Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Selective pulsed chemical vapor deposition of water-free HfO_x on Si in preference to SiCOH and passivated SiO₂



Applied Surface Scienc

Jong Youn Choi^a, Christopher F. Ahles^a, Yunil Cho^b, Ashay Anurag^c, Keith T. Wong^e, Srinivas D. Nemani^e, Ellie Yieh^e, Andrew C. Kummel^{d,*}

^a Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093, United States

^b Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA 92093, United States

^c Department of Nanoengineering, University of California, San Diego, La Jolla CA 92093, United States

^d Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, CA 92093, United States

e Applied Materials, Inc., Santa Clara, CA 95054, United States

ARTICLE INFO

Keywords: Water-free oxide deposition Area-selective deposition Pulsed chemical vapor deposition

ABSTRACT

HfOx was selectively deposited on Si in preference to SiCOH using an oxygen-containing precursor, Hf(O^tBu)₄, via a pulsed chemical vapor deposition. The water-free process avoids nucleation by water on passivated oxide surfaces. The uniform HfO_x film was deposited on Si by the thermal decomposition of the precursor, and the inherent selectivity of HfO_x was retained over SiCOH until ~ 2 nm of HfO_x was deposited on Si at 250 °C. Additional selectivity enhancement was demonstrated by employing molecular surface passivation and reversible adsorption/desorption of the precursor via control of the purge time. 1,1,3,3-tetramethyldisilazane (TMDS) and Bis(dimethylamino)dimethylsilane (DMADMS) were employed to passivate reactive -OH sites on SiO₂ and SiCOH to increase the selectivity to \sim 7 nm HfO_x deposition on Si before any significant nucleation occurred on TMDS passivated SiCOH. It is expected that the selective water-free HfOx deposition can be used for patterning nanoscale structures in MOSFET devices.

1. Introduction

As metal-oxidesemiconductor field effect transistors (MOSFETs) are scaled down to 10 nm nodes or less with three dimensional geometries, a sustainable density scaling becomes a substantial challenge in patterning processes. Conventional patterning techniques (i.e. photolithography) involve the multiple and repetitive processes of deposition and wet/plasma etching with photomasks and resist films [1,2]. However, the complexity of multi-patterning lithography often leads to an unsatisfactory resolution due to an imperfect alignment of masks or limited focal plane of the light source [3-5].

Area-selective atomic layer deposition (AS-ALD) is an alternative method to pattern sub-10 nm features. For example, self-aligned double patterning (SADP) employs lithography in conjunction with a conformal ALD of a spacer which can achieve higher resolution features in three dimensions. Selective oxide deposition eliminates etching steps by depositing an oxide film only on the sidewall of spacer as shown in Fig. S1. AS-ALD selectivity relies on the differential chemical reactivity between the precursors and different substrates so that spontaneous patterning is possible. Therefore, a choice of reactants for a selective

oxide deposition is critical since strongly oxidizing reactants such as H₂O and H₂O₂ easily provide nucleation sites on any surface. For example, previously reported HfOx ALD has employed water (H2O), ozone (O₃), ammonium hydroxide (NH₄OH), hydrogen peroxide (H₂O₂) or oxygen (O2) plasma as oxygen sources [6-12]. These oxidants are effective in forming a high quality HfOx film due to energetically favorable reactions of -OH groups or reactive oxygen species with Hf precursors; however, they can initiate nucleation on most surfaces which should be avoided for selective deposition.

Anderson et al. [13] have demonstrated waterless TiO₂ ALD using TiCl₄ and Ti(OⁱPr)₄, and Atanasov et al. [14] have reported an inherent substrate-dependency of the "water-free" TiO2 process between hydrogen terminated Si (H-Si) and hydroxylated Si (OH-Si). The authors showed that eliminating strong oxidants such as water was critical to obtain selectivity by preventing oxidation of the Si-H terminated surface.

Sayan et al. [15] and Yang et al. [16] previously demonstrated a water-free HfO₂ deposition on Si via a single-source chemical vapor deposition (CVD) process. The authors employed a thermal decomposition of hafnium alkoxides by continuously exposing Si to the

* Corresponding author.

E-mail address: akummel@ucsd.edu (A.C. Kummel).

https://doi.org/10.1016/j.apsusc.2020.145733

Received 10 November 2019; Received in revised form 3 February 2020; Accepted 10 February 2020 Available online 11 February 2020

0169-4332/ © 2020 Published by Elsevier B.V.





Fig. 1. A schematic of the vacuum system. The chamber consisted of a reaction chamber, sample loading chamber and UHV chamber equipped with X-ray photoelectron spectroscopy.

precursors; however, to the best of our knowledge, the selectivity of water-free $\rm HfO_2$ deposition has never been reported nor optimized.

In this study, water-free HfO_x was selectively deposited on Si in preference to SiCOH and passivated SiO_2 by employing hafnium tetra*tert*-butoxide ($Hf(O^{T}Bu)_4$) as a source of both metal and oxygen. The HfO_x deposition was performed via a pulsed CVD process which involved the decomposition of $Hf(O^{T}Bu)_4$. In continuous CVD, a thermally pyrolyzed precursor is generally less sensitive to the initial surface condition which is not desirable for selectivity. However, unlike a conventional CVD process which continuously flows a precursor, $Hf(O^{T}Bu)_4$ was pulsed with a purge. Pulsed CVD enables investigation of the mechanism of selectivity and enhances selectivity by allowing reversibly molecularly absorbed precursors to desorb from the less reactive surface before reacting. The data demonstrate the selective water-free CVD of HfO_x using small molecules passivants and purge control.

2. Experimental

Fig. 1 shows a chamber schematic. A home-built reaction chamber was pumped by a turbopump (Pfeiffer TPU 062) and a backing rotary pump (Edwards RV3). The base pressure of the reaction chamber was 8.0×10^{-7} Torr. The reaction chamber had a manipulator rod with a sample mounting platform made of Cu. A cartridge heater was used to heat the Cu platform and the samples. The precursors and N₂ purge gas had dosing lines pointing at the samples with a 3-inch separation. The dosing was performed using pneumatic valves for the precursor and a leak valve for the purge. The chamber wall and dosing lines for precursors were kept at 150 °C. After the deposition was performed, the processed samples were transferred in-situ into a UHV chamber to characterize the chemical compositions and oxidation states of the films using X-ray photoelectron spectroscopy (XPS). The UHV chamber was pumped by an ion pump (Agilent Varian VacIon 300 StarCell) and had a base pressed of 8.0×10^{-10} Torr. The in-situ transfer was performed

using the manipulators and transfer arm so that the samples were not exposed to the ambient air between the depositions and chemical analyses. For the XPS measurements, a monochromatic Al Ka X-ray source (E = 1487 eV) and a hemispherical analyzer (XM 1000 MkII/ SPHERA, Omicron Nanotechnology) were employed. The anode voltage and filament emission current were set to 10 kV and 25 mA respectively with a hemisphere analyzer pass energy of 50 eV. The focused X-ray beam size on the sample was 0.7-1 mm in diameter. For the surface sensitive measurements, the XPS detector was aligned to 60° from the sample surface normal (i.e. near glancing), but for the detection of the bulk composition of deposited films, 30° from the surface normal was employed. After the XPS data collection, the areas of the XPS peaks were calculated and corrected using their relative sensitivity factors reported in the Casa XPS v2.3 program. The chemical compositions were normalized to the sum of all elements. The morphology of the deposited films were analyzed using ex-situ atomic force microscopy (AFM) (Agilent 5500) in tapping mode.

Passivation of SiO₂ and SiCOH was performed in a separate vacuum chamber where the base pressure was 200 mTorr pumped by a mechanical pump (Edwards RV3). The chamber consisted of a sample stage which had a cartridge heater to heat the samples to a reaction temperature of 70 °C. The chamber walls were kept at 25 °C. SiO₂ samples were loaded in the passivation chamber after degreasing using acetone, methanol and HPLC grade water for 30 s each followed by a 30 s dip in a 0.5% HF(aq) solution. SiCOH samples were degreased using the same process but without the HF clean. 1,1,3,3-tetramethyldisilazane (TMDS) (97%, Sigma Aldrich) and Bis(dimethylamino)dimethylsilane (DMADMS) (> 95%, Sigma Aldrich) were used as passivation agents. The precursor bottles were kept at room temperature. The passivants continuously flowed into the chamber at a constant pressure of 10 Torr for 10 mins using a manual bellows valve. After the passivation process, the passivated SiO₂ and passivated SiCOH samples were removed from vacuum and quickly loaded into a sample loading chamber that was connected to the reaction chamber and UHV chamber



Fig. 2. XPS elemental compositions and the growth rates of HfO_x on H-terminated Si at 250 °C, 200 °C and 150 °C. (a) Elemental composition of HF cleaned Si after sequential doses of Hf(O^tBu)₄ at 250 °C, 200 °C and 150 °C. The elemental composition is normalized to the sum of all elements. (b) The growth rate of HfO_x on H-terminated Si using Hf(O^tBu)₄ at 250 °C, 200 °C and 150 °C. The HfO_x thicknesses were calculated using the substrate attenuation from XPS. The raw data are shown in Fig. S2. The exposure time for the Hf(O^tBu)₄ pulses was 50 ms, and the N₂ purge time was 15 s between the Hf(O^tBu)₄ pulses.

to minimize the contamination from the air transfer.

B-doped Si (0 0 1), SiO₂ and SiCOH were degreased using acetone, methanol and HPLC water sequentially for 30 s. After the degrease, Si and SiO₂ were cleaned in a 0.5% HF(aq) solution for 30 s followed by a HPLC water rinse to remove a native oxide. Two or three samples (i.e. HF cleaned Si and degreased SiCOH or HF cleaned Si, passivated SiO₂ and passivated SiCOH) were loaded together in the sample loading chamber and pumped down to the base pressure of 2.0×10^{-7} Torr. By loading two or three different substrates at the same time, direct comparison of HfO_x selectivity with identical reaction conditions was ensured. Before the deposition, the samples were pre-annealed in the UHV chamber at the corresponding deposition temperatures.

Selective CVD of HfOx was performed using Hafnium tert-butoxide (Hf(O^tBu)₄, 99.99%, Sigma Aldrich) at sample temperatures of 150-250 °C. Hf(O^tBu)₄ was contained in a glass tube that was vacuumsealed to a stainless steel flange and dosing line. The container was kept at 80 °C to increase the vapor pressure of Hf(O^tBu)₄. The exposure of Hf $(O^{t}Bu)_{4}$ per pulse was ~ 6,000 Langmuir calculated using a pressure spike detected by a convectron gauge in the reaction chamber. (1 Langmuir (L) = 1×10^{-6} Torr $\times 1$ s exposure of a gas). This dose was estimated to be 6.67 \times 10¹⁷ based on the pressure rise (6 mTorr), volume of the chamber (4.87 \times 10^{-3} $m^3)$ and wall temperature (150 °C); this was in great excess to the number of precursor molecules, necessary to cover the 0.2 cm² sample surface (~2.16 \times 10¹³) to a thickness of one monolayer. The number of precursor molecules to cover the sample surface was calculated assuming that the Hf(O^tBu)₄ molecules are spherical and considered to be as closely adjacent to each other. The volume of a single $Hf(O^tBu)_4$ molecule (V₁) is

$$V_1 = \frac{V}{N} = \frac{VM}{mN_A} = \frac{M}{\rho N_A} = \frac{4}{3}\pi r^3$$

where V is the total volume of Hf(O^tBu)₄, N = the total number of molecules, N_A is Avogadro number, M is molar mass of Hf(O^tBu)₄, m is a total mass of Hf(O^tBu)₄, ρ is the density of Hf(O^tBu)₄ and r is the radius of a single Hf(O^tBu)₄ molecule. The amount of Hf(O^tBu)₄ molecules per pulse (6000 L) was calculated using an ideal gas law equation.

$$n = \frac{PV}{RT}$$

where P is the Hf(O^tBu)₄ pressure in the chamber, V is the reaction chamber volume, T is the chamber temperature and R is a gas constant. Each pulse of Hf(O^tBu)₄ was separated by a N₂ purge for 15 s. The effect of the purge time on selectivity was determined by varying the purge time between 5 and 60 s at 250 °C. The N₂ purge gas continuously flowed into the reaction chamber at 130 mTorr during the deposition.

3. Results and discussion

 HfO_x single precursor CVD using $Hf(O^tBu)_4$ was performed on HF cleaned Si at three different temperatures, 250 °C, 200 °C and 150 °C. Removal of the native SiO_x on Si using aqueous HF is known to leave the surface Si-H terminated [17]. The HfO_x thickness was calculated using the inelastic mean free path (IMFP) and attenuation length of an electron from the Si substrate as shown below.

$$\lambda = \frac{143}{E^2} + 0.054\sqrt{E}$$

 $I = I_0 \exp(-t/\lambda \sin\theta)$

E is a kinetic energy of electron, I is the intensity of the substrate signal, I_0 is the intensity of the unattenuated substrate signal, t is the thickness of the film on top of the substrate (layer depth), λ is the IMFP of the electrons coming from the substrate and θ is the angle of emitted electron from the surface. The error analysis of the thickness calculation using XPS was performed based on the assumptions that I and I₀ had an absolute error of \pm 1% since all elements in this study had sensitivity factors greater than 0.8. A constant value of $\lambda = 2$ nm at E = 100 eV was employed for Si using the equation above. For the sub-nm thick films, the substrate Si signals showed a high signal to noise ratio (> 30)which led to an uncertainty of two decimal places of nm. For the thicker films of 3-5 nm, the thickness calculation using XPS can be underestimated up to 66% due to the assumption that the electron attenuation length is independent of the material on top of the substrate; this estimate of uncertainty for the thicker films was obtained by a calibration using ellipsometry. For the films thicker than 7 nm, the thicknesses were obtained using ellipsometry with a mean square error (MSE) of 0.6-0.7 nm.

Fig. 2(a) shows the XPS chemical composition of Si after sequential $Hf(O^{t}Bu)_{4}$ doses at 250 °C, 200 °C and 150 °C. The as-loaded HF cleaned Si had 74% Si (depicted in yellow) and all the Si was in an oxidation state of 0 (depicted in grey). There was a total of 26% adventitious hydrocarbon and oxygen on the surface. After 10 pulses of $Hf(O^{t}Bu)_{4}$ at 250 °C, 19% Hf and 45% O were deposited, and the Si substrate peak was attenuated to 21%. After a total of 15 pulses at 250 °C, Hf and O increased to 26% and 59% and the Si substrate was attenuated to 4% which is consistent with continuous growth of HfO_x . There was 5% C on the surface consistent with the presence of butoxide ligands.

At 200 °C, a HfO_x film also continuously grew as the Hf(O^tBu)₄ doses increased. After a total of 150 pulses, the Si substrate was completely buried and HfO_x was deposited with 13% C on the surface. Lastly, at 150 °C only 4% Hf, 17% O and 23% C was deposited on Si after 125 pulses dose which indicates poor nucleation at 150 °C on Si. Note that the raw XPS data are shown in the Fig. S2.



Fig. 3. Selective HfO_x deposition on Si in preference to SiCOH at 200 °C. (a) XPS elemental compositions showed that HfO_x was selectively deposited on Si at 200 °C. (b) HfO_x thicknesses on Si and SiCOH were plotted as a function of $Hf(O^tBu)_4$ doses at 200 °C. \sim 0.7 nm HfO_x was deposited on Si before nucleation occurred on SiCOH. (c) Raw XPS data of Si 2p, O 1 s and Hf 4d show that HfO_x was deposited without forming significant SiO_x at the interface. Note peak shift for O 1 s due to change in bonding from C to Hf. The XPS raw data are shown in Fig. S3. The exposure time for the $Hf(O^tBu)_4$ pulses was 50 ms, and the N₂ purge time was 15 s.

Fig. 2(b) shows the HfO_x thickness on Si as a function of Hf(O^tBu)₄ doses at 150 °C, 200 °C and 250 °C. At 250 °C and 200 °C, HfO_x continuously grew at rates of 1.5 \pm 0.3 Å/pulse and 0.5 \pm 0.1 Å/pulse, respectively. At 150 °C the growth per pulse was negligible since it is beyond the XPS sensitivity limit which is consistent with poor nucleation of Hf(O^tBu)₄ on H-terminated Si at 150 °C.

For investigation of selectivity, the lowest temperature for reasonable pulses CVD growth was chosen since the alkoxide ligands can decompose and promotes a higher density -OH on the surface at higher temperatures which normally diminishes selectivity [13,14]. At 200 °C, the selective pulsed HfOx CVD was observed on Si in preference to SiCOH as shown in Fig. 3. SiCOH is a highly porous silicon oxide doped with carbon with Si-CH₃ termination on the surface [18]. SiCOH is a common low-k material in nearly all logic and memory devices due to its electrical, thermal and chemical compatibility with CMOS fabrication processes [18-20]. Fig. 3(a) shows the chemical compositions of Si and SiCOH after sequential doses of Hf(O^tBu)₄ at 200 °C. After 20 pulses of Hf(O^tBu)₄ on HF cleaned Si, 12% Hf was deposited and O increased from 11% to 31%. The Si substrate was attenuated from 77% to 42%. After another 40 pulses on Si, only 8% of Si was present which is consistent with uniform and rapid HfOx deposition. In contrast, on SiCOH, 20 pulses of Hf(O^tBu)₄ only deposited a trace amount of Hf on the surface. An additional 40 pulses of Hf(O^tBu)₄ on SiCOH deposited 12% Hf and O increased from 38% to 46% while Si was attenuated from 31% to 17%. This indicates that HfO_x deposition at 200 °C showed a nucleation delay on SiCOH which consistent with inherent selectivity.

Fig. 3(b) shows the HfO_x thicknesses on Si and SiCOH calculated using the substrate attenuation from XPS. For the thickness calculation, it was assumed that the HfO_x film on SiCOH was uniform across the surface. The HfO_x thickness after 20 pulses of Hf(O^tBu)₄ on Si and SiCOH was 0.70 \pm 0.02 nm and 0.10 \pm 0.01 nm, respectively. Another 40 pulses deposited 2.4 \pm 0.3 nm of HfO_x on Si and 0.70 \pm 0.06 nm of HfO_x on SiCOH. The inherent selectivity was

retained up to ~ 0.7 nm growth on Si before the HfO_{x} film started to grow on SiCOH.

Fig. 3(c) shows the raw XPS spectra of the Si 2p, O 1 s and Hf 4d orbitals after HfO_x deposition at 200 °C. The Si 2p peak was at an oxidation state of 0 (99.7 eV) after the HF clean. The Si peak intensity decreased as HfO_x was deposited and the Si oxidation state mostly remained at the initial binding energy consistent with Si (0) with a trace amount of an oxidized Si component at 102.6 eV. The absence a large oxidized Si component indicates that the HfO_x CVD at 200 °C occurs without oxidizing more than a monolayer of the Si surface. The O peak of HF cleaned Si was at 532.4 eV which corresponds to the H-C-O bonding from the adventitious hydrocarbon, and the O peak shifted to 531.6 eV consistent with Hf-O bonds. The Hf 4d (214.2 eV and 225.2 eV) peaks became larger in intensity as the number of pulses increased showing the continuous growth of HfO_x.

The surface morphology of the deposited HfO_x film on Si and SiCOH was evaluated using AFM depicted in Fig. 4. Fig. 4(a-b) shows the surface morphologies of HF cleaned Si before and after the HfO_x deposition at 200 °C. The HF cleaned Si surface was flat with a root mean square (RMS) roughness of 0.1 nm. After a total of 60 $Hf(O^tBu)_4$ pulses at 200 °C, the HfO_x film was uniform with an RMS roughness of 2.1 Å. An AFM image of degreased SiCOH had < 2 nm tall chain-like features on the surface which might be due to the porous structure of the film and cross-linking of O-Si-C_xH_y surface termination groups (Fig. 4(c)) [21,22]. Fig. 4(d) shows the SiCOH surface after 60 pulses of $Hf(O^tBu)_4$ at 200 °C. The surface was smooth with a chain-like feature with an RMS roughness of 4.2 Å.

The inherent selectivity of HfO_x on Si was less than 1 nm before growth took place on SiCOH at 200 °C. The selectivity loss could be due to: (1) defect sites (reactive –OH sites) on SiCOH and/or (2) lack of thermal energy or time for $Hf(O^tBu)_4$ to desorb from SiCOH which can initiate nucleation. To test the first hypothesis that the defect sites initiated nucleation of HfO_x , TMDS and DMADMS were employed to



Fig. 4. Surface morphologies of HF cleaned Si and degreased SiCOH before and after HfO_x deposition. (a) AFM image of HF cleaned Si. (b) The surface morphology of HF-Si after the HfO_x deposition at 200 °C. (c) AFM image of degreased SiCOH. (d) AFM image of degreased SiCOH after the HfO_x deposition at 200 °C.

passivate the active –OH sites on SiCOH. The possible chemical reactions are:

and

 $(Si-OH)_2^* + [(CH_3)_2N]_2Si(CH_3)_2(g) \rightarrow (Si-O)_2-Si(CH_3)_2^* + 2(CH_3)_2NH$ (g) for DMADMS

where the asterisk indicates surface species.

 $S = T_G/T_{NG}$ was used as a metric of the selectivity, where T_G is the HfO_x thickness on the growth area and T_{NG} is the HfO_x thickness on the non-growth area. The growth area was Si, and the non-growth areas were SiCOH and passivated SiO₂. The HfO_x thicknesses were calculated using the XPS attenuation method and ellipsometry. As a control, HfO_x deposition was also performed on OH-terminated SiO₂ (HF cleaned SiO₂) at 200 °C. (See Fig. S4) A control sample of OH-terminated SiO₂ showed the same growth rate of HfO_x as on Si which had a selectivity metric of S = 1.1 \pm 0.1.

Fig. 5(a) shows the selective HfO_x deposition on Si in preference to



Fig. 5. XPS elemental compositions and selectivity metric (S) of passivated SiO₂ as a function of HfO_x thickness on Si. (a) Chemical compositions of HF cleaned Si, TMDS passivated SiO₂ and DMADMS passivated SiO₂ after selective HfO_x deposition at 200 °C. (b) Selectivity metric (S) were compared between the different samples. TMDS was the most effective passivant on OH-terminated SiO₂. The HfO_x on Si was 2.9 \pm 0.6 nm before less than a monolayer deposition occurred on TMDS-SiO₂. The DMADMS and TMDS molecular structures are shown on the right. The HfO_x thickness on Si after a total of 150 pulses was measured using ellipsometry. The XPS chemical composition histograms and XPS raw data are shown in Figs. S5 and S6. The exposure time for the Hf(O¹Bu)₄ pulses was 50 ms, and the N₂ purge time was 15 s.

TMDS passivated SiO₂ (TMDS-SiO₂) and DMADMS passivated SiO₂ (DMADMS-SiO₂) using XPS at 200 °C. After 60 pulses of Hf(O^tBu)₄ at 200 °C, 2.9 \pm 0.6 nm HfO_x was deposited on Si (T_G) and the selectivities were S = 2.2 \pm 0.7 for DMADMS-SiO₂, and S = 14.5 \pm 3.3 for TMDS-SiO₂. This significant improvement in selectivity compared to OH-terminated SiO₂ indicates that TMDS is highly effective for passivating –OH groups on the surface. For greater oxide thickness on Si (T_G = 10.7 \pm 0.7 nm), the selectivity for TMDS-SiO₂ decreased while the selectivity for DMADMS-SiO₂ increased from S = 2.2 \pm 0.7 at T_G = 2.9 \pm 0.6 nm to 4.1 \pm 1.5 at T_G = 10.7 \pm 0.7 nm.

In Fig. 5(b), the selectivity of different combinations of passivants and substrates were compared as a function of HfO_x thickness on Si. (D + T) denotes a sequential passivation using DMADMS followed by TMDS and (T + D) denotes a sequential passivation using TMDS followed by DMADMS. (D + T) SiO₂ showed similar selectivity to TMDS-SiO₂ while (T + D) SiO₂ exhibited a similar selectivity as DMADMS-SiO₂ consistent with the final passivant dominating the chemistry due to reversible bonding during the passivation process at 70 °C.

To study the hypothesis that reversible adsorption of the Hf precursor on SiCOH initiates the nucleation, selective HfO_x deposition at 250 °C was performed with different purge times between the Hf $(O^tBu)_4$ pulses. A higher surface temperature was employed to increase the probability that the precursor would desorb from the SiCOH. The purge time between the doses was varied from 5 to 60 sec. Fig. 6(a) shows the timing scheme of the Hf(O^tBu)_4 dosing process with example purge times of 5 s and 60 s. N₂ purge gas was continuously flowed at 130 mTorr.

The HfO_x thicknesses on SiCOH were plotted with respect to the HfO_x thickness on Si in Fig. 6(b). At 250 °C, with 5 s and 15 s purge times, there was ~1 nm HfO_x deposition on Si before a monolayer of HfO_x (~0.25 nm) was deposited on SiCOH which was similar to the selectivity at 200 °C. The selectivity was greatly improved by increasing the purge time to 30 s as shown by the selectivity loss on SiCOH being delayed until 2.3 \pm 0.4 nm of HfO_x deposited on Si. 60 s purge time further increased the selectivity, giving S = 13.6 \pm 0.5 at 3.4 \pm 1.2 nm of HfO_x on Si. This corresponds to a monolayer of HfO_x deposition on SiCOH. The data is consistent with reversible molecular adsorption of the Hf precursor on the SiCOH surface.

The surface morphologies of Si and SiCOH were investigated using AFM after the selective HfO_x deposition at 250 °C with 60 s purge time. Fig. 7(a) shows the Si surface after deposition of a 5.2 nm thick HfO_x film. The HfO_x film was uniform with an RMS roughness of 3.8 Å but

there were a few \sim 3 nm tall particles. Fig. 7(b) shows the SiCOH surface after ~ 0.6 nm of HfO_x was deposited. HfO_x on SiCOH was also uniform, but there were also ~ 6 nm tall particles; note these particles were not observed at 200 °C (See Fig. 4). Even though the HfO_x growth may not be self-limiting, the growth rate was low enough to deposit a smooth film both at 200 °C and 250 °C. The smooth films would be consistent with one monolayer or less being deposited during each precursor pulse and the films being able to smoothen during the purge similar to growth interrupts in molecular beam epitaxy. At 250 °C, the decomposition rate increases compared to 200 °C, and the particles might be formed from the multi-layer decomposition. Alternatively, the particle formation may be also due to gas phase reaction in the proximity of the surface where the temperature can be high enough for the precursors to be decomposed. For both particle formation mechanisms, the decomposition might be suppressed by using a Hf precursor with better thermal stability such as Hafnium isopropoxide (Hf(OⁱPr)₄) [24]. It is noted that the small particles could be nanocrystalytes, but XRD did not shown crystallinity; however, XRD is not sensitive to low densities of 3-6 nm particles. If nanocrystallinity is present, it can be removed by forming oxide alloys with La_2O_3 or TiO_2 [25,26].

Since TMDS was most effective at passivating –OH groups on SiO₂ and 60 s purge time could delay the nucleation on SiCOH, HfO_x deposition with 60 s purge time was performed on TMDS passivated SiO₂ and TMDS passivated SiCOH as shown in Fig. 8. A total of 20 pulses of Hf(O^tBu)₄ deposited 7.5 \pm 0.6 nm thick HfO_x on Si (Fig. 8(a) as measured by ellipsometry). In contrast, there were only 7% Hf and 3% Hf detected on TMDS-SiO₂ and TMDS-SiCOH, corresponding to 0.27 \pm 0.01 nm and 0.12 \pm 0.01 nm thick HfO_x respectively as calculated by the attenuation of the substrates in XPS. The selectivity metrics were S = 28 \pm 2 for TMDS-SiO₂ and S = 62 \pm 5 for TMDS-SiCOH both at 7.5 \pm 0.6 nm HfO_x on Si.

The proposed mechanism of the selective HfO_x deposition is shown in Fig. 9. Fig. 9(a) shows a growth mechanism of HfO_x on Si using Hf $(O^tBu)_4$. $Hf(O^tBu)_4$ first molecularly adsorbs on the H-terminated Si surface and decomposes. The decomposition temperature of $Hf(O^tBu)_4$ is ~ 200 °C [15]. Once the precursor decomposes, the butoxide ligands leave as isobutylene $(C_2H_2(CH_3)_2)$ and $Hf(O^tBu)_4$ transforms to Hf $(O^tBu)_xOH_{4-x}$ (ads). Subsequently, OH groups can react with H-Si bonds to form Si-O-Hf $(O^tBu)_x$. This decomposition of $Hf(O^tBu)_4$ is necessary to deposit HfO_x on Si consistent with the poor nucleation of HfO_x on H-Si at 150 °C as shown in Fig. 2. As the $Hf(O^tBu)_4$ decomposes, the HfO_x film can continuously grow via a reaction of surface-bound $Hf(OH)_x$ and $Hf(O^tBu)_4$.



Fig. 6. Selectivity enhancement of HfO_x on Si versus SiCOH by increasing the purge time between the Hf(O^tBu)₄ pulses at 250 °C. (a) A schematic timing diagram of Hf(O^tBu)₄ doses with a continuous N₂ purge. (b) HfO_x thickness on SiCOH with the respect to HfO_x thickness on Si with different purge times. The selectivity was improved by increasing the purge time between the Hf(O^tBu)₄ pulses. 60 s purge time showed 2.3 \pm 0.4 nm HfO_x deposition on Si before any nucleation occurred on SiCOH. The HfO_x thicknesses were calculated using the substrate attenuation from XPS. The XPS chemical composition histograms and raw data are shown in Figs. S7 and S8. The exposure time for the Hf(O^tBu)₄ pulses was 50 ms.

Fig. 9(b) shows a model for the degreased SiCOH surface after Hf $(O^{t}Bu)_{4}$ dosing. Hf $(O^{t}Bu)_{4}$ first reversibly and molecularly adsorbs on the surface and decomposes at > 200 °C. It should be noted that the concentration of adsorbed species on the SiCOH surface may be less than H-Si surface due to different intermolecular forces between the adsorbate and functional groups on the surface. Since the surface is terminated with O-Si-CH₃ groups, the surface is chemically inert so the decomposed adsorbates, Hf $(O^{t}Bu)_{x}(OH)_{4-x}$ would have a low binding energy which may make decomposition less thermodynamically favorable. This is consistent with the top-most Si atoms on SiCOH being bonded to O (Si-O: 798 kJ/mol) and C (Si-C: 435 kJ/mol) which are harder to break compared to Si-H bonds on Si (298 kJ/mol) [23]. In addition, the Hf atom in Hf $(O^{t}Bu)_{4}$ is already bonded to four oxygens

with strong bond energies of 791 kJ/mol [23]. The energetic stability of both the SiCOH surface and the Hf metal atoms of the precursor are consistent with impeding HfO_x nucleation on the SiCOH surface and the CH₃ termination reducing the physisorption energy. Possible reaction pathway could be described as below;

Si-O-CH₃(s) + Hf(O^tBu)₄(g) \Rightarrow Si-O-CH₃(s) + Hf(O^tBu)₄(ads) \rightarrow Si-O-CH₃(s) + (O^tBu)_xHf(OH)_{4-x}(ads) + 4-xC₄H₈(g)

However, the surface passivation of SiCOH is not perfect so the adsorbed precursor may diffuse and react with the defect –OH sites. This is consistent with better selectivity after passivation by TMDS. Unfortunately, the nucleation sites on the low reactivity surface, SiCOH, are of such low density that XPS cannot be used to confirm the



Fig. 7. Surface morphology of the HfO_x films deposited at 250 °C on Si and SiCOH. (a) HfO_x on H-terminated Si showed a uniform film with an RMS roughness of 3.8 Å. (b) On degreased SiCOH, HfO_x was uniform with \sim 6 nm tall particles. The Hf(O^tBu)₄ pulses were 50 ms with 60 s N₂ purge between the pulses.



Fig. 8. Selectivity enhancement of HfO_x on Si versus TMDS passivated SiO₂ and TMDS passivated SiCo₁. (a) 20 pulses of Hf(O^tBu)₄ with 60 s purge on HF-Si at 250 °C deposited 7.5 \pm 0.6 nm thick HfO_x. (b) On TMDS-SiO₂, 0.27 \pm 0.01 nm thick HfO_x was deposited which gives a selectivity metric of S = 28 \pm 2. (c) On TMDS-SiCOH, 0.12 \pm 0.01 nm thick HfO_x was deposited which gives a selectivity metric of S = 62 \pm 5. The HfO_x thickness on Si after a total of 20 pulses was measured using ellipsometry. The raw XPS spectra are shown in Fig. S9. The exposure time for the Hf (O^tBu)₄ pulses was 50 ms, and the N₂ purge time was 60 s.

identity of the adsorbates which initiate reaction. It is likely that the selectivity is determined by the relative physisorption probabilities on SiCOH and passivated SiO_2 versus Si as well as the density of reactive defect sites such as –OH.

Fig. 9(c) depicts the $Hf(O^tBu)_4$ reaction on passivated SiO₂ using TMDS or DMADMS. Both TMDS and DMADMS react with OH-terminated SiO₂ and ideally form O-Si-CH₃ surface terminations. This is the same surface condition as SiCOH in terms of the topmost Si atoms on the surface bonded to O and CH₃. The subsequent reversible molecular adsorption of $Hf(O^tBu)_4$ followed by the decomposition is analogous to those on SiCOH in Fig. 9(b).

4. Conclusion

This work shows selective deposition of hafnium oxide (HfO_x) on the H-terminated Si and OH-terminated Si surfaces in preference to O-Si-CH_x surfaces using pulsed water-free CVD of $Hf(O^tBu)_4$. The selectivity benefited from the co-reactant free process since commonly used oxygen sources as H₂O or H₂O₂ can readily physisorb or chemisorb on any surface to initiate nucleation. It was demonstrated that pulsed CVD allows for the Hf(O^tBu)₄ precursor to reversibly molecularly adsorb on SiCOH. The reversible precursor adsorption allows further enhancement of selectivity by control of purge time in additional to passivation with small molecules. Using the optimized pulsed CVD process, up to 7.5 \pm 0.6 nm HfO_x was selectively deposited as opposed to the negligible nucleation on TMDS passivated SiCOH; this correspond to a selectivity of S = 62. This was \sim 5 times better combined selectivity (S_{comb} = 465 nm) compared to previously reported selectivity using water based HfO2 ALD [27,28] (S = 30, and $S_{comb} = 90 \text{ nm for } 3.0 \text{ nm HfO}_2 \text{ on Si vs } 0.1 \text{ nm on ODTS SiO}_2)$ in terms of metric which account for selectivity (S = thickness on the growth surface/thickness on nongrowth surface) and the thickness at the max selectivity (t_{max}) : $S_{comb} = S t_{max}$. Furthermore, the previous best selectivity for HfO2 required a 48 hr liquid passivation while the present method requires on 10 min vapor passivation. The pulsed CVD method

has the inherent advantage that selectivity is only needed for one molecule, the oxidants do not attack the passivation layer, and desorption from the nongrowth surface is promoted by high temperature. The pulsed CVD method to control the reversible adsorption of the precursor to improve selectivity could be integrated into the multi-patterning process for sub-10 nm MOSFETs with three-dimensional structures.

CRediT authorship contribution statement

Jong Youn Choi: Validation, Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. Christopher F. Ahles: Validation, Methodology, Formal analysis, Investigation, Data curation, Writing - review & editing. Yunil Cho: Validation, Investigation, Data curation. Ashay Anurag: Validation, Investigation, Data curation. Keith T. Wong: Conceptualization, Writing - review & editing. Srinivas D. Nemani: Conceptualization, Writing - review & editing. Ellie Yieh: Conceptualization, Writing review & editing. Andrew C. Kummel: Validation, Methodology, Resources, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding support from Applied Materials is gratefully acknowledged. The electrical measurements were facilitated by the San Diego Nanotechnology Infrastructure (SDNI) which is supported by the National Science Foundation (NSF) to Nano3 (Grant ECCS-1542148).



Fig. 9. Mechanism of selective HfO_x CVD on Si versus SiCOH and passivated SiO₂. (a) On H-terminated Si, $Hf(O^{t}Bu)_{4}$ adsorbs on the surface and decomposes into $Hf(O^{t}Bu)_{x}OH_{4-x}$. Then OH reacts with H-Si and HfO_{x} continuously grows. (b) CH₃ terminated SiCOH surface is less favorable in adsorption of $Hf(O^{t}Bu)_{4}$ than H-Si surface. The adsorption is reversible which makes decomposition less thermodynamically favorable. Defect OH sites might start nucleation. (c) TMDS and DMADMS reacts with OH-terminated SiO₂ and leaves a O-Si-CH₃ terminated surface which is analogous to the SiCOH surface. $Hf(O^{t}Bu)_{4}$ can be reversibly and molecularly adsorbed on the surface which gives the selectivity.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.145733.

References

- M. Geissler, Y. Xia, Patterning: principles and some new developments, Adv. Mater. 16 (2004) 1249–1269.
- [2] D. Shamiryan, V. Paraschiv, W. Boullart, M.R. Baklanov, Plasma etching: from micro- to nanoelectronics, High Energ. Chem. 43 (2009) 204–212.
- [3] A.J.M. Mackus, A.A. Bol, W.M.M. Kessels, The use of atomic layer deposition in advanced nanopatterning, Nanoscale 6 (2014) 10941–10960.
- [4] L. Li, X. Liu, S. Pal, S. Wang, C.K. Ober, E.P. Giannelis, Extreme ultraviolet resist materials for sub-7 nm patterning, Chem. Soc. Rev. 46 (2017) 4855–4866.
- [5] B. Wu, A. Kumar, Extreme ultraviolet lithography and three dimensional integrated circuit—A review, Appl. Phys. Rev. 1 (2014) 011104.
- [6] Y. Widjaja, C. B. Musgrave, Atomic layer deposition of hafnium oxide: A detailed reaction mechanism from first principles. J. Chem. Phys. 117 (2002) 1931-1934.
 [7] R.L. Puurunen, A. Delabie, S.V. Elshocht, M. Caymax, M.L. Green, B. Brijs,
- O. Richard, H. Bender, T. Conard, I. Hoflijk, W. Vandervorst, D. Hellin, D. Vanhaeren, C. Zhao, S.D. Gendt, M. Heyns, Hafnium oxide films by atomic layer deposition for high- gate dielectric applications: analysis of the density of nanometer-thin films, Appl. Phys. Lett. 86 (2005) 073116.
- [8] M.-J. Choi, H.-H. Park, D.S. Jeong, J.H. Kim, J.-S. Kim, S.K. Kim, Atomic layer deposition of HfO₂ thin films using H₂O₂ as oxidant, Appl. Surf. Sci. 301 (2014) 451–455.
- [9] Y. Senzaki, S. Park, H. Chatham, L. Bartholomew, W. Nieveen, Atomic layer deposition of hafnium oxide and hafnium silicate thin films using liquid precursors and ozone, J. Vac. Sci. Technol., A 22 (2004) 1175–1181.
- [10] E. Oudot, M. Gros-Jean, K. Courouble, F. Bertin, R. Duru, N. Rochat, Christophe Vallée, Hydrogen passivation of silicon/silicon oxide interface by atomic layer

deposited hafnium oxide and impact of silicon oxide underlayer, J. Vac. Sci. Technol., A 36 (2008) 01A116.

- [11] S.X. Lao, R.M. Martin, J.P. Chang, Plasma enhanced atomic layer deposition of HfO₂ and ZrO₂ high-k thin films, J. Vac. Sci. Technol., A 23 (2005) 488–496.
- [12] M.S. Kavrik, E. Thomson, E. Chagarov, K. Tang, S.T. Ueda, V. Hou, T. Aoki, M. Kim, B. Fruhberger, Y. Taur, P.C. McIntyre, A.C. Kummel, Ultralow defect density at sub-0.5 nm HfO₂/SiGe interfaces via selective oxygen, Scavenging. ACS Appl. Mater. Interfaces 10 (2018) 30794–30802.
- [13] V.R. Anderson, A.S. Cavanagh, A.I. Abdulagatov, Z.M. Gibbs, S.M. George, Waterless TiO₂ atomic layer deposition using titanium tetrachloride and titanium Tetraisopropoxide, J. Vac. Sci. Technol., A 32 (2014) 01A114.
- [14] S.E. Atanasov, B. Kalanyan, G.N. Parsons, Inherent substrate-dependent growth initiation and selective-area atomic layer deposition of TiO₂ using "water-free" metal-halide/metal alkoxide reactants, J. Vac. Sci. Technol., A 34 (2016) 01A148.
- [15] S. Sayan, S. Aravamudhan, B.W. Busch, W.H. Schulte, F. Cosandey, G.D. Wilk, T. Gustafsson, E. Garfunkel, Chemical vapor deposition of HfO₂ films on Si (100), J. Vac. Sci. Technol., A 20 (2002) 507–512.
- [16] T.S. Yang, K.-S. An, E.-J. Lee, W. Cho, H.S. Jang, S.K. Park, Y.K. Lee, T.-M. Chung, C.G. Kim, S. Kim, J.-H. Hwang, C. Lee, N.-S. Lee, Yunsoo Kim, Chemical vapor deposition of HfO₂ thin films using the novel single precursor hafnium 3-methyl-3pentoxide, Hf(mp)₄, Chem. Mater. 17 (2005) 6713–6718.
- [17] Y.J. Chabal, G.S. Higashi, K. Raghavachari, Infrared spectroscopy of Si(111) and Si (100) surfaces after HF treatment: hydrogen termination and surface morphology, J. Vac. Sci. Technol., A 7 (1989) 2104–2109.
- [18] B. Narayanan, R. Kumar, P.D. Foo, Properties of low-k SiCOH films prepared by plasma-enhanced chemical vapor deposition using trimethylsilane, Microelectron. J. 33 (2002) 971–974.
- [19] S.M. Gates, G. Dubois, E.T. Ryan, A. Grill, M. Liu, D. Gidley, Adjusting the skeleton and pore structure of porous SiCOH dielectrics, J. Electrochem. Soc. 156 (2009) G156–G162.
- [20] C. Ye, Z. Ning, T. Wang, X. Yu, Y. Wei, X. Qiana, Effect of doping on structure and dielectric property of SiCOH films prepared by decamethylcyclopentasiloxane, J. Electrochem. Soc. 154 (2007) G63–G68.
- [21] G. Li, G. Zheng, Z. Ding, L. Shi, J. Li, Z. Chen, L. Wang, A.A.O. Tay, W. Zhu, Highperformance ultra-low-k fluorine-doped nanoporous organosilica films for inter-

layer dielectric, J. Mater. Sci. 54 (2019) 2379-2391.

- [22] B.R. Kim, J.W. Kang, K.Y. Lee, J.M. Son, M.J. Ko, Physical properties of low-k films based on the co-condensation of methyltrimethoxysilane with a bridged silsesquioxane, J. Mater. Sci. 42 (2007) 4591–4602.
- [23] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substances in SI units. J. Phys. Chem. Ref. Data 11 (1982) 1807.
- [24] C. Wang, S. Yang, Y. Chen, Determination of the vapour pressure curves and vaporization enthalpies of hafnium alkoxides using thermogravimetric analysis, R. Soc. Open Sci. 6 (2019) 181193.
- [25] B. Lee, A. Hande, T.J. Park, K.J. Chung, J. Ahn, M. Rousseau, D. Hong, H. Li, X. Liu,

D. Shenai, J. Kim, ALD of LaHfOx nano-laminates for high-j gate dielectric applications, Microelectron. Eng. 88~(2011)~3385-3388.

- [26] D.H. Triyoso, R.I. Hegde, S. Zollner, M.E. Ramon, S. Kalpat, R. Gregory, X.-D. Wang, J. Jiang, M. Raymond, R. Rai, D. Werho, D. Roan, B.E. White, P.J. Tobin, Impact of titanium addition on film characteristics of HfO₂ gate dielectrics deposited by atomic layer deposition, J. Appl. Phys. 98 (2005) 054104.
- [27] R. Chen, H. Kim, P.C. McIntyre, D.W. Porter, S.F. Bent, Achieving area-selective atomic layer deposition on patterned substrates by selective surface modification, Appl. Phys. Lett. 86 (2015) 191910.
- [28] Q. Tao, G. Jursich, C. Takoudis, Selective atomic layer deposition of HfO₂ on copper patterned silicon substrates, Appl. Phys. Lett. 96 (2010) 192105.