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Physical and electrical characteristics of atomic-layer deposition-HfO₂ films deposited on Si substrates having different silanol Si-OH densities

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In this work, ultrathin HfO_2 films, less than 6 nm in thickness, are deposited by atomic-layer deposition (ALD) on Si substrates that have a variable density of silanol (Si-OH) chemical bonds after oxidizing the Si surface using hot H_2O_2 . Given the surface chemistry needed for proper ALD growth of HfO₂, OH-last surfaces are needed in order to react with the Hf-based precursor during half-cycle of this reaction. The later is important for proper nucleation and uniform growth of ultrathin HfO₂ by ALD. Depending on the immersion time of an initially HF-last Si surface in hot H_2O_2 , ultrathin and nonstoichiometric chemical oxides SiOx are formed presenting a variable density of Si-OH bonds which are measured after Fourier-transform infra red spectroscopy. Following SiOx formation, HfO_2 is directly deposited on these surfaces by ALD using water (H₂O) and tetrakis-dimethylamino-hafnium as precursors. Metal-insulator-semiconductor (MIS) capacitors are then formed using both HfO2/Si and HfO2/SiOx/Si stacked structures and their electrical characteristics are evaluated. It is found that a variable density of Si-OH chemical bonds have an impact on the physical and electrical characteristics of these MIS structures by reducing their atomic surface roughness (R_{rms}) and gate leakage current density (Jg), and at the same time, increasing their flat band voltage (Vfb) for the same immersion times in H₂O₂. Obtaining the lowest R_{rms}, Jg, and Vfb are possible by using intermediate H_2O_2 immersion times between 4 and 8 min, which is also directly related to an intermediate Si-OH bond density. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4769206]

I. INTRODUCTION

In order to obtain high-quality atomic-layer deposition (ALD)-based HfO2 gate oxides having equivalent oxide thickness EOT < 1 nm, it is important to reduce or eliminate a lower dielectric constant material (lower-k when compared with HfO₂) after deposition and/or thermal processing of a HfO₂ thin film on silicon to fully exploit the advantages of a larger HfO₂ dielectric constant. This lower-k interfacial layer (IL) can develop into a Hf-silicate ($Hf_xSi_yO_4$), Hf-silicide (Hf_xSi_y) or even be chemically reduced into a much lower-k SiOx-based material after deposition and/or thermal treatment.^{1,2} Some approaches to reduce/eliminate a persistent Hf silicate-based IL use an ultrathin SiO₂ layer between the silicon substrate and the HfO2. Although this method can effectively suppress the formation of an Hf silicate IL,³ the final EOT is compromised. Another approach to solving the reduction in EOT after ALD of HfO2 is to use HF-last silicon surfaces⁴ or complex chemistries⁵ on the silicon substrates able to withstand the last processing steps for the device under fabrication. On the other hand, direct ALD of HfO₂ on HF-last or H-terminated Si(100) surfaces leads to the challenging problem of inconsistent film nucleation during the first cycles of deposition,^{5,6} thus producing nonuniformities in the thickness and other physical/electrical characteristics of the final material (especially important when considering HfO₂ layers in the ultrathin film regime of less than 5 nm). In order to promote a layer-by-layer ALD film growth of HfO₂ on silicon surfaces, the ALD precursors need to react with adequate initial surface species from the very first ALD cycles (typically highly hydrophilic Si-OH terminated surfaces). The former is obtained if the silicon surface is previously oxidized using a controlled oxidation ambient/ atmosphere instead of a noncontrollable oxidation mechanism (like the native oxide formation that occurs when the silicon substrate is exposed to oxygen inside a clean room). Following a controlled oxidation, specific densities of Si-OH bonds are created on the silicon's surface. These can be used as chemical promoters for subsequent and highly controlled ALD of ultrathin HfO₂ layers. Even though Si-OH bonds are needed for uniform and fully nucleated ALD layers of ultrathin HfO₂, only a few reports correlate the Si-OH density to the morphology and physical characteristics of HfO₂ grown by ALD. Here, we correlate the specific Si-OH densities of ultrathin SiOx (grown by chemical oxidation of silicon in hot H_2O_2) to both the morphology and physical/electrical characteristics of the first cycles of ALD-HfO₂.

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In this work, we grow ultrathin and nonstoichiometric chemical oxides SiOx (whose thickness is less than 1.6 nm after ellipsometry and profilometry measurements) on hydrophilic Si surfaces after exposing HF-last p-type Si substrates [previously Radio Corporation of America (RCA)-cleaned and HF-last treated] to hot H_2O_2 at 75 °C. This way, controlled densities of Si-OH bonds can be obtained during time-

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dependent chemical oxidation of the silicon surface. Immediately after SiOx formation, we deposit ultrathin ALD-HfO₂ films in order to correlate the former Si-OH density (intrinsic to the SiOx surface/bulk) to the quality and uniformity of the physical, chemical, and electrical characteristics of HfO₂. Our aim is, therefore, to obtain the minimum density of Si-OH sites (or minimum immersion time in hot H₂O₂ for this purpose) that are needed as "seed" for promoting more uniform physical and electrical characteristics of ultrathin HfO₂ after atomic layer deposition.

II. EXPERIMENTAL PROCEDURES

Figure 1(a) shows the complete fabrication processing flow for the samples. A simplified schematic of the fabricated structure is shown in Fig. 1(c). In the following paragraphs, we further organize and explain the main stages of silicon surface conditioning, ALD of HfO₂ and the chemical, physical, and electrical characterization.

A. Si-OH bond formation on clean silicon surfaces

P-type silicon wafers having resistivity of 5–10 Ω ·cm and (100) crystalline surfaces were used as substrates. For the initial cleaning procedure, these substrates were degreased by sequential immersion in trichloroethylene and acetone by 10/10 min, respectively, within an ultrasonic vibrator. Then, the substrates were rinsed in deionized water (DI) and gently dried using an ultrahigh purity N₂ pistol blow. After drying, all wafers were

carefully immersed in a 7:1 HF buffer etching solution to eliminate their native oxide, rinsed again in DI, and then immersed in standard RCA cleaning solutions to remove organic and metallic residual contaminants. After RCA cleaning, they were fully rinsed and immersed in a high-purity DI water tank until a DI resistivity of 18 M Ω ·cm was obtained. Finally, these samples were dried using N2, then immersed again in the HF buffer solution to eliminate any chemical oxide grown on the silicon surfaces. Clean and highly hydrophobic HF-last surfaces were thus finally obtained. At this point, all but one sample (used as reference) were simultaneously introduced into a solution containing hot H₂O₂ (30-32 wt. % in H₂O, semiconductor grade, and previously heated at 75 °C). The samples were removed from this solution at different times to promote a timedependent chemical oxidation of the silicon surface and, thus, growth of a SiOx oxide having different densities of Si-OH chemical bonds, like those shown in Fig. 1(b). The wafers' immersion time in hot H_2O_2 ranged from 2 to 32 min at the same temperature.

B. ALD of HfO₂ and MIS device fabrication

After conditioning the silicon surface by chemical oxidation using hot H_2O_2 , HfO_2 was deposited by ALD onto all former samples (both HF-last surface and all SiOx chemical oxides). The precursors used for ALD of HfO_2 were ultrapure H_2O and tetrakis dimethylamino hafnium, both from Sigma-Aldrich. The ALD system was a Savannah S100 from Cambridge Nanotech. During HfO_2 deposition, the chamber



Fig. 1. (Color online) (a) Processing flow for the fabrication of $HfO_2/SiOx$ based MIS capacitors. (b) Schematic of the Si surface having variable Si-OH bond densities after H_2O_2 treatment. (c) Schematic of the final MIS capacitor structure.

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was kept at 275 °C/200 mTorr of temperature/pressure for all 60 deposition cycles. These conditions produced an ultrathin HfO₂ film with \sim 5.4 nm in thickness after ellipsometry and profilometry measurements. Right after ALD of HfO₂, all samples were immediately moved to an e-beam evaporator (Temescal BJD-1800 from Edwards) and the evaporation chamber was vacuumed down to 1×10^{-7} Torr to minimize the exposure time of the HfO2 surfaces to the oxygen present in the atmosphere of the clean room. After reaching proper vacuum conditions, a relatively thick aluminum film \sim 800 nm was then evaporated on top of HfO2 with an evaporation rate of 1–2 Å/s. Later, a thinner \sim 600 nm aluminum layer was evaporated on the back of all the wafers (after native oxide elimination using HF buffer solution). Once fully metalized, all the wafers were covered with positive photoresist using standard spinning/baking conditions and exposed to an UV system (Karl Suss MA6) to define the gate patterns of the MIS structures. A gate capacitor area of 13.34×10^{-4} cm² was used for all MIS devices under test. Following metallization, a last thermal treatment (425 °C in forming gas ambient, 5% H_2 + 95% N₂) was applied to all samples to passivate Si dangling bonds with this H₂-based annealing. The final MIS devices resemble the structure of Fig. 1(c).

C. Chemical, physical, and electrical characterization

The chemical compositional analysis for all films was obtained by Fourier-transform infrared (FTIR) spectrum measurements in absorbance mode with a Bruker Vector-22 system. Also, a relative density of Si-OH chemical bonds was obtained for all samples by calculating the absorption coefficient after normalizing each FTIR spectrum to each oxide thickness. The thickness of each SiOx film was measured and compared using both ellipsometry (Gaertner L117 and Rudolph FE-III systems, both with a HeNe laser of 632.8 nm in wavelength) and atomic-force microscopy (AFM by NanoSurf EasyScan-2 after standard lithography procedures for step definition). The average thicknesses for the SiOx and HfO₂ layers are 1.2–1.6 and 5.4 nm, respectively. Here, it is important to note that the HfO₂ thickness corresponds to the deposition rate provided by the specific deposition conditions that were used and whose value was well correlated to the thickness obtained after AFM measurements. For SiOx, the reported thicknesses are the result of averaging at least ten different ellipsometry and AFM measurements after analyzing ten different spots/steps during those readings. All results had variations within $\pm 5\%$ of the reported average values. Also, atomic surface roughness data for all samples were obtained using AFM and by taking into account ten different spots for each sample. Finally, capacitance-voltage C-V and current-voltage I-V measurements were obtained by using a Keihtley Model 82-DOS Simultaneous C-V system (at 100 kHz) and an HP 4156B Semiconductor Parameter Analyzer, respectively, and by taking into account 20 different samples for each H₂O₂ immersion-time condition. To determine the flat-band voltage Vfb, we plotted $(1/\text{Cox}^2)$ with respect to Vg and found Vfb at the lower knee of this curve. Additionally, we also differentiated this curve and found Vfb at the maximum slope of the left flank.⁷ All electrical measurements were obtained at room temperature.

III. RESULTS AND DISCUSSION

A. SiOx thickness and atomic surface roughness

Figure 2 shows the variation in thickness and atomic surface roughness (by ellipsometry and atomic-force microscopy, respectively) of ultrathin SiOx films after chemical oxidation of Si(100) substrates in hot H_2O_2 . Compared with a native oxide (after only 2 h of exposure of an HF-last silicon surface to the clean room atmosphere), slightly thicker chemical oxides SiOx (about 1.44-1.62 nm) present lower surface roughness (around 0.6-1.0 nm), which are ideal for uniform ALD growth of HfO₂ on SiOx. The inset shows the characteristic atomically flat SiOx surface (area of $1 \ \mu m \times 1 \ \mu m$, with vertical Z axis scale of 100 nm) obtained after chemical oxidation. We also notice a dramatic increase in SiOx surface roughness after increasing the immersion time for more than 8 min. This can be related to a thermal decomposition of the H₂O₂ solution after being used for longer times, thus reducing its effectiveness as an oxidizing agent by the chemical evaporation/decomposition of its active oxygen components.^{8,9} On the other hand, we notice that the average thickness of the chemical oxide SiOx is kept almost constant at between 1.44 and 1.62 nm, thus ensuring a similar SiOx thickness prior to ALD of HfO2 and, therefore, a similar EOT for electrical evaluation purposes. Of course, the final EOT of the total stacked dielectric structure (HfO₂/SiOx) will be greater than 1.44 nm, given our thick SiOx layer. Nevertheless, we want to emphasize the importance of correlating a variable Si-OH bond density with respect to the growth formation of ALD HfO₂ and, therefore, the influence of this important parameter (Si-OH bond density) on the electrical characteristics of the MIS devices.



FIG. 2. (Color online) Physical thickness and atomic surface roughness of ultrathin SiOx films grown on p-type Si(100) substrates after immersion in hot H_2O_2 . The inset shows some typical SiOx surface roughness after AFM measurements (the vertical axis is 100 nm per line). The lowest R_{rms} is obtained after 2–8 min of immersion time in H_2O_2 .

B. Si-OH bond density measurements after FTIR

Figure 3 shows the FTIR spectrum (in absorbance mode and taking into account the specific thicknesses of SiOx after each growth condition) of the absorption coefficient for the Si-OH bonds (rocking, nonbonded mode with maximum peak at $\sim 3652 \text{ cm}^{-1}$).^{10,11} We notice that the immersion time in hot H2O2 of HF-last Si substrates is strongly correlated to the peak intensity of the Si-OH bond so the lowest peak intensity is found for the shortest immersion time in H_2O_2 and the highest peak intensity is found for the longest immersion time. The remaining Si-OH bond peak intensities related to the intermediate immersion times in H₂O₂ are also found in between. In all cases, we demonstrate that by exposing an HF-last Si(100) surface to hot H₂O₂, variable Si-OH bond densities can be obtained, thus providing a suitable surface for controlled ALD growth of ultrathin HfO₂ films whose morphology and interface properties could be relevant for the electrical characteristics of the MIS devices comprising these oxides. The inset in Fig. 3 shows that by integrating the area under each intensity peak curve (with maximum peak intensities centered at a wavenumber of 3652 cm^{-1}), we can normalize the intensity of each Si-OH bond to the physical thickness of each oxide stack (comprising the HfO₂/SiOx structure). We again notice that the lowest area after integration occurs for the shortest immersion time in H_2O_2 , while the highest area corresponds to the longest immersion time in H₂O₂. In between these conditions, we notice a slight reduction followed by an increase in the integrated area of the absorption coefficient for immersion times longer than 4 min. Although a clear monotonic dependence of the Si-OH bond area versus immersion time has not been found, the general trend shows an increase in Si-OH bonds after longer immersion times in H_2O_2 . On the other hand, even though the chemical oxidation process for these samples is not in the gaseous phase and the inset graph shows only the density of Si-OH bonds, this kind of saturation of Si-OH bonds (after longer immersion times in H_2O_2)

Absorption coefficient [cm] 3779 8x10³ Area Immersion time [min] 6x10³ time [min] 3708 32 4x10³ 16 8 4 2x10³ 2 3652 0 3600 3500 3700 3800 3900 4000 Wavenumber [cm]

FIG. 3. (Color online) FTIR spectrum (in absorbance mode) of the absorption coefficient for ultrathin SiOx grown on p-Si(100) after immersion in hot H_2O_2 . The peaks at ~3652 cm⁻¹ are correlated to different Si-OH bond densities. The inset shows the result of integrating the area under the curve for each Si-OH bond peak at its highest intensity. After 2 min of immersion in H_2O_2 , an HF-last silicon surface develops a larger Si-OH bond density.

is not equivalent but somehow similar to the oxidation rate of silicon in the ultrathin oxide regime, where this process is limited by the chemical reaction rate at the surface (not the arrival rate of the molecular oxygen at the SiO₂/Si interface).^{12,13}

C. J-V experimental results

Figure 4 shows the gate current density versus gate voltage characteristics (Jg-Vg) for Al-gated HfO2/SiOx/Si samples in which different Si-OH densities have been previously formed during the chemical oxidation of the Si surface. The data are only shown for the gate injection condition (or accumulation regime in which a negative Vg bias is applied to the gate electrode), where electrons are able to tunnel from the aluminum gate to the substrate via the gate dielectric stack. Even though the specific conduction mechanisms are not shown, we notice similar electron conduction behavior for almost all samples compared with an HF-last silicon sample in which Jg is slightly larger for all the Vg applied (which is expected given its thinner oxide physical thickness). The only deviation from the general conduction behavior is presented by the sample immersed the first 2 min in H_2O_2 . This is thought to be related to an incomplete SiOx formation mechanism given that this sample presented the lowest Si-OH bond density as shown by the inset of Fig. 3. Also, we notice that by using stacked HfO₂/SiOx structures, the gate current density Jg lowers slightly, which is expected since the final EOT increases. Nonetheless, all the samples reach dielectric breakdown around |Vg| = 3.8-4.1 V, which represents a breakdown electric field of Ebd = 6-7 MV/cm (depending on the total physical thickness for each stacked HfO₂/SiOx structure), almost doubling the Ebd reported for an Al/HfO₂/Si MIS structure¹⁴ or HfO2-based metal-insulator-metal structure¹⁵ in which ALD-HfO₂ was grown at similar temperatures.

For the sake of clarity, Fig. 5 shows the previous data with the gate voltage Vg normalized to the physical thickness of each oxide stack, thus directly showing the actual

rea = 13.34x10⁻⁴ cm

time [min]

32

16

8

4

2

0 breakdown

-6

-8

 10^{2}

10[°]

10⁻²

10

10⁻⁶

10⁻⁸

10⁻¹⁰

10⁻¹²

[A/cm²

Gate Current Density Jg



Gate Voltage Vg

-4

-2

[V]

0



FIG. 5. (Color online) Gate leakage current density vs gate electric field characteristics for gate injection conditions. All samples reach breakdown for Ebd = 6-7 MV/cm. With the exception of the sample oxidized for only 2 min, the same conduction mechanism can be observed before all samples reach breakdown.

gate electric field Eg applied to each sample. We clearly notice that the same gate leakage current density flows for most of the samples before they reach breakdown, the only exception being the sample immersed in H₂O₂ for 2 min. The Ebd for all samples is between 6 and 7 MV/cm, which suggests a high resistance for dielectric breakdown of this HfO2 under gate injection conditions and, therefore, its high electrical resistance for charge injection. After hard breakdown, we notice the characteristic high leakage current condition (ON state) of these HfO2-based MIS capacitors in which an electrical window between the OFF/ON states comprises almost 7 orders of magnitude, which is quite useful for high-performance nonvolatile memory applications such as the emerging resistive random access memory or resistive random-access-memory device (usually based in a metal-insulator-metal stacked structure and the recently discovered memristive effect¹⁶). In the memristive device, an oxide layer reaches dielectric breakdown after applying proper bias to the gate electrode, thus producing a high leakage current flow. This high conduction state is then reversed to a low conduction state or low leakage current flow by applying another biasing condition. Therefore, the "memory window" (HIGH to LOW ratio) of this device is an important parameter that is related to the different levels of gate leakage current found in those conduction states and that usually comprises only a few orders or magnitude. Even though not shown, a full J-V postbreakdown characteristic is similar to a rectifying junction characteristic (specifically, to a Schottky diode). This makes sense if we think of a filamentary conduction path being formed after breakdown, in which a metal-semiconductor junction would be formed by the aluminum of the metal gate making contact with the p-type silicon substrate through this filamentary path. Because of the differences in their work functions, the metal-semiconductor contact would end up presenting rectifying characteristics.

The gate leakage current density Jg at a gate voltage |Vg| = 1 V lies between 4 and 18 nA/cm², so we have obtained an



FIG. 6. (Color online) Simultaneous comparison of Jg at |Vfb-1| and Vfb characteristics to each H_2O_2 immersion-time condition. The lowest Jg at |Vfb-1| is obtained between 4 and 16 min of immersion time while the Vfb is kept almost constant between -0.9 and -1.0 V for the same conditions.

ultralow gate leakage current density for this Vg applied. On the other hand, if we plot Jg at a gate voltage Vg = |Vfb - 1| V (thus normalizing with respect to each flat band voltage Vfb value), we will obtain the data of Fig. 6, in which the main J–V and C–V parameters are both presented and compared with respect to each immersion time in H₂O₂. It is interesting to notice a similar trend in Fig. 6 with respect to that of the inset in Fig. 3, where the different Si-OH bond densities (normalized to the gate dielectric stack thickness after integration) exert a direct influence on the electrical J–V and C–V characteristics as well. Finally, we notice that the lowest Jg obtained at |Vfb - 1| corresponds to the intermediate Si-OH bond densities that were formed after immersion of HF-last silicon substrates in H₂O₂ by 4–16 min.

D. C-V experimental results

Figure 7 shows the normalized capacitance versus voltage C–V characteristics of all the samples under study. Compared



FIG. 7. (Color online) Normalized capacitance vs gate voltage characteristics for all studied samples. Compared to our reference sample, all silicon surfaces being chemically oxidized in H_2O_2 present a shift to the left side of the C–V plot, which is characteristic of an increase in positive charge.

with our reference sample (direct ALD of HfO₂ on an HF-last silicon surface), all silicon substrates that were chemically oxidized in H₂O₂ present a shift to the left of the C-V plot, which is characteristic of an increase in fixed positive charge and possibly located at the HfO₂/SiOx interface. For the longest immersion time in H₂O₂, we obtain the largest Vfb = -1.5 V, whereas the other samples remain within a Vfb around -0.9 to -1.0 V. Given the technological importance of having a properly passivated interface between a HfO₂/Si abrupt interface, it would be necessary to fabricate metal-oxide-semiconductor field-effect transistor devices in order to locally measure the interface-states density Dit and correlate this important parameter to each of the immersion conditions we have used so far. From these C-V curves, we can only suggest that better HfO2/Si interface properties can be found for samples having a SiOx-based IL in between, given the ability of SiOx to passivate silicon dangling defects,^{17,18} thus producing smooth C–V curves with a large slope when going from accumulation to inversion regimes. In Fig. 6, we have correlated the Vfb parameter to each immersion-time condition, suggesting that a longer immersion time will introduce a larger density of positive charge at the HfO₂/SiOx/Si stacked structure, thus largely shifting Vfb down to -1.5 V.

IV. SUMMARY AND CONCLUSIONS

By promoting a variable Si-OH bond density on HF-last silicon surfaces after immersion in hot H_2O_2 (producing the chemical oxidation of the silicon surface), we were able to measure and correlate this chemical property to the physical and electric characteristics of MIS capacitors based on ALD HfO₂. We have found that after using a relatively constant SiOx thickness having variable Si-OH bond densities, the atomic surface roughness R_{rms} of the SiOx IL can be dramatically reduced to ~ 5 A (ideal for uniform ALD of ultrathin HfO₂ layers) by using H₂O₂ immersion times between 2 and 8 min. On the other hand, the peaks in the absorption coefficient of the Si-OH bonds were found at 3652 cm^{-1} , where larger Si-OH bond densities are obtained after using immersion times longer than 2 min, as expected. From the J-V characteristics, very low gate leakage current densities Jg are found for all samples, while the electric field for breakdown Ebd lies between 6 and 7 MV/cm, thus suggesting a highquality HfO₂ material having high resistance for dielectric breakdown and for which a broad ON/OFF window could be used for nonvolatile memory applications with high scalability. Also, the C–V characteristics show an increase in Vfb for all samples when compared with HfO₂ directly deposited on an HF-last silicon surface. By correlating the Si-OH bond densities to all these physical and electrical characteristics, we find that in order to obtain the combined characteristics of lowest R_{rms} , Jg, and Vfb, we need to use intermediate H₂O₂ immersion times between 4 and 8 min of HF-last silicon surfaces. Finally, a further study of the influence of specific Si-OH bond densities promoted by several other mechanisms (O₃ oxidation, wet/dry/plasma oxidation, etc.) with respect to even thinner HfO₂ layers is important to compare the possible advantages other Si-OH bond forming methods have with respect to our simple, yet reproducible, silicon surface conditioning technique.

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