements and error in the SE fit, is very small and of the order of the data marker. Initially, the growth rate decreases as a function of temperature indicative of precursor condensation on the substrate. Then the growth rate reaches a minimum of ~1.2 Å/cycle at 250 °C and increases marginally at higher temperatures. The temperature where the minimum in the growth rate is achieved is regarded as the optimal temperature for ALD growth.<sup>13</sup> In Fig. 1(b) we present the effect of the purge pulse length on the growth rate at 250 °C. For purge pulses longer than 10 s the growth rate remains practically constant indicating ad-

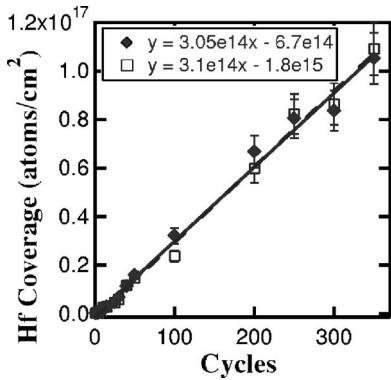


FIG. 2. Hf surface coverage as measured by RBS vs the number of process cycles for films deposited on H-terminated Si surfaces (diamond) and SC1 chemical oxide (square). The data were fitted to a straight line and the “best-line” equation is included in the plot.

equate purging. Based on that data the depositions were performed at 250 °C using a 15-1-15-1 s (purge, TEMAH, purge, H<sub>2</sub>O) pulse sequence.

The composition of thick films was analyzed by XPS (data not shown). A survey scan was used to determine all the elements present in the film and the area of the Hf 4f, C 1s, O 1s, and N 1s peaks was integrated and scaled by the atomic sensitivity factors provided by the instrument supplier to provide atomic percent (at. %) composition.<sup>14</sup> The films are nearly stoichiometric HfO<sub>2</sub> (O/Hf~1.9) with low concentration of bonded C impurities (2.9 at. %).

The linearity of the film growth on H-terminated Si and SC1 chemical oxide starting surfaces was evaluated by RBS. In Fig. 2 we show the measured Hf atom surface coverage as a function of cycle number for a series of films ranging from 1 to 350 cycles. The data are fitted using linear regression and the equations of the lines are shown on the graph. Initially, we observe slow growth that stabilizes after ~50 process cycles. To examine the initial nucleation period we display the growth rate as a function of cycle number in Fig. 3. We observe that for both starting surfaces it takes ~45 cycles for the growth rate to approach a steady state value of  $3.1 \times 10^{14}$  Hf atoms/cm<sup>2</sup>. To study the initial film nucleation on both starting surfaces we focus on the first 30 process cycles on each surface [Fig. 3(b)]. We observe that initially the Hf coverage rate on the Si-H surface lags significantly behind the chemical oxide surface, but the coverage rate equalizes after the 6th process cycle.

The condition of the H-terminated surface during deposition is very important, and in order to detect the formation of interfacial layers we used ARXPS to detect the core electrons from the Si 2p level for a series of very thin films ranging from 4 to 25 process cycles. Figure 4 shows the normalized spectra for these films at takeoff angles ranging from 0° to 60° in 15° steps. The substrate peak at 99.3 eV and a higher binding energy peak are evident in all spectra. The location of the high binding energy peak shifts marginally to lower binding energies as the film grows; for the four cycle film it is centered at ~103.1 eV while for the 15 cycle film it is centered at ~102.5 eV. For the 25 cycle sample the peak is very broad and appears centered at ~102 eV. The intensity of the interfacial layer peak increases compared to

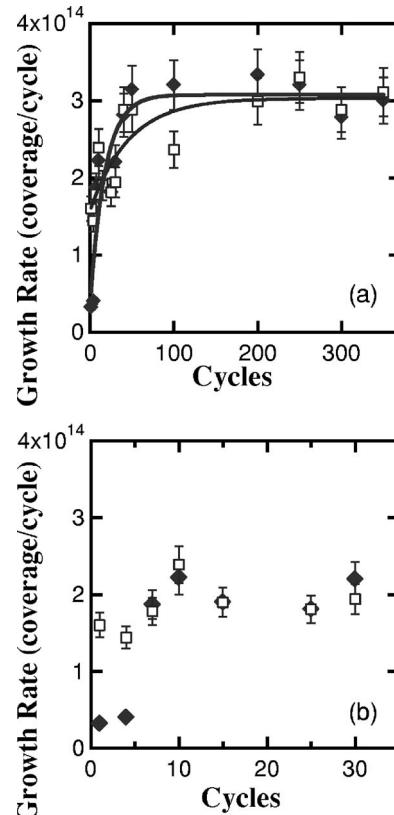


FIG. 3. (a) Growth rate as a function of cycle number for films deposited on H-terminated Si surfaces (diamond) and SC1 chemical oxide (square). It takes ~45 process cycles for the growth rate to reach its steady state value of  $3.1 \times 10^{14}$  atoms/cm<sup>2</sup>. (b) Growth rate for the first 30 cycles. For the first 5 cycles the H-terminated surface shows substantially lower Hf surface coverage than the SC1 chemical oxide. After the 7th cycle the growth rate becomes similar. The lines in Fig. 3(a) are only used as a guide to the eye and do not represent an attempt to model the data.

the substrate peak as we proceed to more shallow probing angles and the ratio  $R$  of the intensity of the two peaks can be used to provide a measure for the thickness of the interfacial layer according to the formula described by Powell and Jablonski:<sup>15</sup>

$$\ln\left(1 + \frac{R}{K}\right) = \frac{d}{\lambda \cos \theta}, \quad (1)$$

where  $K=0.7$  is the relative sensitivity factor for the two peaks,  $\lambda=3.47$  nm is the effective attenuation length of the Si 2p electrons,  $\theta$  is the takeoff angle, and  $d$  is interfacial layer thickness. A plot of  $\ln(1+R/K)$  vs  $1/\lambda \cos \theta$  should result in a straight line through the origin with a slope equal to the thickness of the interfacial layer. In Fig. 5 we show the plots for the five films (4, 7, 10, 15, and 25 cycles) we examined using this technique. The data for each film were fitted to a simple linear function ( $y=ax$ ) and the best lines are plotted for each data set with the derived interfacial layer thickness  $d$  shown on the plot. The error bars in the plots represent the propagated error in the function from the peak intensity integration; a flat 10% error was assumed for each peak intensity (including error in the peak fit and noise in the data) and propagated through Eq. (1) using standard error analysis methods to arrive at ~14% error for each data point. For all the films the interfacial layer thickness is calculated

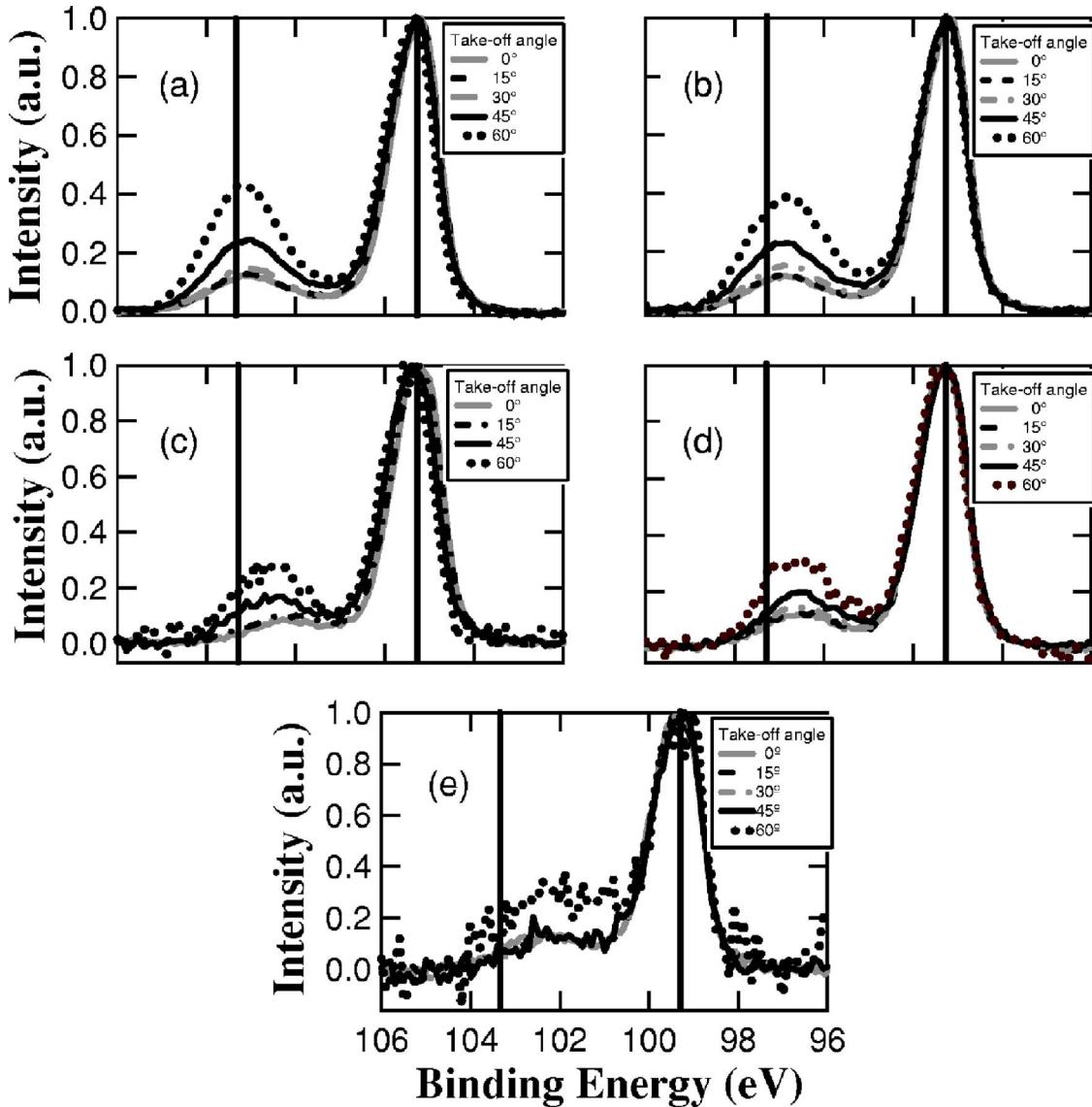


FIG. 4. Angle-resolved high resolution Si 2p XP spectra for a series of very thin films on H-terminated Si. (a) 4, (b) 7, (c) 10, (d) 15, and (e) 25 cycles. The take off angle is measured with respect to the sample normal.

between 6.1 and 6.7 Å and is practically unaffected from the number of ALD process cycles the sample has experienced. The 25 cycle film represents the upper limit of the overlaying HfO<sub>2</sub> film thickness for which this technique can provide reliable data. For thicker films we used HRTEM to obtain a direct measurement for the thickness of the interfacial layer and we present this data for a 50 cycle film on a H-terminated surface in Fig. 6. The high contrast strip represents the interfacial layer and based on the length scale supplied on the bottom of the image, the thickness of the interfacial layer for that film is ~7 Å, in good agreement with the measurements obtained using ARXPS.

The film thickness was measured using SE for films deposited on both chemical oxide and H-terminated Si and the results are shown in Fig. 7. The measurements for the films deposited on the SC1 surface were corrected for the thickness of the chemical oxide (15 Å). We observe that for depositions exceeding 100 cycles, the films deposited on the Si-H surfaces are ~5% optically thicker than similar films deposited on the chemical oxide layer. The surface roughness

of the films was examined using atomic force microscopy and the results are summarized in Table I. For the 30 cycle depositions we only have data from films deposited on native oxide and H-terminated Si surfaces. For that thickness there is no discernible difference in the surface roughness between the two starting surfaces. However, for the 350 cycle samples the films deposited on Si-H exhibit a significant increase in the root-mean-square (rms) surface roughness compared to those deposited on the SC1 surface, 2.1 vs 1.7 nm, respectively. AFM data for a 30 and a 350 cycle film on a HF-last surface is shown in Figs. 8(a) and 8(b), respectively, and for a 350 cycle on SC1 chemical oxide starting surface in Fig. 8(c). The difference in the film surface roughness is apparent.

#### IV. DISCUSSION

ALD is a thin film deposition technique that depends on favorable, cyclical chemistry for thin film nucleation and growth. Until recently, it had been thought that an OH-terminated starting surface was necessary for the growth of

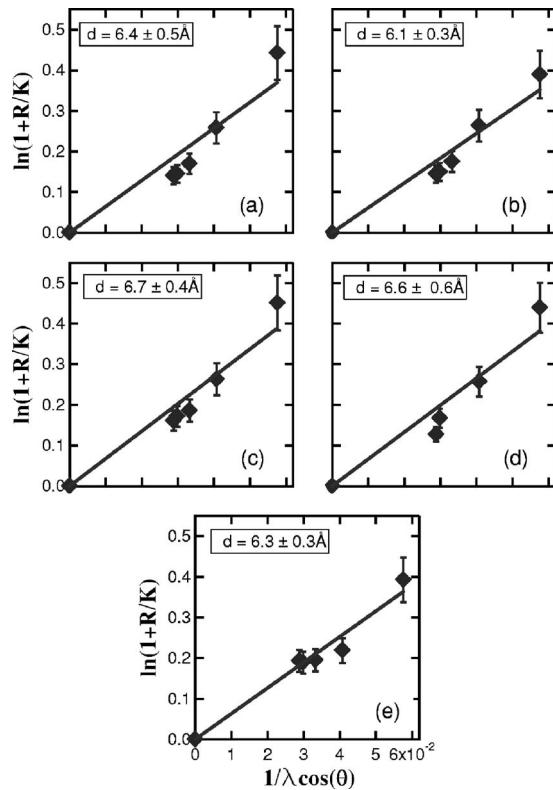


FIG. 5. Plots of  $\ln(1+R/K)$  vs  $1/\lambda \cos \theta$  for the same films as in Fig. 4. (a) 4, (b) 7, (c) 10, (d) 15, and (e) 25 cycles. The takeoff angle is measured with respect to the sample normal. The straight line in each plot represents the least-squares fit line to the data.

high quality metal oxide thin films.<sup>8,16</sup> Inert starting surfaces such as H-terminated silicon were found to impose significant nucleation barriers for certain ALD processes resulting in a very slow nucleation period or “incubation period”<sup>17</sup> and rough, three-dimensional, and nonlinear growth.<sup>18</sup> However, some recent results indicate that the earlier picture may not be accurate. For the trimethyl aluminum/H<sub>2</sub>O system it is reported that the precursor reactivity with the Si-H surface controls the nucleation of Al<sub>2</sub>O<sub>3</sub> films and not the reactions of H<sub>2</sub>O with the Si-H surface.<sup>19,20</sup> Ho *et al.* have shown

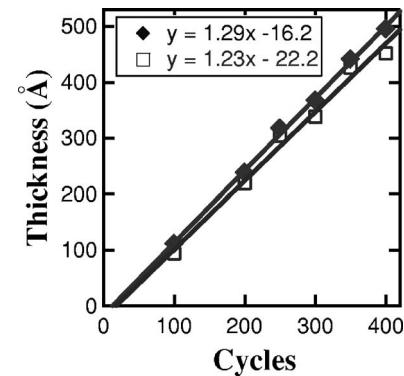


FIG. 7. Film thickness measured by SE as a function of process cycles for films deposited on H-terminated Si (diamond) and SC1 chemical oxide (square). The films deposited on the H-terminated surface are ~5% optically thicker than similar films deposited on the SC1 surface. The data were fitted to a straight line and the best-line equation is included in the plot.

efficient film nucleation on Si-H for a HfO<sub>2</sub> process from TEMAH and D<sub>2</sub>O at 100 °C.<sup>10</sup> For our process, RBS measurements indicate that deposition on a chemically “inert” surface such as hydrogen terminated Si results in reduced nucleation efficiency for the first five cycles compared to the more “reactive” chemical oxide surface. ARXPS measurements reveal that after four ALD cycles an interfacial layer consisting of a SiO<sub>x</sub>/Hf-silicate mixture is present. Due to a lack of *in situ* techniques, we are unable to determine whether this interfacial layer is formed during the ALD process or postdeposition. Recent *in situ* Fourier-transform infrared studies have shown that for a TEMAH/D<sub>2</sub>O process<sup>10</sup> after 30 ALD cycles, 50% of the original Si-H surface sites remain unreacted and hydrogen desorption was detected after even 100 ALD cycles for a TDEAH/H<sub>2</sub>O process.<sup>21</sup> In this case, it is possible that the interface contains unreacted Si-H bonds that oxidize during ambient air exposure. H-terminated Si substrates left in the ambient have been shown to oxidize after a few hours of exposure.<sup>22</sup> A more plausible explanation is that the interface oxidation occurs during the first few ALD cycles. Initially, poor Hf coverage is measured by RBS and the unprotected Si-H surface is exposed to large doses of H<sub>2</sub>O. As a result an interfacial layer is formed that provides a suitable surface for HfO<sub>2</sub> nucleation and the growth rate on HF-last matches that of the SC1 surface. Once full HfO<sub>2</sub> surface coverage is achieved the interface is protected from further oxidation.

The analysis based on the ARXPS and the HRTEM data indicates that the thickness of the interfacial layer remains

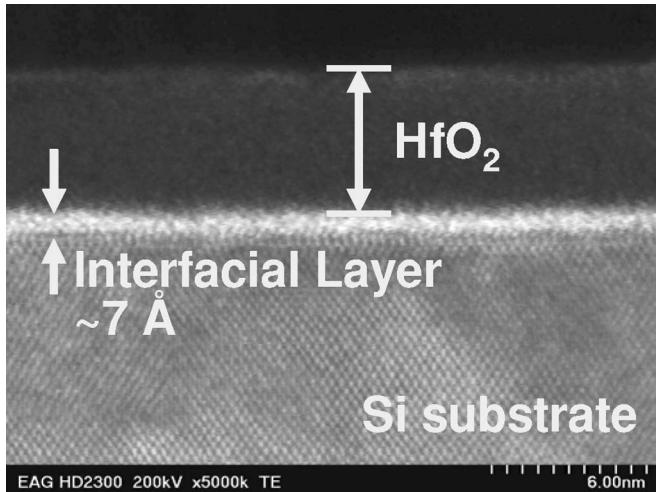


FIG. 6. A HRTEM image for a 50 cycle film on H-terminated Si. The thickness of the interfacial layer is ~7 Å.

TABLE I. rms roughness for a series of films on different starting surfaces. The films deposited on the H-terminated surface exhibit higher roughness than those deposited on the SC1 chemical oxide.

No. of cycles	Starting surface	rms roughness (nm)
350	H-terminated	2.1
350	SC1	1.7
100	H-terminated	0.3
100	SC1	0.2
30	H-terminated	0.1
30	Native oxide	0.1

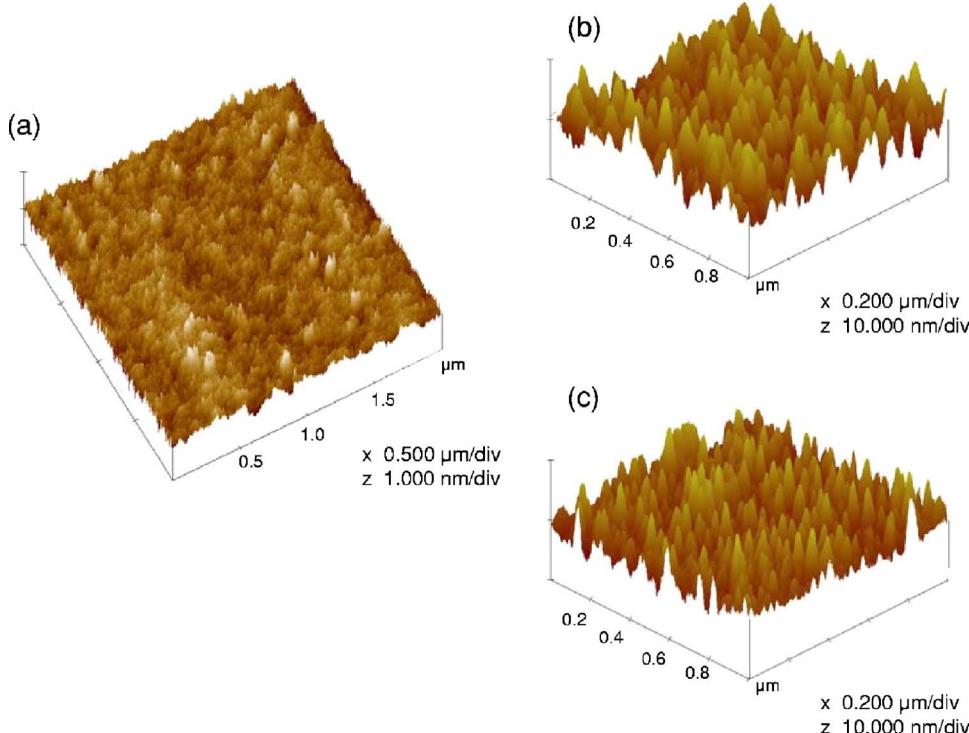


FIG. 8. AFM images for (a) 30 cycle film on H-terminated Si, (b) 350 cycle film on H-terminated Si, and (c) 350 cycle film on SC1 chemical oxide.

practically unchanged for the first 50 process cycles. There is excellent agreement between the interface thickness analysis performed with the ARXPS measurements and the HRTEM data, corroborating earlier results for the potential of the technique to accurately measure the thickness of silicate-based interfacial layers for ultrathin films.<sup>23</sup> From the XPS data we see that as the film thickness increases the binding energy for the interfacial layer shifts to lower energy. The binding energy of the interfacial layer peak is compatible with the formation of  $\text{SiO}_2$  for the first 4–7 cycles and silicate composition for the thicker films. Because the thickness of the interfacial layer does not increase with film thickness the shift in the binding energy of the interfacial layer can be explained in terms of second neighbor effects; the presence of the Hf atoms in the film bulk affects the energy levels of the Si atoms in the interfacial layer.<sup>24</sup>

The data suggest that for the specific process the presence of a suitable starting surface is required for film nucleation, but once the film nucleation begins then there is no additional growth of the interfacial layer. Composition measurements performed on thick films (600 cycles) reveal the formation of practically stoichiometric  $\text{HfO}_2$  and no excess oxygen is detected in the films. The absence of excess oxygen in the film bulk may account for the stability in the thickness of the interfacial layer.

For both starting surfaces we find that a 40 cycle-long surface “conditioning” period is required for the growth rate to reach its steady state value of  $3.1 \times 10^{14}$  atoms/cm<sup>2</sup>. The RBS data regarding film growth shows qualitative similarities with observations for the growth on H-terminated surfaces of  $\text{HfO}_2$  films from  $\text{HfCl}_4$  and  $\text{H}_2\text{O}$ ,<sup>25</sup>  $\text{ZrO}_2$  from  $\text{ZrCl}_4$  and  $\text{H}_2\text{O}$ ,<sup>18</sup>  $\text{Al}_2\text{O}_3$  from  $\text{AlMe}_3$  and  $\text{H}_2\text{O}$ ,<sup>18</sup> and W films from  $\text{WF}_6$  and  $\text{H}_2$ .<sup>26</sup> Alam *et al.*<sup>25</sup> proposed a three region film growth model, consisting of initial, transitional, and linear

regimes and our data conform to that observation. Our initial growth regime lasts ~7 cycles, followed by a transition region from 7 to 45 cycles which displays an increasing growth rate and a steady state growth regime after the 45th cycle. Furthermore, it has been suggested that the films deposited on H-terminated surfaces are more porous.<sup>27</sup> While we are not equipped to measure film porosity directly, the combination of the RBS, SE, and AFM data we have collected for our films seem to corroborate such an observation. More specifically, the measured RBS growth rate equates to ~1.1 Å/cycle which is in excellent agreement with the growth rate of 1.2 Å/cycle on SC1 measured by SE. This observation indicates that the  $\text{HfO}_2$  films deposited on the SC1 surface have optical properties close to the bulk and that the SE thickness determination is accurate. The AFM measurements of the film surface roughness indicate a consistently higher surface roughness for the films deposited on the Si-H surface compared to the SC1 surface. For thick (>100 cycles) films deposited simultaneously on both surfaces, the RBS measurements suggest similar surface atom density while the SE data suggest that the films deposited on the H-terminated surfaces are 5% optically thicker than the films deposited on the SC1 chemical oxide. Higher film porosity in addition to the increased surface roughness can explain this observation.

## V. CONCLUSIONS

In this article we have compared the nucleation of  $\text{HfO}_2$  films from TEMAH and  $\text{H}_2\text{O}$  on SC1 chemical oxide and H-terminated Si. RBS measurements of the surface atom density for very low cycle films (1–7 cycles) reveal that initially the H-terminated surface poses a significant nucleation barrier. However, this barrier is overcome after the sixth process cycle and may coincide with the formation of a

$\text{SiO}_x/\text{SiOHf}$  interfacial layer, which is detected by ARXPS and HRTEM and determined to be  $\sim 7 \text{ \AA}$  thick. Once formed, the thickness of the silicate layer remains unchanged for films as thick as 50 cycles. Although same-cycle films on the two starting surfaces have similar surface atom densities as measured by RBS, SE measurements suggest that the films deposited on the H-terminated surface are  $\sim 5\%$  optically thicker than similar films deposited on the SC1 chemical oxide. This increase in the optical thickness is accompanied by substantial surface roughening as detected by AFM. These results are consistent with increased porosity for the films deposited on H-terminated surfaces suggested by Green *et al.*<sup>27</sup>

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