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**Steven Consiglio, Kandabara Tapily, Robert D. Clark,
Toshio Hasegawa, Fumitaka Amano, Gert J. Leusink,
Jean Jordan-Sweet, Relja Vasić, Manasa Medikonda, and
Alain C. Diebold**

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Engineering crystallinity of atomic layer deposited gate stacks containing ultrathin HfO_2 and a Ti-based metal gate: Effects of postmetal gate anneal and integration schemes

Steven Consiglio,^{a)} Kandabara Tapily, Robert D. Clark, Toshio Hasegawa, Fumitaka Amano, and Gert J. Leusink

TEL Technology Center, America, LLC, 255 Fuller Rd., Albany, New York 12203

Jean Jordan-Sweet

IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

Relja Vasić, Manasa Medikonda, and Alain C. Diebold

SUNY College of Nanoscale Science and Engineering, 257 Fuller Rd., Albany, New York 12203

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In this study, the authors examined the effects of different annealing schemes on crystallinity in atomic layer deposition (ALD) grown Ti-containing metal gates and ultrathin ALD HfO_2 high-k dielectric layers, and corresponding electrical results in metal oxide semiconductor capacitor (MOSCAP) devices. The authors investigated the effect of a postmetal deposition anneal (PMA) on the underlying HfO_2 , which was deposited using either a standard ALD process or a process which utilized a cyclical deposition and annealing scheme (termed DADA). The effect of the starting substrate surface, either chemically grown SiO_2 or H-terminated Si, on HfO_2 crystallinity was also studied. For 40 cycle ALD HfO_2 ($\sim 32 \text{ \AA}$) with a TiN overlayer, a transition from an amorphous state to a cubic phase was observed with the application of a PMA treatment. Evidence of the orthorhombic phase of HfO_2 with some level of texturing was observed for 40 cycle DADA processed films annealed with a TiN cap. Concomitantly a cubic (111) texture was observed for TiN deposited on DADA processed HfO_2 and subjected to a PMA. Suppression of crystallinity for HfO_2 deposited on H-terminated Si and annealed with a TiN layer was observed which illustrates the need for an adequate nucleation layer for uniform grain growth and increased atomic ordering. The authors also investigated metal gate stacks with a bilayer of TiN overlying Ti which showed reflections from both cubic TiN and hexagonal $\text{TiN}_{0.3}$ in the as-deposited state and after annealing clear evidence of silicidation (TiSi_x) was observed. In MOSCAP structures with 40 cycle ALD HfO_2 and a TiN overlayer subjected to a PMA, although the cubic phase of HfO_2 was stabilized, there was no associated improvement in device scaling. This study highlights the importance of the initial crystalline state and nucleation of HfO_2 as well as the thermal stability of the capping metal layer material when engineering dielectric layer crystallinity by means of a postmetal cap anneal. For ultrathin HfO_2 integrated in advanced metal oxide semiconductor structures, the benefits of the stabilization of a higher-k phase through postmetal gate anneal may not be fully realized due to increased leakage along grain boundaries or decrease in effective k due to changes in the lower-k interfacial layer. © 2014 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4869162>]

I. INTRODUCTION

With the recent introduction of HfO_2 -based gate dielectrics in advanced metal oxide semiconductor field effect transistors (MOSFETs), the inherent limitations to scaling the equivalent oxide thickness (EOT) of the SiO_2 -based gate dielectric have been successfully overcome.¹ In order to continue this trend in decreasing EOT, further scaling of the HfO_2 -based gate dielectric is desirable. This can be achieved by decreasing the thickness of the gate dielectric, which should lead to an increase in leakage current density, or by increasing its effective dielectric constant (k-value). In this regard, the k value of HfO_2 thin films may be altered by engineering its crystalline phase in accordance with theoretical studies which predict that the cubic and tetragonal

crystalline phases of HfO_2 , which can be stabilized at elevated temperatures, possess a higher k value, 29 and 70, respectively, than that of the monoclinic phase ($k=16$), which is thermodynamically preferred at ambient conditions.² The amorphous phase of HfO_2 , which is typically observed for thin films deposited using low-temperature deposition techniques, is also predicted to possess a k value comparable to that of the monoclinic phase.³ In addition to the cubic, tetragonal, and monoclinic phases (space groups $\text{Fm}\bar{3}\text{m}$, $\text{P4}_2/\text{nmc}$, and $\text{P2}_1/\text{c}$, respectively), which are all considered to be low pressure phases, the orthorhombic phase also exists and it can be stabilized at elevated pressures.⁴ There are two well-known orthorhombic phases, namely, orthorhombic-I and orthorhombic-II (space groups Pbca and Pnma , respectively), and it has been shown using first-principles calculations that HfO_2 undergoes a structural transformation from monoclinic to orthorhombic-I followed

^{a)}Electronic mail: steve.consiglio@us.tel.com

by orthorhombic-II with an increase in pressure.⁵ In contrast to the k -values of the low temperature phases, the predicted k -values for orthorhombic phases of HfO_2 are not as well understood. First-principles calculations of the orthorhombic phases of the structurally similar ZrO_2 predict comparable or slightly lower orientationally averaged k -values to that of the monoclinic phase.⁶ The orthorhombic phase of HfO_2 has also recently been shown experimentally to exhibit a similar k value to that of the monoclinic one ($k \sim 16$ – 20).⁷ Recently, phase stabilization of a noncentrosymmetric and ferroelectric orthorhombic phase (space group $\text{Pbc}2_1$) in HfO_2 -based films has also been claimed, in contrast to the previously mentioned crystalline phases, which are all centrosymmetric, offering the promise of novel applications of phase stabilized HfO_2 .^{8–15}

Various doping or alloying schemes, which utilize the addition of other metal oxides into thin HfO_2 films, such as ZrO_2 , Al_2O_3 , SiO_2 , rare earth oxides, and alkaline earth oxides, with the goal of stabilization of the metastable higher- k phases, have been thoroughly investigated.^{16–23} Another approach that may offer a viable method to engineer the phase of pure HfO_2 is by depositing a metal gate on top of a thin HfO_2 film and then subjecting the film stack to a postmetal deposition anneal (PMA). Of the candidate metal gate materials, Ti-based metal gates, and in particular TiN, have been thoroughly evaluated and have found utilization in advanced MOSFET structures.²⁴ In this regard, recent studies have demonstrated stabilization of metastable phases of pure HfO_2 through the use of a Ti-containing overlayer followed by a PMA.^{25–30} Triyoso *et al.* utilized a 7 nm TiN capping layer followed by a 1000 °C N_2 anneal to modify the microstructure of atomic layer deposited (ALD) HfO_2 from fully monoclinic, in the case of uncapped HfO_2 , to a mixture of monoclinic and non-monoclinic phases, for capped HfO_2 , and attributed the metastable phase formation to the constraint of volume expansion due to annealing as a result of mechanical constraint from the TiN overlayer.²⁵ Toriumi and co-workers have similarly reported the stabilization of the higher- k cubic phase for HfO_2 grown by rf-sputtering and subjected to a postgate electrode anneal.^{26,27} One drawback that was pointed out was that the mechanism of gate-electrode induced compressive stress and concomitant oxygen vacancy formation, which helps stabilize the cubic phase, leads to a deleterious oxidation of the underlying Si when starting from a direct-contact (HF-last) Si substrate, thus limiting the ultimate k -value scaling using this approach.²⁷ In order to overcome this obstacle, Morita *et al.* have investigated the inclusion of a sputter deposited Ti metal layer, with a high affinity for oxygen, as an oxygen-controlling layer in the gate electrode and subjected it to a postmetal anneal.^{28–30} In these studies, it was shown that with proper control of the Ti layer thickness and PMA conditions, deleterious oxidation of the Si substrate can be avoided while also stabilizing the higher- k cubic phase of HfO_2 .

With the introduction of nonplanar device structures, such as the Tri-Gate,³¹ an ALD approach for both dielectric and metal gate deposition would be highly desirable given

the accurate thickness control, uniformity, and conformality that can be afforded from such a process.^{32,33} Accordingly, in this study, we investigated an all ALD approach for HfO_2 and metal gate deposition and pursued a straightforward means to engineer the phase of ultrathin HfO_2 in the stack by a post metal cap anneal with a Ti-based metal gate, including TiN and TiN/Ti bilayers. The all ALD approach combined with controlled phase engineering may offer a viable method to deposit conformal gate stacks on three-dimensional device structures with scaled electrical thickness.

II. EXPERIMENT

The starting substrate surface used in this study consisted of a thin (~ 8 – 10 Å) chemically grown oxide (SiO_2) layer on 300 mm Si wafers. A subset of samples were subjected to a gaseous etching processing which removed the thin SiO_2 layer by a treatment in an HF/NH_3 ambient followed by sublimation of by-products using an elevated temperature treatment resulting in an H-terminated Si surface (Si-H) prior to HfO_2 deposition.^{34–36} This process, which is referred to as chemical oxide removal (COR), was performed on a TEL CertasTM wafer processing system. ALD of HfO_2 was performed in a shower-head type reactor on a TEL TriasTM platform at a wafer temperature of 250 °C using tetrakis(ethylmethylamino) hafnium with H_2O as a coreactant. A total number of HfO_2 ALD cycles of 40 were used in this study, which resulted in an as-deposited film thickness of ~ 32 Å. A subset of the ALD grown HfO_2 was processed using a cyclical deposition and annealing scheme, which has been described in detailed previously and is denoted as DADA.^{37,38} The DADA process incorporates an *in-situ* anneal (N_2 ambient at 800 °C) performed in a clustered thermal anneal chamber after each 20 cycles of ALD film growth. For the 40 cycle ALD HfO_2 films used in this study, the DADA process consisted of two deposition and anneal iterations, respectively. The Ti-based metal layers were deposited using ALD in a shower-head type reactor using TiCl_4 . TiN layers of ~ 5 nm were deposited using 180 ALD cycles with NH_3 as a coreactant at 400 °C wafer temperature. TiN/Ti layers were deposited using 750 cycles or 1250 cycles to target ~ 5 nm and ~ 7 nm of Ti, respectively, with the use of a plasma-based reducing agent, followed by 2 nm ALD TiN deposited *in-situ*. For the TiN/Ti bilayer deposition a wafer temperature of 450 °C was used. The postmetal cap anneal (PMA) consisted of a 60 s anneal in a rapid thermal anneal chamber at 800 °C in N_2 using a ramp rate of 50 °C/s.

As-deposited dielectric stack film thickness (ALD HfO_2 and SiO_2 interface) was assessed using an in-line KLA Tencor spectroscopic ellipsometer (SE) and as-deposited HfO_2 thickness (without SiO_2 interface) was determined by x-ray reflectivity (XRR). The subtraction of SE and XRR measured thickness was used to estimate the interfacial SiO_2 thickness.³⁹ XRR was also performed after postmetal anneal to estimate the resultant thickness of the HfO_2 layer, Ti-based metal gate, and oxidized thickness of the top surface of the metal layer (TiO_2).

Grazing incidence in-plane x-ray diffraction (GIIXRD) measurements, which enable the in-plane ordering of

ultrathin films to be probed, were performed on beamline X20A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using x-rays with wavelength of 1.5482 Å. In this configuration, the x-ray beam angle of incidence was set to 0.5°, and the detector was scanned in the plane of the film. Collected spectra were compared to standard reference patterns for monoclinic, tetragonal, and orthorhombic HfO₂ from the Standard Joint Committee for Powder Diffraction Spectra Powder Diffraction Files (PDF).⁴⁰ The d-spacings for cubic HfO₂ were calculated using the lattice constant $a = 5.08$ Å.⁵ The orthorhombic Pbc2₁ phase was also considered based on d-spacing calculations using the lattice constants of $a = 5.30$ Å, $a = 5.11$ Å, and $a = 5.10$ Å.⁴¹ In order to investigate details of preferred orientation and film texture, x-ray pole figure measurements were also performed on beamline X20A at the NSLS using x-rays with wavelength of 1.5482 Å. The pole figure represents an angular distribution of a chosen crystal direction with respect to the specimen coordinate system. For the pole figure measurements, a linear detector was used to collect scans over ~90° ranges of both azimuthal (ϕ) and tilt angles (ψ) at a given 2θ value, allowing for orientation mapping for a specific lattice spacing. The tilt angle ψ measures the amount of tilting of the sample normal with respect to the scattering vector. Use of the linear detector allowed for the simultaneous measurement of 640 pole figures in a 2θ range of 20°–60°. The acquisition was performed using a step size of 1° for both the rotation of the sample about its normal and the tilting of the sample. The data were used to construct a continuous array of pole figures over a range of d-spacings for each sample. The pole figures were converted into diffracted intensity contour maps (two-dimensional representations) of ψ versus d-spacing by integrating each of the 640 pole figures (each d-spacing value) over the azimuthal angle (ϕ).^{21,42,43}

Cross-sectional transmission electron microscopy (TEM) measurements were obtained using an FEI Tecnai G2 F20 system. Focused ion beam precision sample preparation was performed using an FEI Nova600. Wedge polishing and ion milling was performed using a Gatan 691 PIPS.

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo VG Scientific Theta Probe system. The binding energy of the Hf4f and Ti2p photoelectrons were examined to assess the change in bonding states of Hf and Ti in the film stack from the different postmetal gate anneal and processing schemes.

For metal oxide semiconductor capacitor (MOSCAP) testing, we utilized the same experimental splits as described earlier for the film stacks deposited for physical characterization using 5 nm TiN metal gate, either with or without PMA step. Following the ALD TiN deposition and postprocessing, a 50 nm layer of physical vapor deposited TiN was deposited. The complete MOSCAP process flow is outlined in Fig. 1. The MOS structures were characterized by capacitance–voltage (C-V) and current–voltage (I-V) measurements using an Agilent Technologies 4284A precision LCR meter and 3485A multimeter, respectively. EOT and flatband voltage (V_{fb}) values were extracted from C-V data by the Hauser model.⁴⁴

Fig. 1. (Color online) Outline of MOSCAP process flow featuring ALD HfO₂ with ALD TiN and postmetal anneal experimental splits.

III. RESULTS AND DISCUSSION

A. Stacks with TiN metal gate—physical analysis

The as-deposited dielectric stack (HfO₂ + SiO₂), HfO₂ film, and interfacial SiO₂ thickness values for 40 cycle films deposited on chemical oxide or Si-H are displayed in Table I. It is shown here that the Si-H starting surface results in a thinner SiO₂ interfacial layer (by ~3 Å) than the case of the chemical oxide starting surface, based on the SE-XRR calculation. The HfO₂ film deposited on Si-H is also slightly thinner than the film deposited on chemical oxide, which is attributed to the decreased nucleation density of the film deposited on the less reactive Si-H.⁴⁵ The DADA processed film deposited on chemical oxide possessed a lower HfO₂ thickness than the unannealed film, which is attributed to film densification that occurs during the high temperature interleaved treatment. The DADA processed film also possessed slightly lower interfacial SiO₂ thickness, which is consistent with previous reports of SiO_x uptake into the HfO₂ film and low levels of Si incorporation as a result of the DADA process.³⁷

Figure 2 shows the GIIXRD spectra for stacks containing HfO₂ deposited using 40 ALD cycles with a ~5 nm TiN metal capping layer. The spectra for the as deposited stack with no postmetal anneal (PMA) contains no discernible peaks due to reflections that can be attributed to HfO₂ crystallinity but only a broad shoulder in the region 28–33° (two theta), which is indicative of a primarily amorphous HfO₂ or a nanocrystalline matrix. Multiple reflections from the cubic phase of TiN (Ref. 46) are evident in the as deposited stack spectra, which indicates that the TiN is polycrystalline in its as deposited form. With the addition of the PMA step following the metal deposition, clear signatures of the metastable cubic HfO₂ phase are evident as shown in the upper overlaid spectra in Fig. 2. Although the cubic and tetragonal phases are often difficult to differentiate in XRD, in this instance, the cubic phase is in better agreement in peak positioning than the tetragonal phase and certain peaks due to the asymmetry in the tetragonal phase, such as (202), are not present. In this case, the use of the in-plane measurement configuration allows for the unambiguous determination of the presence of the cubic phase whereas for conventional

TABLE I. Thickness measurements for 40 cycle HfO_2 with TiN capping with and without postmetal anneal (PMA) including spectroscopic ellipsometry (SE), XRR, and interfacial SiO_2 (SE-XRR) estimation for pre metal deposition stacks, as well as XRR derived thickness for completed postprocessed film stacks. Chemical oxide starting surface is denoted as Chem ox and H-terminated Si is denoted as Si-H. ALD std denotes standard ALD process and the ALD process with interspersed anneal is denoted DADA.

Starting surface	HfO_2 deposition	PMA	Premetal deposition thickness (Å)					Postprocessing thickness (Å) XRR [center]		
			SE [mean]	SE [1σ]	SE [center]	XRR [center]	SE-XRR [center]	TiO_2	TiN	HO_2
Chem ox	ALD std	No	41.9	0.5	41.9	31.8	10.1	11.4	45.8	29.6
Si-H	ALD std	Yes	36.7	0.3	36.1	29.2	6.9	12.0	43.1	25.5
Chem ox	ALD std	Yes	42.0	0.4	41.8	31.8	10.0	11.8	43.0	26.6
Chem ox	DADA	Yes	36.7	0.4	37.0	28.0	9.0	10.6	44.5	26.0

XRD, difficulty in differentiating cubic, tetragonal, and orthorhombic phases is problematic due to peak overlaps for the strong intensity peak near $30\text{--}31^\circ$ (two theta).^{40,47} The PMA treated film deposited on the hydroxyl terminated chemical oxide starting surface shows multiple strong reflections from the cubic HfO_2 phase indicating that the PMA step with TiN capping layer can act as an efficient metastable phase stabilization treatment consistent with previous reports on metal nitride capping layer anneal stabilization.^{25–27} The importance of HfO_2 starting from an initial amorphous state prior to a cap anneal in order to obtain a cubic phase was also similarly reported by Toriumi and co-workers.²⁷ The 40 cycle HfO_2 layer deposited with the same process but on an H-terminated substrate (Si-H) shows a clear difference in the level of crystallinity as compared to the case of the chemical oxide starting surface. For the case of Si-H, the cubic phase is still observed but the intensity of the peaks associated with reflections for cubic HfO_2 is reduced. This reduction in peak intensity indicates that there is some suppression of crystallinity for films deposited on a direct contact interface most likely due the

effects of poor nucleation on this surface (lack of sufficient density of reactive surface sites) and subsequent poor grain nucleation and coalescence.⁴⁵ In contrast, the chemical oxide layer, with its high density of reactive surface hydroxyl groups, acts as a nucleation layer for the uniform growth of HfO_2 . As shown in the TEM micrographs in Fig. 3, both the HfO_2 film and film–substrate ($\text{HfO}_2\text{--SiO}_2$) interface appear more uniform and smooth with the addition of the chemical oxide starting surface. The TEM micrograph of the PMA treated stack on chemical oxide shows a well ordered HfO_2 dielectric layer whereas the image of the stack on Si-H starting surface shows a region of atomic ordering adjacent to an amorphous region. Comparing the interfacial SiO_2 oxide layer thickness for the as deposited stack and PMA treated stacks by TEM, it does not appear that this interfacial layer thickness is increased, which is in contrast to a reported claim of an oxygen release mechanism and concomitant oxidation of the underlying substrate as an effect of PMA treatment.²⁷ It should be pointed out that the results shown in Ref. 27 were for HfO_2 films deposited on a direct contact (HF last) Si substrate and the oxidation of the underlying Si may be different when an existing interfacial layer is present. In Fig. 3(c), the TEM micrograph of the PMA treated HfO_2 film deposited on Si-H does show an oxidized interface, but it is not clear if this is due to oxygen release during PMA, oxidation during HfO_2 ALD growth, or to a measurement induced oxidation, which can occur during TEM measurement, as pointed out in a recent review by Rai *et al.*⁴⁸ The intensity of reflections from cubic TiN in Fig. 2 shows no major changes between both cases of PMA and compared with the case of as deposited stack, thus demonstrating the stability of this metal capping layer and its lack of reaction with the underlying layers as well as stability of the cubic TiN phase and average grain size.

In addition to the investigation of atomic ordering by GIIXRD, the metal cation chemical bonding states of both Hf and Ti were examined by XPS of the Hf 4f and Ti 2p photoelectron core levels. As shown in Fig. 4(a), there is a shift toward higher Hf 4f peak binding energy of $\sim 0.5\text{ eV}$ after PMA for films deposited on both chemical oxide and Si-H. The O 2s peak, which appears in the binding energy range of $\sim 20\text{--}23\text{ eV}$, does not exhibit a noticeable peak binding energy shift, which indicates that the observed shift in the Hf 4f binding energy is due to a change in the Hf bonding

Fig. 2. (Color online) GIIXRD spectra of 40 cycle HfO_2 with TiN and no postmetal anneal (PMA) on chemical oxide (as dep, chem ox), with TiN and postmetal anneal on chemical oxide (PMA, chem ox) and with TiN and postmetal anneal on H-terminated Si (PMA, Si-H).

FIG. 3. TEM images of 40 cycle HfO₂ with TiN and (a) no PMA on chemical oxide (as dep, chem ox), (b) PMA on chemical oxide (PMA, chem ox), and (c) PMA on H-terminated Si (PMA, Si-H).

environment and not due to a measurement artifact such as sample charging. This shift in binding energy may be due to an increase in oxygen-deficiency after PMA consistent with what has been reported by other groups.^{49,50} For instance,

Cho *et al.* examined the Hf 4f level of oxygen-deficient HfO_x and correlated this binding energy shift with a shorter Hf-O bond length as measured by extended x-ray absorption fine structure.⁵⁰ A correlation between a shorter Hf-O bond length is also consistent with the formation of the denser cubic phase as opposed to the less dense amorphous phase in the case of the as deposited stack. Another possibility for the shift in the Hf 4f spectra after PMA could be low levels of Si uptake into the HfO₂ film, as it has been shown that the second nearest neighbor effect between Si and Hf in a hafnium silicate film (a Hf-O-Si bond arrangement) may give rise to an increase in binding energy of the Hf 4f core level.⁵¹ The shift due to silicate-like bonding is believed to be less likely since low levels of Si incorporation in HfO₂ have been shown both experimentally⁴⁷ and theoretically⁵² to stabilize the tetragonal phase as opposed to the cubic phase, which is observed in our study. The Hf 4f core level spectrum of HfO₂ deposited on Si-H shows a more broadened peak at the lower energy side than the spectrum of HfO₂ deposited on chemical oxide, which is consistent with the presence of the amorphous phase in addition to contributions from the cubic phase. It is well known that metastable phases of HfO₂ can be stabilized by oxygen vacancies and this mechanism is one of the main factors which prompted investigations of HfO₂ doping using lower valency metal oxides.^{52,53} In addition to differences in the Hf 4f spectra as a result of PMA, the Ti 2p spectra were also observed to change, although no clear differences in the Ti 2p spectra were observed between stacks with chemical oxide or Si-H starting surfaces and subjected to PMA as shown in Fig. 4(b). The spectra shown were all normalized to the Ti-O bonding state for the Ti 2p_{3/2} core level photoelectron associated with TiO₂. The Ti-O bonding state is expected for air exposed TiN surfaces, and based on XRR fittings of the completed stacks (Table I), this TiO₂ layer was estimated to be ~11–12 Å. After PMA, a decrease in intensity of the lower binding energy shoulder of the Ti 2p_{3/2} state was observed. This lower energy portion of the spectra is attributed to Ti in a bonding configuration coordinated with N. In keeping with the peak binding energies as outlined in Esaka *et al.*, we assigned the lower energy portion (454–457 eV) to two distinct states of Ti bonding, either a TiN configuration or a N-Ti-O configuration, which lies between the TiO₂ and TiN peak positions.⁵⁴ As shown in

FIG. 4. (Color online) XPS core level spectra for (a) Hf4f, O2s and (b) Ti2p from 40 cycle HfO₂ with TiN and no PMA on chemical oxide (chem ox), PMA on chemical oxide (chem ox), and PMA on H-terminated Si (Si-H). Hf4f binding energy shift of 0.5 eV after PMA was observed. A lack of shift in the O2s spectra indicates that sample charging is not a contributing factor in binding energy shift.

Fig. 5, the Ti $2p_{3/2}$ and $2p_{1/2}$ spectra can be adequately fit with the three bonding states of Ti. These bonding states were fit using Voigt functions with a Shirley background subtraction and a $Ti2p_{3/2}$ and $Ti2p_{1/2}$ energy difference of 5.6 eV⁵⁴ along with an intensity ratio of 2 were fixed. The peak binding energy, full width at half maximum (FWHM) and Ti atomic percent for each bonding state is also tabulated in Table II. Based on the peak fits, the percentage of the intermediate N-Ti-O bonding state is reduced following the PMA step and the TiN % is subsequently increased. As the TiO_2 bonding state percentage is not significantly increased, it does not appear that there is a detectable signature of O gettering in the metal layer due to the PMA step. Therefore, any increase in O deficiency or vacancies in the underlying HfO_2 does not result in an oxidation of the overlying TiN layer, and this metal layer does not appear to be susceptible to further oxidation following an additional higher temperature treatment.

Figure 6 displays the GIIXRD spectrum for the DADA processed 40 cycle HfO_2 films subjected to PMA treatment. Compared to the as deposited, amorphous HfO_2 deposited using 40 ALD cycles, the DADA processing method has been shown to result in a highly ordered crystalline film with increased atomic ordering compared to performing only a single postdeposition anneal.³⁸ It has also been shown by GIIXRD that the DADA processed 40 cycle ALD HfO_2 film shows signature reflections from a non-monoclinic phase (tetragonal and/or orthorhombic).³⁸ Thus, by investigating the PMA treatment of DADA processed films we are able to evaluate the effect of a metal cap anneal on the resultant crystalline structure of a film, which has the presence of non-monoclinic metastable phase prior to the treatment. Comparing to the case of starting in an amorphous phase

TABLE II. XPS fitting results for Ti $2p_{3/2}$ core level photoelectrons for 40 cycle HfO_2 and TiN overlayer with and without postmetal anneal (PMA) processing.

Sample	Ti $2p_{3/2}$ bonding state	Peak Binding Energy (eV)	FWHM (eV)	Atomic %
TiN (5 nm)—as dep	TiO_2 (Ti-O)	458.4	1.5	42.0
	TiON (N-Ti-O)	456.6	2.4	49.0
	TiN (Ti-N)	455.2	1.1	9.0
TiN (5 nm)—PMA	TiO_2 (Ti-O)	458.4	1.5	43.3
	TiON (N-Ti-O)	456.7	2.3	42.5
	TiN (Ti-N)	455.2	1.3	14.2

which leads to a cubic phase post-PMA (Fig. 2), the resultant crystal structure for the DADA film treated using PMA takes on a very different form. Although there are some ambiguities due to peak overlaps from monoclinic and non-monoclinic phases as shown in Fig. 6, there is a peak at $\sim 54^\circ$ associated with a region (highlighted in Fig. 6) that is strictly due to the orthorhombic phase. The orthorhombic phases with space groups $Pbca$ and $Pbc2_1$ are labeled in this figure, and since these structures exhibit peak overlaps, it is shown that the possibility of either or both orthorhombic structure being present exists. The energy of these phases as a function of cell volume have also been calculated to lie within close range of each other so it is difficult to suggest a thermodynamic basis for suggesting the existence of one over the other.⁴¹ The strong intensity peak which is aligned with the expected position of $Pbc2_1$ (222) at $\sim 62.5^\circ$ (not labeled) is most likely due to in-plane reflections from the (220) planes of cubic TiN since an in-plane alignment of $Pbc2_1$ should also exhibit peaks due to the (111) reflection.

Fig. 5. (Color online) XPS $Ti2p$ core level spectra of 40 cycle HfO_2 deposited on chemical oxide with TiN cap and either no PMA or PMA. Raw data, fitted peaks, and background are shown with solid lines. Fitted data are overlaid with raw data and are shown with dashed lines.

Fig. 6. (Color online) GIIXRD spectrum of 40 cycle HfO_2 processed using cyclical deposition and anneal method (DADA) with TiN and PMA on chemical oxide. The designated region which encompasses the peak at $\sim 54^\circ$ degrees indicates strictly orthorhombic region.

In Fig. 6, there are no discernible reflections from a strictly monoclinic peak position. Although it is difficult to distinguish between these two orthorhombic phases the possibility of the centrosymmetric $\text{Pbc}2_1$ is consistent with recent reports on Si-doped HfO_2 being stabilized in this phase after annealing with a TiN capping layer.^{8,9} We have previously reported on Si uptake in thin HfO_2 films which were processed using the DADA method,³⁷ and this low level of Si incorporation combined with a TiN cap anneal could possibly drive this stabilized orthorhombic phase. Further studies would need to be done to assess the precise nature of this phase and determine if a noncentrosymmetric phase is present.

In addition to differences in crystalline phase, differences in texture were also observed, as shown in the diffracted intensity contour maps (Fig. 7) for both as deposited and DADA processed 40 cycle HfO_2 films subject to PMA. By representing the pole figure data in this fashion, a fiber

texture can be identified by the presence of high intensity spots (diffraction features), with a preferred orientation showing up as a spot near tilt angle $\psi \sim 0^\circ$, and the elongation of spots along the ψ axis is due to a variation of this orientation, a so-called texture “width.”⁴² It should be mentioned that the high intensity spots in the contour maps, which are circled, are due to peaks from Si lattice planes. For the case of the as deposited HfO_2 subject to PMA [Fig. 7(a)], there are no signatures of texturing of either HfO_2 or TiN. The TiN metal layer remains in a randomly aligned polycrystalline state, and the HfO_2 , which starts from an amorphous state, is converted to a polycrystalline cubic phase with no preferred orientation. The highly disordered initial state of the HfO_2 leads to a random alignment of crystals upon annealing with the TiN overlayer. The same PMA treatment on the DADA processed film shows some level of texturing for both TiN and HfO_2 as labeled in Fig. 7(b). The weak intensity spot close to $2.5 \text{ \AA}$ d-spacings is attributed to (111) planes of cubic TiN oriented nearly parallel to the substrate while the spot at $\sim 2.1 \text{ \AA}$ can be assigned to (200) planes. For a cubic (111) textured film, the peak associated with the (111) d-spacing should be very weak or absent for the measurement in the in-plane configuration and this is what is observed in Fig. 6. The strong intensity of the cubic (220) peak for TiN when measured in the in-plane configuration is also consistent with the (111) texturing shown in Fig. 7. For cubic (111) texturing, there will be {110} planes oriented normal to the film surface which will give rise to a higher intensity peak for cubic (220) measured in the in-plane configuration. For instance, [111] planes are perpendicular to both [1-10] and [-110], while [110] planes are perpendicular to [-111] and [1-11]. In Fig. 7, the broad intensity spot centered at $\sim 3 \text{ \AA}$ d-spacing ($\sim 2.8\text{--}3.2 \text{ \AA}$) is a signature of planes of crystalline HfO_2 oriented parallel to the substrate. Since this peak is fairly broad it is difficult to assign a distinct phase or d-spacing as it may encompass one or more of the following d-spacings: M(111), M(-111), O(211), T(111), or C(111). There is also a broad and elongated spot at $\sim 2.6 \text{ \AA}$ d spacing, which may be assigned to one or more of the following d spacings: M(002), M(020), O(020), T(002), T(200), or C(200).

B. Stacks with TiN/Ti bilayer metal gate—physical analysis

Figure 8 displays the GIIXRD spectra comparison of the as deposited stack containing TiN with the stack containing the TiN (2 nm)/Ti (7 nm) bilayer as well as comparison between PMA treated bilayer stacks with either 7 nm or 5 nm of Ti. In the previous study by Morita *et al.*, it was shown that a layer of PVD Ti interposed between HfO_2 and TiN and subjected to a 800°C PMA step can lead to a significant EOT reduction and it was also shown that the EOT was decreased as the Ti layer thickness increased from 5 to 7 nm.²⁸ Accordingly, in this study, we sought to evaluate the effect of similar thickness Ti layer on the crystallinity of underlying ultrathin HfO_2 and using an all ALD approach. As shown in Fig. 8, the as deposited bilayer stack with 7 nm

FIG. 7. (Color online) Diffracted intensity contour map as a function of tilt angle (ψ) for (a) as deposited 40 cycle HfO_2 (ALD std) and (b) 40 cycle HfO_2 processed using cyclical deposition and anneal method (DADA). Both samples were deposited on chemical oxide, capped with TiN and subjected to a postmetal cap anneal (PMA). The high intensity spots in the contour maps which are circled are due to peaks from Si lattice planes. The dark blue regions for low values of ψ are due to orientations that are not measured due to the detector geometry.

Fig. 8. (Color online) GIIXRD spectra of 40 cycle HfO_2 with $\text{TiN}(5\text{ nm})$ and $\text{TiN}(2\text{ nm})/\text{Ti}(7\text{ nm})$ with no postmetal anneal (as dep) and 40 cycle HfO_2 with $\text{TiN}(2\text{ nm})/\text{Ti}(5\text{ nm})$ and $\text{TiN}(2\text{ nm})/\text{Ti}(7\text{ nm})$ with postmetal anneal (PMA). All of the HfO_2 films were deposited on a chemical oxide starting surface.

Ti shows reflections from both the TiN cubic phase and a secondary phase which can be indexed to hexagonal $\text{TiN}_{0.3}$.⁵⁵ Following a PMA treatment, a new set of reflections emerges, which are not able to be indexed to Ti, TiN compounds, or HfO_2 , and these reflections are notated by the two theta values in Fig. 8. Further evaluation of these new reflections suggests that these peaks are due to a Ti silicide compound as outlined in Table III, which lists the closest associated two theta values.⁵⁶ In particular, the hexagonal phase of Ti_5Si_3 can be indexed to the d-spacings at 41.24° , 51.49° , and 67.13° two theta. For the 7 nm Ti containing stack, PMA treatment does not show any clear, unambiguous signs of non-monoclinic HfO_2 formation. For the thinner 5 nm Ti-containing stack a reflection from cubic (111), or possibly tetragonal (111), HfO_2 can be seen, although this peak is greatly suppressed compared to the similar case of TiN metal gate as shown in Fig. 2.

In Fig. 9(a) the Ti 2p core level spectra from the 40 cycle ALD HfO_2 containing stacks with either TiN or TiN

(2 nm)/Ti (7 nm) are normalized and overlaid. For the unannealed bilayer metal containing stacks, the low binding energy edge shifts to a lower binding energy compared to the unannealed TiN containing stack, which is consistent with N-deficient TiN and the presence of $\text{TiN}_{0.3}$ as shown in the GIIXRD spectrum. Following the PMA treatment, the presence of Ti silicide for the bilayer metal containing stacks is also consistent with a low binding energy peak, which appears in the Ti 2p spectra as shown in Fig. 9(b). The TiSi_x phase should give rise to a lower binding energy peak in the Ti 2p_{3/2} spectra compared to TiN.⁵⁷ Although the binding energy values of Ti and TiSi_x are close in value,^{58,59} the lack of reflections in the GIIXRD spectra corresponding to pure Ti suggests that this peak is due to a silicide phase and not Ti metal. Further evidence of the occurrence of a silicidation reaction is shown in the TEM micrographs in Fig. 10, which shows both as deposited and PMA treated stacks with $\text{TiN}(2\text{ nm})/\text{Ti}(7\text{ nm})$. Signs of silicidation are apparent even for the as deposited stack and following the PMA treatment the Si substrate appears fully reacted. The Ti deposition process is also shown to result in large granular structures and highly nonuniform film. Similar results were obtained for stacks deposited on Si-H as also shown in Fig. 10. These results outline some of the difficulties of integrating a Ti layer deposited by an all ALD approach as opposed to a PVD Ti layer, which has been used as an oxygen-controlling layer for additional scaling with the use of a PMA treatment on stacks deposited on direct contact HF treated Si.^{28–30} Even for the case of preannealed HfO_2 deposited by the DADA method evidence of silicidation is observed as shown in the GIIXRD spectrum in Fig. 11.

C. MOSCAP testing with TiN metal gate

Due to difficulties in preventing silicidation reactions when using an interposed Ti layer in the bilayer metal gate as well as the nonuniform deposition as shown in the TEM image of Fig. 10, the use of an ALD Ti layer was not tested in MOSCAP structures, and the device testing consisted of experimental splits using only the TiN overlayer. Figure 12(a) displays EOT versus leakage current density at flat-band voltage (V_{fb}) – 1 V and Fig. 12(b) displays the EOT versus V_{fb} from these MOSCAP devices. The data points

TABLE III. Peak positions in GIIXRD spectra from Ti-containing metal gate, following a postmetal anneal (PMA) treatment, which are unable to be indexed to HfO_2 , TiN_x , or Ti phases. Peak positions, which are closest matches for TiSi_x phases along with Miller indices (hkl), are tabulated. (H=hexagonal, O=orthorhombic, T=tetragonal).

PDF	29-1362		72-2115		27-0907		23-1079		71-0187	
Phase	Ti_5Si_3 (H)		TiSi (O)		Ti_5Si_4 (T)		Ti_5Si_4 (O)		TiSi_2 (O)	
Peak (2theta)	Closest peak (2theta)	hkl	Closest peak (2theta)	hkl	Closest peak (2theta)	hkl	Closest peak (2theta)	hkl	Closest peak (2theta)	hkl
26.53	27.79	200	27.65	200	27.65	201	28.18	004	–	–
41.24	41.16	111	41.83	112	41.84	115	41.58	301	42.46	004
51.49	51.31	310	50.78	200	52.83	314	51.78	026	50.01	313
67.13	67.03	213	–	–	69.56	218	67.68	334	67.65	315
89.92	–	–	–	–	–	–	–	–	–	–

FIG. 9. (Color online) Ti2p XPS spectra overlay of stacks containing 40 cycle HfO_2 with (a) TiN(5 nm) and TiN(2 nm)/Ti(7 nm) with no postmetal anneal and (b) TiN(2 nm)/Ti(7 nm) with and without PMA. All of the HfO_2 films were deposited on a chemical oxide starting surface.

plotted for EOT, leakage current density (J_g), and V_{fb} represent mean values for the measurements on a full 300 mm wafer. The EOT, J_g , and V_{fb} values are also tabulated in Table IV. Although a cubic phase is obtained for the standard ALD HfO_2 process with a PMA treatment, both the EOT and J_g are increased as compared to the non-PMA MOSCAP. The benefit of obtaining a higher-k phase of HfO_2 may not be fully realized due to other physical changes that occur in the gate stack following a PMA treatment. The previous work by Migita *et al.*, which demonstrated higher-k cubic phase stabilization, also showed that for ultrathin films (on the order of 3 nm or less) an increase in EOT compared to non-PMA treated monoclinic HfO_2 was obtained.²⁷ In their study, they attributed this increase in EOT to oxidation of the underlying lower-k interface. In our study, a similar mechanism may be occurring, and although there is no significantly measurable change in the interfacial thickness based on the TEM images in Fig. 3, a slight thickness change (below the measurement limit of TEM) or a change in the associated k value of the interface cannot be ruled out. An increase in the V_{fb} value for PMA treatment as shown in Table IV may also be related to an associated increase in the interface thickness consistent with reported effect of so-called V_{fb} roll-off for thinner SiO_2 interfaces in $\text{HfO}_2/\text{SiO}_2$ structures.⁶⁰ The study from Migita *et al.*²⁷ also does not report the associated leakage from their scaled devices so the increase in leakage we observe in our study cannot be directly compared with their study. The polycrystalline nature of the cubic HfO_2 films in the post-PMA treated devices may pose a drawback due to increased leakage current due to grain boundaries compared to the as-deposited amorphous HfO_2 .^{61,62} Migita *et al.* have also shown similar optical bandgap for cubic and monoclinic HfO_2 in their study which suggest that leakage due to reduced band offsets may not be an issue for cubic phase stabilized HfO_2 .²⁷ For the film stack deposited on the COR treated substrate and subjected to PMA, a decrease in EOT of 1.2 Å compared to the same stack deposited on chemical oxide and treated with PMA is shown, which is most likely attributed to the

FIG. 10. TEM images of 40 cycle HfO_2 with (a) TiN(2 nm)/Ti(7 nm) and no PMA on chemical oxide (as dep, chem ox), (b) TiN(2 nm)/Ti(7 nm) and PMA on chemical oxide (PMA, chem ox), and (c) TiN(2 nm)/Ti(7 nm) and PMA on H-terminated Si (PMA, Si-H).

FIG. 11. (Color online) Comparison of GIXRD spectrum of 40 cycle HfO_2 processed using DADA with either TiN or TiN(2 nm)/Ti(7 nm) and PMA on chemical oxide. The designated region which encompasses the peak at ~ 54 degrees indicates strictly orthorhombic region.

interface scaling due to the COR treatment. A scaled interface would also be consistent with the observed lowered V_{fb} , compared to both the as-deposited and PMA treated stacks on chemical oxide, and the aforementioned V_{fb} roll-off effect.⁶⁰ Although this treatment results in a scaled EOT, it does not offer an electrical benefit in terms of leakage since it is increased by an order of magnitude for the PMA case and two orders of magnitude for the non-PMA case. In terms of leakage, the DADA processed film stack followed by PMA has relatively the same leakage as the non-PMA stack with the standard ALD HfO_2 process but it suffers from the drawback of an increased EOT. A similar interfacial oxide growth may occur in the case of the DADA film subjected to PMA as seen in the standard ALD processed HfO_2 film treated by PMA. Since both cases show an increase in V_{fb} compared to the case of no PMA treatment this change is also consistent with the phenomenon of V_{fb} roll-off.⁶⁰ Regarding the difference in leakage current density, in the case of the DADA process the more uniform textured film may be less prone to grain boundary leakage as compared to the case of the polycrystalline, randomly orientated grains in the cubic phase stabilized HfO_2 . The DADA process has also previously been shown to lead to reduced leakage compared to the case of a postdeposition anneal only, which was shown to be due to decreased impurity levels and trap assisted tunneling as a result of the interspersed annealing treatment.⁶³

IV. SUMMARY AND CONCLUSIONS

In this study, we examined the effects of post metal deposition anneal using an ALD grown Ti-based metal gate and various processing schemes for ultrathin ALD HfO_2 growth,

FIG. 12. (Color online) Mean EOT vs (a) mean $J_g @ V_{fb} - 1 \text{ V}$ and (b) mean V_{fb} for MOSCAP structures with 40 cycle ALD HfO_2 and 5 nm TiN metal gate, outlining the effects of PMA treatment on device properties. The starting substrate consisted of chemical oxide except for the experimental split which received COR treatment. Error bars represent standard deviation of each measurement.

including an interspersed anneal and a Si-H starting surface, on the crystallinity of both the metal gate and high-k dielectric. For 40 cycle ALD HfO_2 ($\sim 32 \text{ \AA}$) with TiN overlayer, a transition from an amorphous state to a cubic phase was observed with the application of a PMA treatment. Evidence of the orthorhombic phase was observed for 40 cycle HfO_2

TABLE IV. EOT, leakage current density at flatband voltage minus 1 V ($J_g @ V_{fb} - 1 \text{ V}$), and flatband voltage (V_{fb}) (all mean values) for MOSCAP structures with 40 cycle ALD HfO_2 and 5 nm TiN metal gate. Chemical oxide starting surface is denoted as Chem ox and H-terminated Si is denoted as Si-H. ALD std denotes standard ALD process and the ALD process with interspersed anneal is denoted DADA.

Starting surface	HfO ₂ deposition	PMA	EOT [nm]	$J_g @ V_{fb} - 1 \text{ V}$ (A)	V_{fb} (V)
Chem ox	ALD std	No	1.13	8.72×10^{-4}	-0.186
Si-H	ALD std	Yes	1.08	1.35×10^{-1}	-0.202
Chem ox	ALD std	Yes	1.24	9.54×10^{-3}	-0.141
Chem ox	DADA	Yes	1.25	1.11×10^{-3}	-0.167

films processed using a cyclical deposition and anneal (DADA) followed by an anneal with a TiN cap. The textured DADA film was also observed to influence the texture of the overlying TiN and a cubic (111) preferred orientation was obtained following a PMA treatment. We observed suppression of crystallinity for HfO₂ deposited on H terminated Si and annealed with a TiN layer, which illustrates the need for an adequate nucleation layer for uniform grain growth and increased atomic ordering. In the investigation of bilayer of TiN overlying Ti we observed reflections from both cubic TiN and hexagonal TiN_{0.3} in the as-deposited state and after annealing clear evidence of silicidation (TiSi_x) was observed. In MOSCAP structures with 40 cycle ALD HfO₂ and TiN overlayer subjected to a PMA, there was no associated improvement in device scaling, despite the stabilization of the cubic phase of HfO₂. This study highlights the importance of the initial crystalline state and nucleation of HfO₂ as well as the thermal stability of the capping metal layer material when engineering dielectric layer crystallinity by means of a postmetal cap anneal. For ultrathin HfO₂, the benefits of the stabilization of a higher-k phase may not be fully realized due to the additional constraints of increased leakage due to grain boundaries or change in effective k due to changes in the lower-k interfacial layer.

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