

Growth and interface of HfO₂ films on H-terminated Si from a TDMAH and H₂O atomic layer deposition process

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HfO₂ thin films have been deposited by an atomic layer deposition (ALD) process using alternating pulses of tetrakis(dimethyl)amino hafnium and H₂O precursors at a substrate temperature of 200–325 °C. The initial stage of film growth on OH- and H-terminated Si(100) surfaces is investigated using Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), and spectroscopic ellipsometry (SE). The authors observe an initial growth barrier on the Si-H surface for the first approximately four process cycles, where film growth is more efficient on the OH-terminated surface. Both starting surfaces require about 15 cycles to reach a steady growth rate per cycle, with the OH-terminated surface displaying a slightly higher growth rate of 2.7×10^{14} Hf/cm² compared to 2.4×10^{14} Hf/cm² for Si-H. Combining the RBS and SE data we conclude that the films deposited on the OH-terminated surface are denser than those deposited on the Si-H surface. Angle-resolved XPS measurements reveal the formation of an ~ 8 Å interfacial layer after four ALD cycles on the H-terminated surface for a deposition temperature of 250 °C, and transmission electron microscopy verifies that the thickness of the interfacial layer does not change substantially between the 4th and the 25th process cycles. The interfacial layer appears to depend weakly on the deposition temperature from 200 to 325 °C, ranging from 6.9 to 8.4 Å.

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I. INTRODUCTION

As the field effect transistor feature size continues to shrink below the 65 nm level, new gate oxide materials must be implemented to replace the conventional SiO₂ gate dielectric and to meet stringent device requirements such as low leakage current and equivalent oxide thickness (EOT).¹ Hafnium-based oxides including hafnium silicate and nitrated Hf silicate are favorable materials for this application due to a higher dielectric constant compared to SiO₂, good electrical properties, and thermal stability with Si.^{2,3} However, stoichiometric HfO₂ has proven difficult to work with due to structural changes from amorphous to crystalline phases during high temperature anneals^{4,5} followed by eventual film breakdown,⁶ and interfacial layers forming during deposition which increase the EOT of the gate stack.^{7,8}

Atomic layer deposition (ALD) is an excellent technique for growing high quality conformal thin films such as those required in transistor gate stacks,⁹ and a number of precursors and ALD processes are available for the deposition of HfO₂.^{3,7,10} However, the initial growth mechanism of HfO₂ on differently prepared silicon starting surfaces is not well understood. Liu *et al.* proposed a surface reaction model for two-step ALD growth on OH-terminated Si, where surface

OH groups are required to initiate a chemical reaction with an organic amide Hf precursor.¹¹ Experiment has shown that this is a desirable surface for HfO₂ deposition with uniform growth rates even at early stages of film growth.^{12–14} Conversely, there are many different reports about HfO₂ growth characteristics on hydrogen-terminated Si (Si-H or HF last) and the development of the interfacial structure during initial film growth. Alam and Green showed a nucleation barrier lasting ~ 25 ALD cycles using a HfCl₄/H₂O process at 300 °C,¹² which was verified by Chung *et al.*;¹⁵ Wang *et al.* demonstrated nearly identical early stage growth rates on OH- and H-terminated surfaces with a tetrakis(ethylmethyl)amino hafnium (TEMAH) and D₂O low-temperature ALD process at 100 °C, with virtually no interfacial layer.¹⁶ Kukli *et al.* did not report a growth barrier with the tetrakis(dimethyl)amino hafnium (TDMAH) and H₂O process, but showed a significant interfacial layer of ~ 20 Å for HfO₂ deposited on Si-H.⁷ Niinistö *et al.* reported both a significant growth barrier and a 5–10 Å interfacial layer using cyclopentadienyl-type precursors and H₂O for HfO₂ growth at 350–400 °C.¹⁷ Previous work by the authors showed a growth barrier of five to seven cycles on a H-terminated Si surface using a TEMAH/H₂O ALD process at 250 °C and the formation of about 7 Å of interfacial SiO_x.¹³ The diverse behavior observed at the initial film growth stage demonstrates that HfO₂ ALD is a complicated function of substrate preparation, precursor type, and deposition conditions, which

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has been discussed elsewhere for systems such as trimethylaluminum(TMA)/H₂O ALD.¹⁸ A comparison of different HfO₂ precursors under similar conditions should decrease experimental variability and enhance the understanding of the initial growth process of thin ALD HfO₂ films.

In this article, we examine HfO₂ nucleation and growth on both Si–H and Si–OH surfaces using a TDMAH/H₂O ALD process at a deposition temperature of 200–325 °C under process conditions similar to our previous study of the TEMAH/H₂O system. We find that the Si–H surface experiences an initial growth barrier of about four ALD cycles; afterward, both OH- and H-terminated surfaces display similar growth rates. Angle-resolved x-ray photoemission spectroscopy (ARXPS) measurements show that an ~8 Å nearly stoichiometric SiO₂ interfacial layer forms during the first four ALD cycles on the Si–H surface. ARXPS and high resolution transmission electron microscopy (HRTEM) measurements verify that the interfacial layer remains practically constant in thickness from 4 to 25 ALD cycles.

II. EXPERIMENT

HfO₂ films were grown in a homemade, hot-wall stainless steel flow tube ALD reactor. The reactor details and sample surface preparation techniques have been described previously.¹³ Films were deposited at a substrate temperature of 275 °C while using a 30 s N₂ purge time, which reflects the optimum ALD conditions for HfO₂ growth (data not shown). TDMAH was purchased from Sigma Aldrich and transferred to a 100 ml stainless steel vessel; during the experiment the TDMAH vessel was kept at 70 °C. The H₂O vessel was maintained at room temperature throughout deposition, ~24 °C. A constant flow of ultrahigh purity N₂ gas [25 SCCM (SCCM denotes cubic centimeter per minute at STP) was used to maintain a flow tube process pressure of ~225 mTorr during deposition. Low-resistivity (0.001–0.005 Ω cm) *p*-type Si(100) wafers were used to prepare the OH—(SiO₂ chemical oxide) (Ref. 19) and H-terminated surfaces for HfO₂ deposition. The Si–H surface has been shown to be stable in air for hours before appreciable oxidation was observed.²⁰ However, the reoxidation of the Si surface is accelerated at higher temperatures.²¹ To maintain the H-terminated Si surface intact for deposition, the predeposition reactor purge time was kept at ~30 min after sample loading. 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 Woollam α -SE spectroscopic ellipsometer with a spectral range of 380–900 nm (180 wavelengths). The optical constants for HfO₂ were obtained by the library provided by the vendor. Compositional analysis of the samples was performed *ex situ* by a Kratos ultra-XPS spectrometer at 0° takeoff angle with 0.5 eV step size for survey scans and 0.1 eV step size for high-resolution

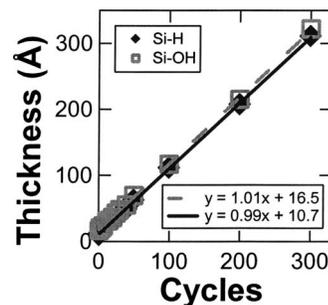


FIG. 1. Spectroscopic ellipsometry measurements of HfO₂ film thickness on chemical oxide (square) and Si–H (diamond) show identical, linear growth rates of 1.0 Å/cycle. The vertical intercepts correspond to the thickness of SiO₂ chemical oxide underlayer and the interfacial layer formed on the Si–H surface.

scans. All takeoff angles were measured with respect to the surface normal. The films deposited at 250 °C were analyzed using the Mg *K*α source ($h\nu=1253.6$ eV), while the samples deposited at 200, 225, 275, and 325 °C were analyzed using the Al *K*α source ($h\nu=1486.6$ eV) of the spectrometer. The samples were not sputtered cleaned before the XPS analysis to remove residual hydrocarbon contamination. Sample charging effects were partially compensated by using the system's electron flood gun neutralizer. For the angle-resolved scans of the Si 2*p* core electron peak, the Si 2*p* substrate peak was used to calibrate the energy scale and set at a binding energy of 99.3 eV. For the elemental scans, the C 1*s* peak was set at 285 eV. Rutherford backscattering spectrometry (RBS) measurements were made using a 1.2 MeV He⁺ beam obtained from a National Electrostatics 5SDH-2 positive ion accelerator. The backscattering angle was 170° and the spectra were collected using a surface barrier detector subtending approximately 5 msn. The raw RBS data were fitted using the simulation program RUMP.²² HR-TEM data were provided by Evans analytical group.

III. RESULTS

SE measurements of HfO₂ films ranging from 1 to 300 ALD cycles show identical, linear growth rates of 1.0 Å/cycle for both Si–OH and Si–H starting surfaces (Fig. 1). The positive intercepts in the plot indicate the thicknesses of the chemical oxide layer and interfacial layer for the OH- and H-terminated surfaces, which are 16.5 and 10.7 Å, respectively. The error was calculated by combining a standard deviation in SE measurements (a typical 1 × 1 cm² sample was measured at five different points) with the uncertainty of the fit, and is on the order of 1 Å. Film growth was further investigated using RBS by analyzing the hafnium surface coverage. The Si–OH surface displays a slightly higher coverage rate of 2.7 × 10¹⁴ Hf/cm² cycle, compared to 2.4 × 10¹⁴ Hf/cm² cycle for the Si–H surface [Fig. 2(a)]. To examine the initial HfO₂ film formation on the Si–H starting surface, we look at the average hafnium coverage shown in Fig. 2(b); the *x* axis is plotted on a logarithmic scale in order to display the entire data range. The Si–H surface exhibits a growth barrier for the first approximately four ALD cycles,

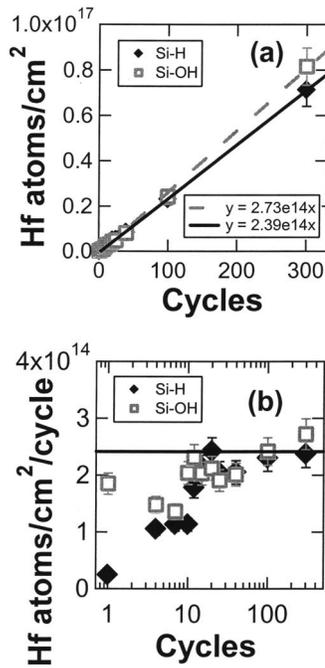


FIG. 2. (a) Hf coverage as measured by RBS for 1–300 cycle HfO₂ films on Si–H and Si–OH starting surfaces. The Si–OH surface displays slightly higher Hf coverage of 2.7×10^{14} Hf/cm² cycle compared to 2.4×10^{14} for Si–H. (b) Average Hf coverage rates on Si–H and Si–OH starting surfaces. A four cycle growth barrier is observed for the Si–H surface. Both surfaces require about 15–20 cycles to reach steady-state coverage rates, shown by the horizontal bar on the figure.

characterized by a significantly reduced growth rate compared to the Si–OH surface. Both starting surfaces require 15–20 cycles to reach steady-state coverage rates.

ARXPS was utilized to study the evolution of the HfO₂/Si interface for the Si–H surface during the period where steady-state Hf coverage is attained. The Si 2*p* peak for samples of 4, 7, 10, 15, and 25 ALD cycles at 250°C was examined with a series of scans ranging from 0° to 55°, measured from the sample normal. Normalized spectra from the 4 and 25 cycle samples are shown in Figs. 3(a) and 3(b),

respectively. The secondary peak located at a binding energy of 103 eV corresponds to the interfacial layer (IL) and shifts marginally toward lower binding energy between 4 and 25 cycles. The positive ~4 eV shift with respect to the substrate peak implies that the IL is comprised of nearly stoichiometric SiO₂. We used the method outlined by Jablonski and Powell in order to calculate the interfacial layer thickness over the 4–25 cycle period.²³ For a given sample, both the Si⁰ and Si⁴⁺ peaks were background corrected, integrated, and fitted to the equation

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

where R is the intensity ratio of the Si⁴⁺ 2*p* to the Si⁰ 2*p* peak, $K=0.7$ is the relative sensitivity factor, θ is the take-off angle, d is the interfacial layer thickness, and λ is the effective attenuation coefficient, with a value of $\lambda=3.01$ nm for the Si 2*p* photoelectrons produced by the Mg source and $\lambda=3.47$ nm for the Si 2*p* photoelectrons produced by the Al source. In this analysis, the HfO₂ overlayer is assumed to be uniform and to attenuate evenly both the Si⁰ and Si⁴⁺ signals; as a result the thickness of the HfO₂ film does not affect the calculations. Similar approaches have been used for the quantitative examination of IL for various other systems.^{24–26} The values for the constants λ and K in Eq. (1) are taken from literature and a 10% error is estimated as a reasonable uncertainty that accounts for differences among the reported values.^{25,27} A flat 10% error was assumed for all peak intensity integrations as well; the uncertainties are then propagated through Eq. (1) to arrive at an uncertainty value for each data point. The data are fitted to a straight line through the origin ($y=ax$) where the slope represents the ratio d/λ . The 4 and 25 cycle data are presented in Fig. 4 and show interfacial layers of 8.4 ± 1.2 and 8.7 ± 1.3 Å, respectively. The uncertainty in the film thickness reflects the quality of the fit and the uncertainty in λ . All the uncertainties quoted in this article are 1σ . Results for all five samples are summarized in Fig. 5 and illustrate that the interfacial layer remains unchanged, within the uncertainty

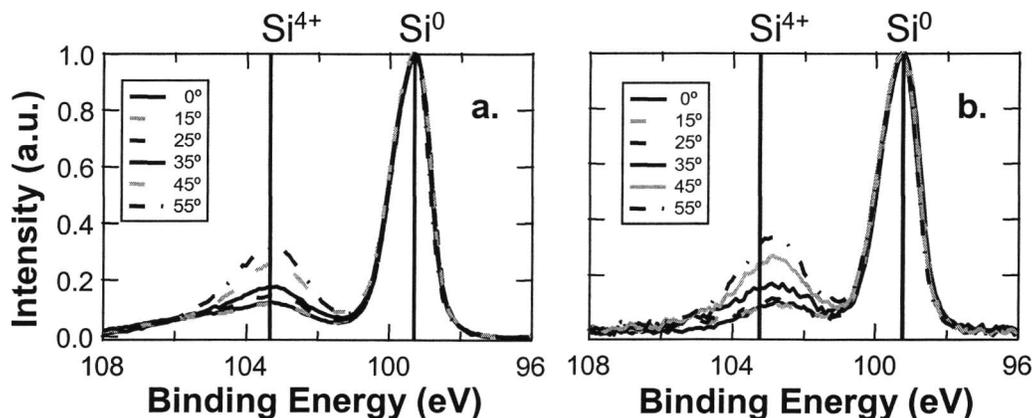


FIG. 3. ARXPS scans of the Si 2*p* core electron region at 0°–55° takeoff angles measured from the sample normal for (a) 4 and (b) 25 cycle samples on Si–H. The secondary peak corresponds to Si⁴⁺ (energy shift of 4 eV for the four cycle sample) and its binding energy does not change substantially between 4 and 25 process cycles.

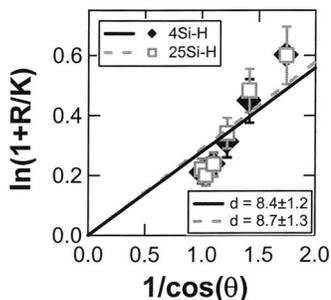


FIG. 4. Linear fit of the Si⁴⁺/Si⁰ XPS data shown in Fig. 3 to Eq. (1). The straight lines represent linear fits to the data and the slope is equal to d/λ .

of the measurement, from 4 to 25 ALD cycles, ranging from 7.4 to 8.9 Å. In order to verify the accuracy of this technique, HRTEM data were taken for the same 25 cycle sample that was used for ARXPS, and are shown in Fig. 6. The HRTEM image displays an interfacial layer of 10 ± 2 Å, shown by the high contrast layer, which agrees within the error limits with the values derived from the ARXPS measurements as well as the IL thickness taken from the SE growth curve.

To explore the temperature dependence of the interfacial layer thickness, several 15 cycle samples were grown on a Si-H surface at substrate temperatures of 200, 225, 275, and 325 °C. The previous ARXPS analysis was applied and the results are shown in Fig. 7. A very weak temperature dependence is detected as the IL thickness changes from 6.9 Å at 200 °C to 8.2 Å at 325 °C; the error for each temperature is shown in the plot.

IV. DISCUSSION

It is well known that substrate surface preparation can affect significantly the initial film growth during an ALD process. OH-rich surfaces such as chemical oxide layers result in immediate linear ALD growth, whereas Si-H surfaces represent the opposite extreme and may display long growth barriers and islandlike initial growth.^{28,29} In general, thin film growth with metal organic precursors such as TEMA (Ref. 30) or TMA (Ref. 31) shows a weaker dependence on surface functionalization compared to chlorinated reagents,¹⁹ and our results conform to this trend as well. RBS measure-

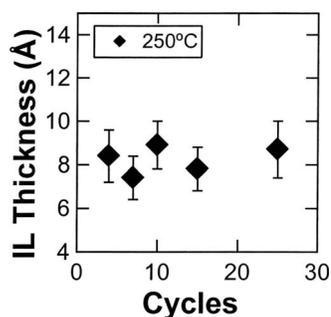


FIG. 5. Thickness of the interfacial layer as a function of cycle number for HfO₂ films on Si-H surfaces at 250°. The interfacial layer remains nearly constant at ~ 8 Å. The error bars represent 1σ limits.

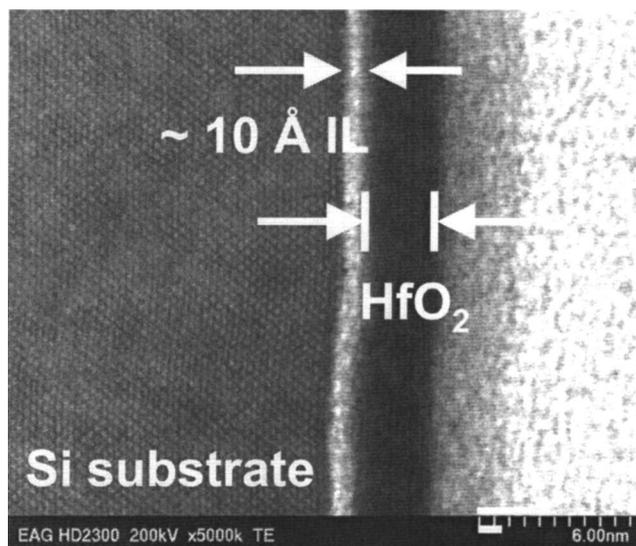


FIG. 6. HRTEM image of a 25 cycle HfO₂ film on Si-H; the interfacial layer is evident by the white strip between the Si substrate and HfO₂ layer and its thickness is 10 ± 2 Å.

ments for samples of 1–300 cycles point to an initial growth barrier of about four ALD cycles on the Si-H surface, where Hf coverage lags behind that on an OH-rich chemical oxide surface. In addition, the Si-OH surface displays a higher Hf coverage rate of 2.7×10^{14} Hf/cm² cycle compared to 2.4×10^{14} Hf/cm² cycle for Si-H, even though optical techniques (SE) indicate identical growth rates. Combining the RBS and SE data and using the bulk density of 2.77×10^{22} Hf/cm³ for HfO₂ we find that the films on Si-OH reach about 95% of bulk crystalline HfO₂ density, while films on Si-H are about 85% dense. Low film density on the Si-H surface may be due to film porosity resulting from initial islandlike growth.²⁸

ARXPS evaluation of the interfacial region for films grown on Si-H surfaces indicates the formation of ~ 8 Å of nearly stoichiometric interfacial SiO₂. The IL thickness measured with ARXPS agrees well with both the value determined from HRTEM scans of a 25 cycle sample (10 ± 2 Å) and with the IL thickness taken from the SE growth curve (~ 10.7 Å, shown by the vertical intercept). Lack of *in situ*

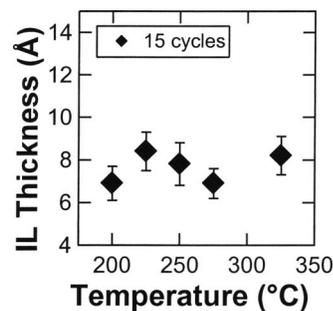


FIG. 7. Interfacial layer thickness measurements for a series of 15 cycle HfO₂ films deposited at substrate temperatures ranging from 200 to 325 °C. The IL thickness ranges from 6.9 to 8.4 Å. The error bars represent 1σ limits.

diagnostic tools does not allow direct determination of whether the IL is formed during the process or after postdeposition ambient exposure. The IL thickness is practically unchanged for films up to 25 cycles. The low cycle films are noncoalesced due to low surface coverage and as such susceptible to postdeposition oxidation. The HRTEM data show that the 25 cycle film is coalesced, and our recent investigation of the HfO₂/GaAs interface has shown that a 15 cycle film deposited with the TDMAH/H₂O chemistry on an oxide-free GaAs surface protects the surface from postdeposition oxidation.³² In addition, the Hf surface coverage of the Si-H for the first four ALD cycles is significantly lower than that for the Si-OH surface and similar beyond that point. Formation of the IL during the initial four process cycles would provide a surface amenable to efficient film growth and result in the subsequent enhanced Hf coverage detected by RBS. Based on the above discussion we conclude that the most probable cause of the IL is oxidation during the first four ALD cycles. The SiO₂ layer subsequently stabilizes the interface and prevents further oxidation of the surface for the remainder of the ALD process.

In previous work we examined the early growth and interface of HfO₂ ALD films on Si surfaces using the TEMAH precursor that belongs to the same amide precursor family as TDMAH.¹³ For the TEMAH chemistry an IL thickness of $\sim 6.5 \pm 1.0$ Å was measured, somewhat thinner than the IL obtained for the current TDMAH process. This difference can be explained by the different film stoichiometries obtained in the two processes and/or a steric hindrance effect. More specifically, elemental XPS measurements indicate that the HfO₂ films from the TDMAH chemistry are oxygen-rich (O/Hf=2.2) compared to films obtained with the TEMAH/H₂O process (O/Hf=1.9). The presence of excess oxygen in the TDMAH films may enhance the Si surface oxidation. In addition, the TDMAH molecule is smaller in size than the TEMAH molecule and as a result may allow the oxidizing species to reach more easily the Si substrate during the initial HfO₂ growth.

Several models of ALD growth that have been proposed describe the role of the OH surface group in the ALD process. Puurunen found a linear correlation between OH surface concentration and Al surface concentration for a TMA ALD process.³³ Nyns *et al.* showed that initial Hf surface coverage for the first five cycles of a HfCl₄ ALD process is a linear function of the SiO₂ underlayer (grown either chemically or thermally) and saturates at a SiO₂ thickness of ~ 8 Å.³⁴ In both cases, the OH surface density is directly related to the amount of adsorbed precursor. Our results agree well with this picture; the hydrogen termination provides an unreactive surface for TDMAH, and initially only a small fraction of a monolayer is adsorbed (2.4×10^{13} Hf/cm² for the first cycle compared to 1.9×10^{14} Hf/cm² for the Si-OH surface). The bare Si surface is then exposed to several large doses of H₂O and TDMAH over the next few cycles, and a SiO₂ layer subsequently develops. This provides an OH-rich surface for the TDMAH half reaction, and the growth rate reaches that of the SCl

chemical oxide surface. Both surfaces reach a steady-state growth per cycle (GPC) by about 15 cycles. The current results mirror our previous conclusions for the TEMAH/H₂O process, where a similar four cycle growth barrier is observed on the Si-H surface. The GPC results from both experiments may be qualitatively described by a model from Lim *et al.* of ALD growth, consisting of an initial transient region followed by steady-state growth.^{35,36}

The IL also appears to stabilize the film interface since no noticeable change in thickness or composition occurs from 4 to 25 cycles. Triyoso *et al.* observed similar stabilization behavior with a TEMAH/O₃ process; a 10 Å IL develops on a Si-H surface during the ALD process and does not change even after a high temperature postdeposition anneal (PDA) at 900 °C.³⁷ Our films have not been examined after PDA treatments. However, it is interesting to note that the IL exhibits little change, ranging from 6.9 to 8.4 Å, when the deposition temperature is varied from 200 to 325 °C. Process temperatures above the ALD window may result in chemical vapor deposition (CVD)-like growth, where the initial surface coverage may be poor due to islanding of the HfO₂ film. For the temperature range used in this work, the GPC increases marginally by 0.2 and 0.4 Å/cycle at 200 and 325 °C, respectively. This shows that the current process is still far removed from pure CVD growth. It is possible that the variation in the process temperature results in density, morphology, and composition variations of the HfO₂ film.^{38,39} However, to a first approximation the approach used to evaluate the ARXPS data for the Si⁴⁺ and Si⁰ peaks does not depend on the properties of the overlayer because the calculation for the IL thickness uses the ratio of the Si⁴⁺ and Si⁰ peaks and not absolute intensities. Both the Si⁴⁺ and Si⁰ photoelectrons are very similar in energy and transverse the same, very thin, HfO₂ layer. As a result, their intensity is attenuated by the same exponential factor. In reality, neglecting electron scattering effects and assuming an exponential photoelectron current decay introduce error into the XPS calculations. If electron scattering is considered, Jablonski and Powell suggest that the value of λ deviates from the typical inelastic mean free path by at most 10% under conditions similar to this experiment.²³ The uncertainty in λ included in the evaluation of IL thickness accounts for this source of error.

Deposition temperatures as low as 100 °C have resulted in HfO₂ growth without any interfacial layer formation for a TEMAH/D₂O chemistry, and it was shown that the metal organic precursor and not the D₂O oxidizing agent reacts with the passivated Si-H surface and initiates growth.⁴⁰ In light of our results, it appears that the interfacial layer growth is temperature activated; once the surface hydrogen is removed (whether by TDMAH, H₂O, or a combination of the two), the higher temperature together with H₂O exposure encourages substrate oxidation. Further investigation into the interfacial SiO₂ growth for a broader process temperature range may provide more insight into the substrate oxidation process.

V. CONCLUSIONS

In this article, we have examined initial HfO₂ growth on Si-H and SCl chemical oxide surfaces using a TDMAH and H₂O ALD process, as well as the IL formation during early film growth. The data suggest that surface functionalization affects the initial growth of HfO₂ from TDMAH and H₂O at 275 °C. The Si-H surface displays a growth barrier of about four cycles compared to the SCl surface. During that initial period, an ~8 Å SiO₂ interfacial layer develops, which provides the necessary OH-dense surface for HfO₂ nucleation. Steady-state growth rates on Si-H and Si-OH surfaces are similar. The interfacial layer composition and thickness does not change substantially from 4 through 25 process cycles, as verified with ARXPS and HRTEM, implying that this layer stabilizes the film interface for the remainder of the ALD process. These results closely mirror those from our previous study of the TEMA/H₂O ALD system.¹³ In summary, our results show that for the TDMAH/H₂O ALD chemistry, a SiO₂ interfacial layer develops to stabilize the HfO₂/Si interface and provide suitable OH surface density for HfO₂ nucleation and subsequent steady-state growth.

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