

Kinetics Of Charge Generation During Formation Of Hf And Zr Silicate Dielectrics

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ABSTRACT

Understanding charged defects in high dielectric constant insulators is a critical challenge for advanced devices. We have formed thin Zr and Hf silicates by oxidation of thin metal films sputtered on clean Si(100) and studied the effect of oxidation time (15 to 300s) and temperature (600 or 900°C) on the flatband voltage using capacitance vs. voltage measurements. We find that the thermal budget during oxidation and the type of oxidizing agent (slow vs. fast) affect the amount of fixed charge in the film significantly. Oxidation of 0.8nm of Zr metal on Si at 600°C in N₂O for 15s results in EOT=1.2nm and a shift in the flatband voltage by ~-0.2V indicating generation of positive fixed charge. Oxidation of similar films for 300s result in EOT=2.8nm and shift of the flatband voltage by ~-0.95V. Hf films oxidized in N₂O also show increased concentrations of fixed charge for longer oxidation times. By comparison, Si oxidized in the same environment does not show this extent of flatband voltage shift. A significantly reduced charge generation rate is observed for Hf oxidation under low O₂ partial pressure. Extended oxidations (up to 1h) result in increased EOT and a slight decrease in the charged defect state density. Forming Gas Anneal (FGA) results in partial neutralization of the charge. FGA after the Al gate deposition also leads to significant decrease of the EOT (from 2.7 to 2.1nm) indicating significant reaction of the film with the gate metal. X-ray photoelectron spectroscopy for thin films indicates formation of Zr and Hf-silicates. However, for thick Hf films the low O₂ oxidation process results in less silicon incorporation in the film as compared to films oxidized in N₂O. Results suggest that understanding oxidation mechanisms will be important in isolating and controlling fixed charge in high-k dielectrics.

INTRODUCTION

Approaching the tunneling limit for the SiO₂ gate dielectric in CMOS devices has fueled research for an alternative material with a higher dielectric constant that will permit the use of physically thicker films. Several prospective materials are currently under investigation, mainly oxides and silicates of group III and IV metals. Formation of low-k interfacial layers and significant concentration of fixed charge are two of the main shortcomings of most materials investigated to date.¹ For some materials, fixed charge appears to be an intrinsic property and as such, very hard to neutralize.² In other cases, charge is generated as a result of processing conditions. Formation of interfacial layers and mixing of Si in the film are also shown to occur as a result of the deposition process.³ In this article, we present our findings regarding the effect of the oxidation rate and thermal budget on the Si content and the amount of charged defects detected in ultra-thin Hf and Zr-based high-k films on Si.

EXPERIMENTAL

We deposit 0.8-1.0nm of Hf or Zr metal on cleaned Si(100) substrates using dc sputtering as described by Chambers.⁴ After metal deposition, the films are oxidized ex-situ in a tube furnace at 600°C in the presence of N₂O, a process that is known to cause rapid oxidation. Another set of metal films is oxidized using the impurity O₂ present in dry N₂ at atmospheric pressure, following the procedure initially described by B. H. Lee et al.⁵ As a control experiment, several clean silicon substrates are oxidized in N₂O for 20 to 60 min which produces ~1.8 to 2.5nm of SiO₂.

Metal-Insulator-Semiconductor capacitors are fabricated by resistive heating evaporation of Al through shadow masks. Capacitance vs. voltage (CV) measurements are performed with a HP4284 impedance meter at 1MHz. Capacitor surface areas (typically 4x10⁻⁴cm²) is determined by optical microscopy. The NCSU program⁶ that corrects for quantum mechanical effects is used to obtain the Equivalent Oxide Thickness (EOT) and the position of the flatband voltage. For each sample the CV characteristics for several capacitors are measured and the results are averaged. Compositional analysis of the samples is performed by X-ray Photoelectron Spectroscopy (XPS) using a Riber LAS3000 (MAC2 analyzer, Mg K α (h ν =1253.6 eV) non-monochromatic X-ray source) at 75° take-off-angle with 0.1eV step size. We compensate for sample charge effects by setting the adventitious C1s peak to a binding energy of 285.0 eV.

RESULTS AND DISCUSSION

Figure 1a shows the CV curves for 0.8nm Zr films oxidized in N₂O at 600°C for 15 to 300s. Figures 1b and 1c present the flatband voltage (V_{FB}) and the equivalent oxide thickness (EOT) as a function of the oxidation time respectively. The data points represent the average of measurements on several capacitors of the same sample and the error bars represent one standard deviation. If no error bar is shown, the size of the error bar is equal to (or less than) the size of the data point symbol. The expected position of V_{FB} , calculated from the vacuum work function of the Al gate and the doping of the Si substrate is ~0V. We find that an increase in the oxidation time leads to smaller capacitances and more negative shift in the CV curve. The EOT more than doubles, from ~1.2nm for 15s oxidation to 2.8nm for 300s oxidation, due to the formation of a

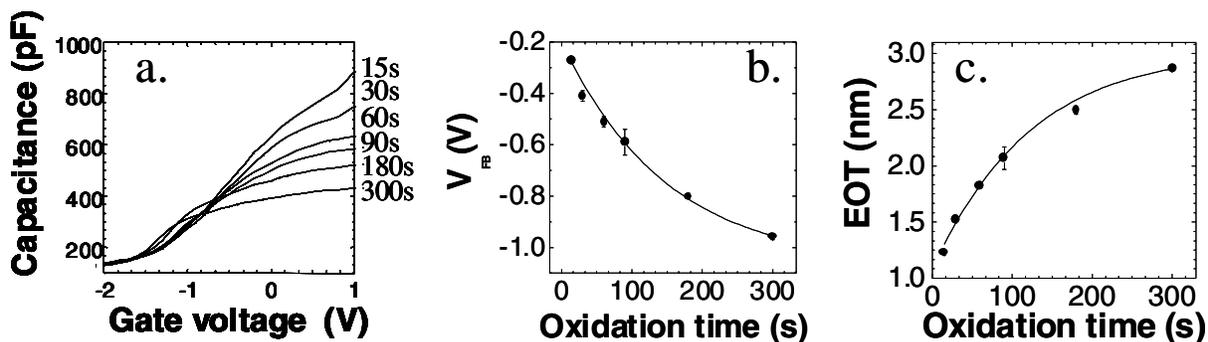


Figure 1. Capacitance vs. Voltage curves (Fig. 1a) for 0.8nm Zr-metal films oxidized in N₂O with Al gates as a function of oxidation time (legend). The flatband voltage (V_{FB}) (Fig. 1b) and EOT (Fig. 1c) vs. oxidation time plots show that extended oxidation results in oxidation of the interface that is accompanied by generation of positive fixed charge in the film.

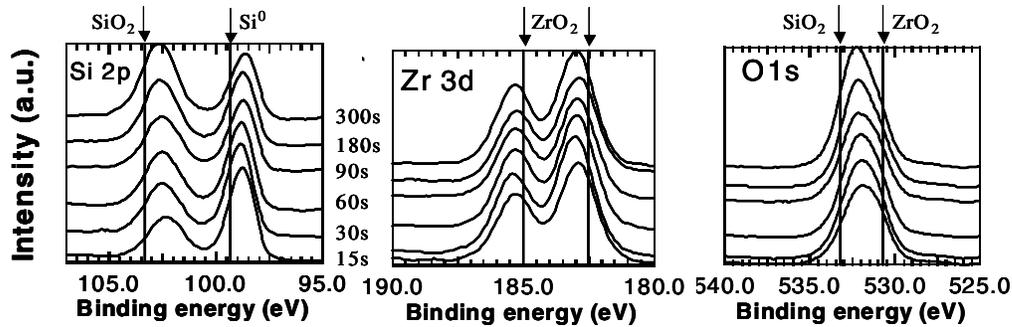


Figure 2. Si2p, Zr3d and O1s XP spectra for 0.8nm Zr metal films on Si oxidized at 600°C in N₂O. The oxidation time is given in the legend. The film is ZrSiO with a substantial SiO₂ interfacial layer.

thick interfacial layer. The flatband voltage shifts from $\sim -0.25\text{V}$ for the 15s process to $\sim -0.95\text{V}$ for the 300s process, indicating the generation of substantial amounts of positive fixed charge in the film.

Si2p, Zr3d and O1s XP spectra for the Zr samples are shown in Fig. 2. The location and width of the Si2p peak at $\sim 102.5\text{eV}$, O1s peak at $\sim 532\text{eV}$ indicates that the films are silicates^{7,8} with SiO₂ at the interface. The ratio of the ZrSiO/SiO₂ to the substrate Si⁰ peak areas increases with oxidation indicating further oxidation of the interface. The Si⁰ peak is detected for all samples and appears at a lower binding energy than expected. Opila et al. have reported and explained the relationship between fixed charge and the position of the Si⁰ peak in XP spectra for Hf and Zr silicate films.⁹ The shift in Si⁰ peak in our films can be explained by the existence of fixed charge in the layers that the substrate photoelectrons have to transverse.

Figure 3a shows the CV curves for 0.8nm Hf-metal films oxidized in N₂O at 600°C for 30 to 300s. In general, we find that an increase in the oxidation times leads to smaller capacitances (i.e. thicker films) but the shape and position of the curve remains practically unchanged for oxidation up to 120s. For the sample oxidized for 300s we observe a reduction in the capacitance and a significant shift of the curve to more negative voltage. Figure 1b is a plot of the C-V curves for 0.8nm Hf films oxidized in the N₂ ambient for 45, 90 and 300s. The capacitance of the gate stack decreases with longer oxidation, but the rate of decline is significantly slower than for N₂O oxidation, and the position of the curve is not significantly affected.

Fig. 4a presents the equivalent oxide thickness (EOT) as a function of the oxidation time

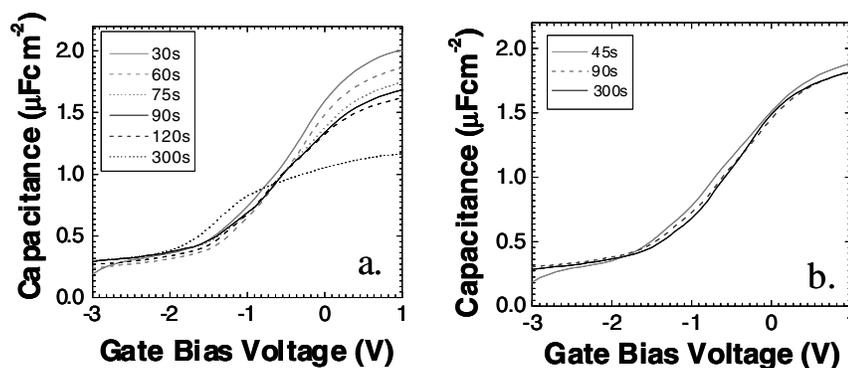


Figure 3. Capacitance vs. Voltage measurements for 8Å Hf-metal films oxidized in N₂O (Fig. 3a) and N₂ (Fig. 3b) with Al gates as a function of oxidation time (legend).

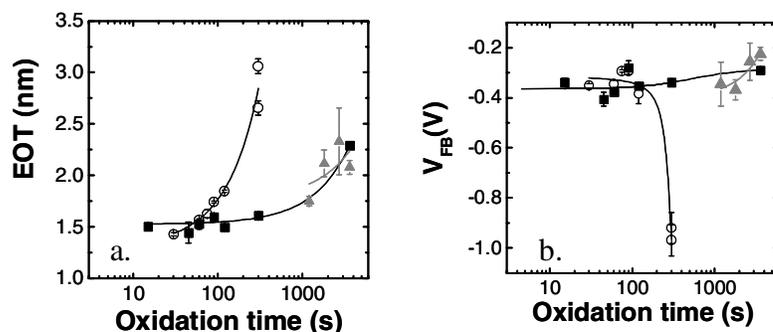


Figure 4. Equivalent Oxide Thickness (EOT) and flatband voltage V_{FB} vs. oxidation time for 0.8nm Hf-metal films oxidized in N_2 (squares) and N_2O (circles), and for H-terminated Si oxidized in N_2O (triangles).

for Hf films oxidized by N_2 and N_2O , and the control SiO_2 films. For oxidation in N_2O (circles), the EOT increases by almost a factor of two, from ~ 1.4 nm for 30s oxidation to 2.6nm for 300s oxidation. The N_2 process (squares in Fig. 4a) results in negligible increase in the EOT from 1.5nm to ~ 1.6 nm for oxidation between 15 and 300s, and increases to ~ 2.3 nm after 1h oxidation. The EOT for the control SiO_2 film data (triangles) oxidized in N_2O varies between 1.6 and 2.2nm, comparable in thickness to the interfacial layer produced during N_2O oxidation of Hf-metal films. The SiO_2 data exhibit significant scattering, which is probably due to the poor quality of SiO_2 produced with this technique. Figure 4b shows the flatband voltage (V_{FB}) vs. oxidation time for N_2O (open circles), N_2 ambient (solid squares), and control SiO_2 films (triangles). For the N_2 process, prolonged exposure leads to marginal reduction in the V_{FB} from ~ -0.375 to -0.3 V. For the N_2O process, the V_{FB} is comparable to that for the N_2 process and remains almost constant at -0.35 V for oxidations up to 120s. For 300s, though, V_{FB} becomes substantially more negative. For the control SiO_2 films, V_{FB} decreases somewhat for longer oxidation times, tracking fairly well the trend exhibited by the N_2 process.

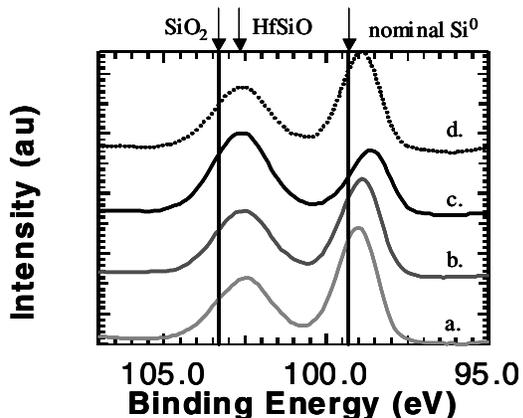


Figure 5. XP spectra for 0.8nm Hf-metal films oxidized in N_2O for (a) 30s (b) 90s (c) 300s and (d) N_2 for 300s. Spectra (a), (b) and (d) are practically identical and correspond to samples with comparable electrical properties. The $HfSiO_x/SiO_2$ peak is enhanced in spectrum (c), result of the fast interface oxidation achieved in N_2O .

$Si2p$ XP spectra for some of the samples from Figure 4 are shown in Fig. 5. The substrate peak Si^0 can be detected for these samples and the peak at ~ 102.5 eV indicates that the films are silicates^{7,8} with some SiO_2 at the interface. For the samples (a) and (b) oxidized in N_2O for 30 and 90s respectively, the ratio of the $HfSiO_x/SiO_2$ to the Si^0 peak areas is approximately the same and less than 1. However, for sample (c) oxidized in N_2O for 300s we observe substantial oxidation of the interface as evidenced by the increase in the $HfSiO_x/SiO_2$ peak area. The spectrum for the sample (d) oxidized for 300s in N_2 is comparable to spectrum (a) oxidized for 30 seconds in N_2O . The Si^0 peaks appear at a lower binding energy than expected

corroborating similar observations for the Zr-based films. Based on the electrical and the XPS data for both the Hf and Zr films we can conclude that the increase in the EOT results from an increase in the thickness of the SiO₂ interfacial layer. In general, it is believed that SiO₂ leads to a better quality silicon interface than metal oxide. For N₂O oxidation we find that rapid oxidation of the interface is accompanied by trapping of charge in both the Hf and Zr films. The data indicate that the growth rate of the interfacial layer correlates with the amount of charge generated in the film. For the Zr-based films, it appears that the amount of charge trapped in the film is proportional to the thickness of interface layer, which is proportional to the oxidation time. The Hf-based films appear more resistant to the generation of charged defects. For oxidation times in N₂O up to 120s there is no substantial effect. However, oxidation in N₂O at 600°C in for 300s results to the growth of $\sim 1.5 \pm 0.2$ nm of interfacial SiO₂ and a substantial shift of the flatband voltage. For the control samples, much slower growth of 1.6-2.2nm of SiO₂ on Si in N₂O in 20-60 min leads to significantly lower trapped charge. For the Hf samples oxidized in O-deficient environment growth of 0.7nm of interfacial SiO₂ at 600°C in 1h also results in marginal reduction in the amount of charge in the film. It appears that the defect generation mechanism involves participation of the metal atoms. High growth rate of the interfacial layer facilitates trapping of hetero-atoms near the interface. Where the covalent SiO₂ network is disrupted by the introduction of ionic bonding due to the metal atom, defects are generated. This mechanism may cause the difference in the film quality observed for fast vs. slow oxidation. It is not clear, though, why there is difference in the quality of the Hf and Zr films oxidized in N₂O.

Generation of positive fixed charge has been observed during postdeposition reoxidation of ZrO₂/SiO₂ gate stacks formed by atomic layer deposition, and the fixed charge has been attributed to formation of overcoordinated O center induced by a large density of H atoms originating from the H₂O precursor.¹⁰ Our process is H₂O free, and IR measurements on thick samples do not show any appreciable absorption of H₂O even after long ambient exposures.¹¹ Clearly more detailed experiments are required to trace the origin of this type of charge.

FGA (10%H₂ in N₂ for 30min at 400°C) performed on the Hf-based samples results in partial neutralization of the charges when performed before metallization, and almost complete removal after Al deposition. In the latter case, however, neutralization of the charge is accompanied by significant increase in the gate capacitance indicative of reaction at the dielectric-gate metal interface. FGA performed on Zr samples after the deposition of the Al gate also indicates significant reaction of the film with the gate metal. While, FGA may remove part of these defects, from a reliability standpoint it is desirable to avoid introducing the charges in the first place, as further thermal treatment and stress on the device may lead to desorption of the

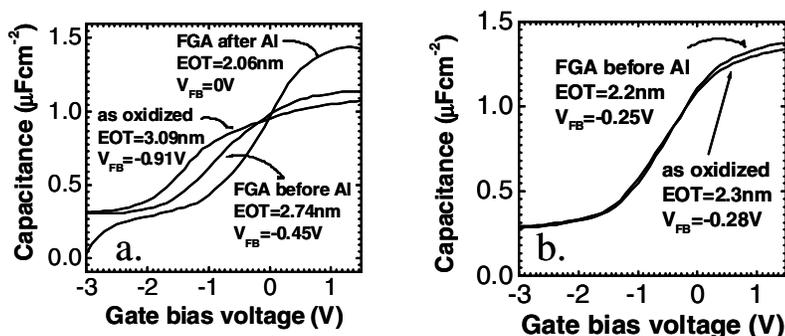


Figure 6. The effect of FGA on the CV curves of Hf films oxidized in N₂O (a) and N₂ (b).

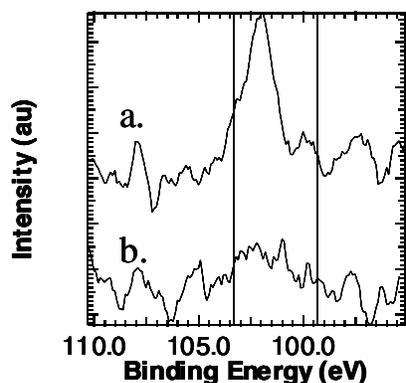


Figure 7. Si 2p XP spectra for 45nm Hf-metal films oxidized in (a) N_2O and (b) N_2 . The film oxidized in N_2O shows Si incorporation in the film.

H-atoms and regeneration of the defects, which will deteriorate carrier mobility in devices significantly.

The effect of the oxidizing agent on the film composition was also examined. Figure 7 displays the Si2p XP spectra for two similar thick (~ 45 nm metal) Hf-based films, one oxidized in N_2O for 10min (sample (a)) and the other oxidized in N_2 (sample(b)) for 10min. We observe that for the film oxidized in N_2O there is a peak at ~ 102 eV indicative of silicate bonding in the film. For the film oxidized at low O_2 partial pressure this spectral region is practically flat. The O1s and Hf4d spectra are consistent with formation of a top silicate layer for sample (a) and a HfO_2 layer for sample (b). It appears that fast oxidation of a Hf-metal film results not only in significant oxidation of the dielectric/Si

interface but also promotes Si incorporation in the bulk of the film. These findings are consistent with observations reported by Rangarajan et al.¹² for CVD Hf-based high-k films.

ACKNOWLEDGMENTS

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