

Charge generation during oxidation of thin Hf metal films on silicon

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Abstract

Oxidation of Hf metal films on Si appears to follow different charge generation rules than the traditional oxidation of Si described in detail by Deal et al. [B.E. Deal, M. Sklar, A.S. Grove, E.H. Snow, J. Electrochem. Soc. 114 (1967) 226]. Oxidation of thin Hf metal films on silicon in oxygen rich environments to form Hf-silicate results in rapid growth of silicon oxide interfacial layers and generation of significant charge concentration in the films. Oxidation of Hf in oxygen-deficient environment leads to improved control of the interface with much thinner interfacial layers and substantial reduction in the charge present in the films. Results from capacitance vs. voltage and X-ray photoelectron spectroscopy measurements are compared to correlate charge with chemical structure evolution during oxidation and dielectric layer formation. It is demonstrated that processing conditions may influence the quality of the Hf dielectric film significantly by generating positive charge that is not intrinsic to the material.

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1. Introduction

The search for a replacement material for the SiO₂ gate dielectric in *Complimentary Metal Oxide Semiconductor* devices [1] has led to the evaluation of the properties of several high dielectric constant materials, mainly oxides and silicates of groups III and IV metals [2,3]. One of the major shortcomings of most candidate materials is the large amount of charge in the film that degrades the carrier mobility in devices [2]. For some of these materials the charge is mainly inherent and as such difficult to neutralize [4].

Extensive research of the Si oxidation process by Deal et al. [5] established the guidelines for the formation of high quality SiO₂ films. The main conclusion of this work was that oxidation or post deposition inert anneals at high temperatures lead to significantly reduced concentrations of fixed charge in the SiO₂ film. This conclusion was somewhat arbitrarily extended to the oxidation of other metal films on Si and there is the widespread belief that formation of a SiO₂ interfacial layer although it may

reduce the overall gate stack capacitance offers a better quality interface in return. In this article we demonstrate that oxidation of Hf metal on Si can be different from oxidation of Si in terms of charge generation in the film. More specifically, it is shown that fast growth of the SiO₂ interfacial layer directly correlates with increased amounts of charge in the produced Hf-silicate film. This is achieved by comparing the electrical properties of HfSiO_x films prepared by oxidation of thin Hf-metal films in O-rich and O-deficient environments and correlating it to film composition measurements obtained by X-ray photoelectron spectroscopy (XPS).

2. Experimental details

Thin Hf metal films were deposited on H-terminated Si(100) substrates via *direct current or radio frequency* sputtering following the techniques described in earlier work [6]. After deposition of the metal, the films were oxidized ex-situ in a tube furnace or in a Rapid Thermal Anneal (RTA) instrument. The furnace oxidations were performed at 600 °C either in the presence of N₂O, or using the impurity O₂ or H₂O present in dry N₂ at atmospheric pressure, following the procedure initially described by B.H. Lee et al. [7]. The nominal concentration of

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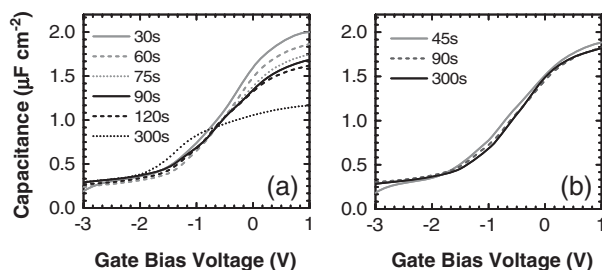


Fig. 1. Capacitance vs. voltage measurements for 0.8 nm Hf-metal films oxidized in N_2O (a) and N_2 (b) with Al gates as a function of oxidation time (legend). Oxidation in N_2O for 300 s results in substantial reduction of the capacitance and generation of positive fixed charge in the films. Oxidation up to 300 s in N_2 does not have a significant effect in the electrical properties of the films.

O_2 and H_2O in the N_2 gas was given as <5 ppm by the gas supplier (National Welders). The RTA oxidations were performed in dry air at temperatures ranging from 400 to 700 °C. The RTA chamber was purged with Ar at high air flow rates for several minutes before and after the anneal and the samples were removed only when the chamber temperature was below 200 °C to prevent undesirable reactions of the film with atmospheric components such as H_2O or CO_2 . The nominal concentration of O_2 and H_2O in the Ar gas was given as <5 ppm and <3 ppm respectively by the gas supplier (National Welders). The nominal concentration of H_2O in the dry air mixture was given as <8 ppm by the gas supplier (National Welders). The initial Hf-metal film thickness was determined by extrapolating linear time vs. step height measurements made using thicker films.

After oxidation, samples from the same run were used for compositional analysis via XPS, and for electrical characterization. XPS measurements were performed with a Riber LAS3000 (MAC2 analyzer, Mg $K\alpha$ $h\nu=1253.6$ eV, non-monochromatic X-ray source) at 75° take-off-angle with 0.1 eV step size. The energy scale was calibrated by setting the adventitious C 1s peak to a binding energy of 285.0 eV. Al top and back-contacts were formed by resistive-heating evaporation using shadow masks. Capacitance vs. voltage ($C-V$) measurements were performed with an HP 4284A impedance meter at 1 MHz. Typical capacitor area, as determined by digital photography, was 4×10^{-4} cm². Flatband voltage (V_{FB}) and equivalent oxide thickness (EOT) were obtained by processing the $C-V$ characteristics with the NCSU $C-V$ program that includes corrections for the quantum mechanical effects.[8] Some samples were annealed in forming gas (FGA) (10% H_2 in N_2) for 30 min at 400 °C using a standard Tylan furnace available in the NCSU cleanroom.

3. Results

Initially, we compare the results for N_2O vs. N_2 oxidation in the tube furnace. Fig. 1(a) shows the $C-V$ curves for 0.8 nm Hf-metal films oxidized in the tube furnace in N_2O at 600 °C for 30 to 300 s. In general, an increase in the oxidation time leads to smaller capacitances (i.e. thicker interface layers) but the shape and position of the curve

remains practically unchanged for oxidations up to 120 s. For the sample oxidized for 300 s a reduction in the capacitance and a significant shift of the curve to more negative voltage is observed. Fig. 1(b) plots the $C-V$ curves for 0.8 nm Hf films oxidized in a N_2 ambient for 45, 90 and 300 s. Even in this environment there is enough impurity O, probably in the form of O_2 and H_2O , to form metal oxide as evidenced by the capacitance measurements. The capacitance of the gate stack decreases marginally with longer oxidation, and the position of the curve is not significantly affected.

Fig. 2(a) presents the EOT as a function of the oxidation time and Fig. 2(b) presents the V_{FB} vs. oxidation time for films obtained by the two processes. The expected position of V_{FB} , calculated from the work function of the Al gate and the doping of the Si substrate is ~ 0 V. 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.

For the N_2O (circles) process the key observations are: (i) the EOT is proportional to the oxidation time and increases by almost a factor of two, from ~ 1.4 nm for 30 s oxidation to 2.8 nm for 300 s oxidation, in the conditions examined; (ii) the V_{FB} remains almost constant at -0.35 V for oxidations up to 120 s. At this point it appears that a turning point in the oxidation process is reached and longer oxidations (300 s) result in a substantially more negative V_{FB} . This particular data point is the average over several capacitors on two different samples processed in the span of several weeks.

For the N_2 process (squares) the key findings are: (i) the EOT increases marginally for oxidations up to 300 s; (ii) the small increase in the EOT from 1.5 nm to ~ 1.6 nm for oxidation between 15 and 300 s, is accompanied by a marginal reduction in the V_{FB} from ~ -0.375 to -0.3 V; (iii) to obtain an increase in the EOT comparable to the N_2O process, a 3600 s oxidation in this O deficient environment is required. This film, unlike the films oxidized in N_2O , exhibits the highest EOT but the lowest shift in the V_{FB} .

Clearly a substantial difference in the electrical quality of the films prepared in O rich and O deficient environments in the tube furnace is observed. To investigate further the charge

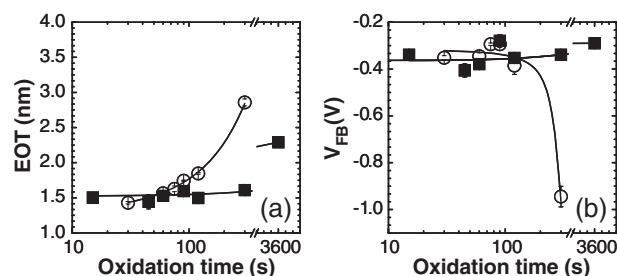


Fig. 2. Equivalent oxide thickness (EOT) and flatband voltage V_{FB} vs. oxidation time for 0.8 nm Hf-metal films oxidized in N_2 (squares) and N_2O (circles). Oxidation of Hf-metal on Si in N_2O leads to growth of thick interfacial layers that is accompanied by the generation of large amounts of charge in the case of 300 s oxidation time. Oxidation of Hf-metal on Si in N_2 and Si in N_2O leads to significantly reduced charge generation.

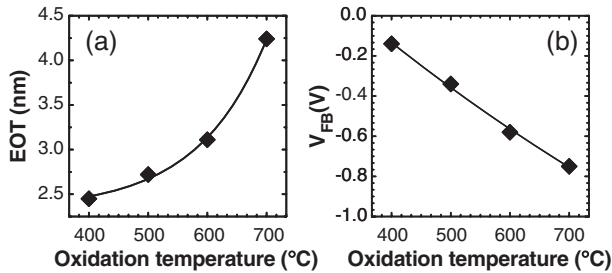


Fig. 3. Equivalent oxide thickness (EOT) and flatband voltage V_{FB} vs. oxidation temperature for 2.5 nm Hf-metal films oxidized in dry air from 2 min in an RTA. Oxidation of Hf-metal on Si at higher temperatures leads to growth of thick interfacial layers that is accompanied by the generation of large amounts of charge as evidenced by the shift in V_{FB} .

generation during fast oxidation another set of Hf-metal films was oxidized in dry air in the much cleaner environment of an RTA for 2 min at temperatures ranging from 400 °C to 700 °C. Figs. 3 (a) and (b) show the EOT and flatband voltage vs. oxidation temperature for the RTA oxidized films, respectively. As the oxidation temperature increases, the flatband voltage becomes more negative, indicative of positive charge generation in the films [9]. At the same time the EOT of the gate stack increases due to the formation of a low-k interfacial layer. The electrical characteristics of the air-RTA annealed films mirror that of the N_2O -furnace films indicating a similar charge generation mechanism.

To investigate whether a similar charge generation mechanism is responsible for the observations for the two fast oxidizing processes (N_2O -furnace vs. air-RTA) we plot (Fig. 4) the shift in the V_{FB} (ΔV_{FB}) vs. the increase in the interfacial layer thickness (ΔEOT). We assume that the increase in the EOT is exclusively due to the growth of the SiO_2 interfacial layer. For the samples oxidized in air the V_{FB} and EOT obtained for the 400 °C oxidation is treated as the baseline measurement. The situation is more complex for the samples oxidized in N_2O . Oxidation from 15 to 75 s does not affect the EOT substantially and the corresponding shift in the V_{FB} exhibits a marginal reduction. At 90 s oxidation time there is a sizable increase in

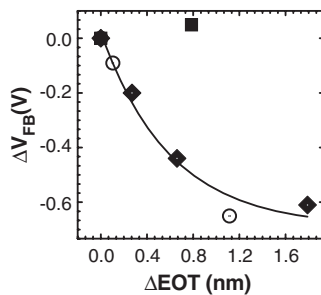


Fig. 4. Shift in the V_{FB} as a function of the interfacial layer thickness increase. For the samples oxidized in the RTA (diamonds) the V_{FB} and EOT obtained for the 400 °C oxidation is treated as the baseline measurement. For the samples oxidized in the tube furnace in N_2O at 600 °C (circles) the V_{FB} and EOT obtained for the 90 s oxidation is treated as the baseline measurement. Just for comparison purposes the long time (3600 s) N_2 oxidation point (square) is included in the graph.

the EOT and longer oxidation times reinforce this trend. At the same time the shift in the V_{FB} becomes substantially more negative. So for the samples oxidized in N_2O , the measurements for the 90 s sample are used as a baseline. Fig. 4 shows that the trend exhibited by the two sets of data is very similar suggesting a common mechanism for the generation of the charge in the films during the growth of the interfacial layer, despite the difference in the oxidation medium and method. Just for comparison purposes the long time (3600 s) N_2 oxidation point (square) is included in the graph.

Hf 4f, Si 2p and O 1s XP spectra for some of the samples are shown in Fig. 5. From the spectra it is obvious that the composition of the films is compatible with Hf-silicate [10,11] with some SiO_2 at the interface. From the Si 2p spectra, it is seen that the substrate peak Si^0 can be detected for all samples. The peak at ~ 102.5 eV is a mixture of SiO_2 and $HfSiO_x$ bonding. For the samples (i) and (ii) oxidized in N_2O for 30 and 90 s, 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 (iii) oxidized in N_2O for 300 s a substantial increase in the $HfSiO_x/SiO_2$ peak area is observed, which is now larger than the Si^0 peak. This increase in the $HfSiO_x/SiO_2$ peak area can be

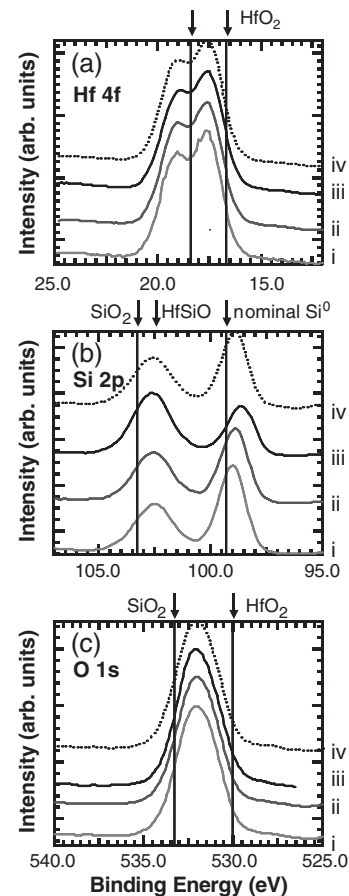


Fig. 5. Hf 4f, Si 2p and O 1s spectra for 0.8 nm-metal films oxidized in (i) N_2O for 30 s, (ii) N_2O for 90 s, (iii) N_2O for 300 s and (iv) N_2 for 300 s. Spectra (i), (ii) and (iv) are practically identical and correspond to samples with comparable electrical properties. We can observe the growth of the SiO_2 peak in the Si 2p spectrum for sample (iii), result of the fast interface oxidation achieved in N_2O .

interpreted in terms of growth of a thick interfacial SiO_2 layer. The spectrum for the sample (iv) oxidized for 300 s in N_2 is comparable to spectrum (i) oxidized for 30 s in N_2O , confirming the observations based on the electrical data that oxidation in N_2 results in much less interfacial SiO_2 .

4. Discussion

It is well established that for thermal oxidation of Si, higher thermal budget during oxidation either in the form of elevated temperature or longer oxidation or post deposition inert anneals causes significant reduction in the concentration of fixed charge in the film [5]. There is increasing evidence that the HfO_x/Si interface behaves substantially differently [12–14] than the well studied SiO_2/Si interface. The results described in this article show that there is a distinct difference in the electrical quality of the films produced during fast and slow oxidation of Hf metal on Si. In the case of fast oxidation (N_2O and dry air) rapid oxidation of the interface is accompanied by generation of charge in the film.

The rapid oxidation of the interface during the N_2O and dry air processes is evidenced by the increase in the EOT (decreased capacitance per unit area) and corroborated by the XP spectra. The electrical and the XPS data indicate that the increase in the EOT stems from an increase in the thickness of the SiO_2 interfacial layer. In general, it is believed that a Si/ SiO_2 interface is superior to a metal oxide/Si interface. The key finding of this work is that for the case of Hf-metal on Si there is a correlation between the growth rate of the interfacial layer and the amount of charge generated in the film. More specifically, fast growth of the interfacial layer such as when using N_2O or air as oxidizers, results in the generation of a substantial concentration of fixed charge. Oxidation of the Hf/Si interface in an oxygen deficient environment leads to thinner interfacial layers and less charge detection in the films. The specific results that support this conclusion are: growth of ~ 1.6 nm of interfacial SiO_2 at 600 °C in N_2O in 300 s results in -0.65 eV shift in the flatband voltage. For dry air oxidation increasing the oxidation temperature from 400 to 700 °C results in the growth of ~ 2.0 nm of additional interfacial SiO_2 in 120 s that is accompanied by a ~ -0.6 V shift of the flatband voltage (from ~ -0.2 V to ~ -0.8 V). The fact that this trend is reproducible both in the case of the furnace and the strictly controlled RTA oxidation demonstrates that the observed correlation is linked to some fundamental change in the quality of the interface and is not a side effect of poor film formation. Fig. 4 demonstrates that the charge generation mechanism is similar for the furnace (N_2O) and RTA (air) oxidations, and does not depend on the initial Hf metal film thickness. By comparison, very slow growth of 0.7 nm of interfacial SiO_2 at 600 °C in N_2 in 3600 s results in marginal reduction in the amount of charge in the film.

As a further test for the validity of our conclusions we evaluated the quality of SiO_2 films grown by oxidation of clean Si in N_2O at 600 °C in the tube furnace for 20–60 min to produce ~ 1.8 – 2.5 nm of SiO_2 . For these control SiO_2 films an increase in the oxidation time results in marginal reduction of

the amount of charge present in the film, in agreement with the well-established Si oxidation studies by Deal et al. [5].

Recent studies have demonstrated trapping of Hf atoms in SiO_2 interlayers during rapid thermal annealing of HfO_2 films on Si and suggest that these defects affect the charge transport through the film [13]. Rashkeev et al. [13] suggest the introduction of ionic bonding due to the metal atom disrupts the integrity of the covalent SiO_2 , and defects are generated. *In our study, fast oxidation of the Hf/Si interface results in the rapid growth of the SiO_2 interfacial layer, and this likely leads to the entrapment of Hf atoms in the SiO_2 interfacial layer similar to the observations of Rashkeev et al.* The presence of the Hf impurity then produces energy levels inside the Si energy gap and the C – V curves obtained in the course of this work corroborate that conclusion; the rising part of the curves is stretched over 2V, indicative of interface traps distributed evenly over the bandgap.

Gavartin et al. [13] have suggested that Atomic Layer Deposition HfO_2 films may be rich in oxygen vacancies and interstitial atoms. These vacancies can drift towards the interface resulting in the formation of Si–Hf bonds that can act as hole traps and a source of fixed charge. This explanation can partially explain the charge generation during fast oxidation but it does not account for the absence of this effect during the slow oxidation.

Generation of positive fixed charge has also been observed during postdeposition reoxidation of $\text{ZrO}_2/\text{SiO}_2$ 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 H_2O precursor [15]. Our process is H_2O free, and IR measurements on thick samples do not show any appreciable absorption of H_2O even after long ambient exposures [16]. Clearly more detailed experiments are required to trace the origin of this type of charge.

The correlation between growth of interfacial SiO_2 and presence of charge in the film is corroborated by the XPS data. The substrate Si^0 peaks appear at a lower binding energy than expected. Opila et al. have reported and explained the relationship between fixed charge and the position of the Si^0 peak in XP spectra for Hf and Zr silicate films [17]. The shift in Si^0 peak in our films can be explained by the existence of charge in the layers that the substrate photoelectrons have to transverse. For samples (i), (ii) and (iv) that exhibit comparable amounts of charge (V_{FB} shifted by ~ -0.35 V) the substrate peak appears at ~ 98.9 eV (Fig. 4) shifted by ~ -0.4 V from the nominal value of 99.3 eV. For sample (iii), which exhibits an additional ~ -0.6 V shift in the V_{FB} , the Si^0 peak is shifted by ~ -0.5 eV more than for the other samples.

FGA (data not shown) results in partial neutralization of the charges when performed before Al gate deposition and almost complete removal after Al deposition for the films oxidized in N_2O . *At the same time the stretch out of the C – V curves is reduced by about 30%.* In both cases, however, neutralization of the charge is accompanied by significant increase in the gate capacitance, indicative of reaction at the dielectric-gate metal interface. For the case of N_2 oxidation, FGA does not have an

effect on either the flatband voltage or the EOT. This may suggest that the ~ -0.4 V shift in the V_{FB} may be due to fixed or oxide charge, as FGA is known to passivate interface charge [18]. While, FGA may remove part of these defects, processes that avoid charge generation are generally preferred as further thermal treatment and stress on the device may lead to desorption of the H-atoms and regeneration of the defects, which will deteriorate carrier mobility in devices significantly.

5. Conclusions

There increasingly mounting evidence that oxidation of thin Hf-metal films on Si is a very complex process and very different from oxidation of Si. Fast oxidation leads to growth of thick interfacial layers and the generation of significant concentration of charge in the film. Slow oxidation allows better control of the interface and results in significantly reduced charge in the film. FGA on capacitors with Al gates yields inconclusive results due to reaction in the gate metal/dielectric interface.

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