Charge generation during oxidation of thin Hf metal films on silicon

Theodosia Gougousi *, David B. Terry, Gregory N. Parsons

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC 27695, USA

Received 1 November 2005; received in revised form 1 February 2006; accepted 1 February 2006
Available online 15 March 2006

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.

© 2006 Elsevier B.V. All rights reserved.

PACS: 73.61.Ng; 77.55.+f

Keywords: Hafnium oxide; Charge defects; Dielectrics; Interfaces; Oxidation

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 HfSiOₓ 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...
Some samples were annealed in forming gas (FGA) (10% H2 in atmospheric components such as H2O or O2). 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 H2O or CO2. The nominal concentration of O2 and H2O in the Ar gas was given as <5 ppm and <3 ppm respectively by the gas supplier (National Welders). The nominal concentration of H2O 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 Kα hv=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 (VFB) 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% H2 in N2) for 30 min at 400 °C using a standard Tylan furnace available in the NCSU cleanroom.

3. Results

Initially, we compare the results for N2O vs. N2 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 N2O 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 N2 ambient for 45, 90 and 300 s. Even in this environment there is enough impurity O, probably in the form of O2 and H2O, 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.

O2 and H2O in the N2 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 H2O or CO2. The nominal concentration of O2 and H2O in the Ar gas was given as <5 ppm and <3 ppm respectively 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 Kα hv=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 (VFB) 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% H2 in N2) for 30 min at 400 °C using a standard Tylan furnace available in the NCSU cleanroom.

Fig. 1. Capacitance vs. voltage measurements for 0.8 nm Hf-metal films oxidized in N2O (a) and N2 (b) with Al gates as a function of oxidation time (legend). Oxidation in N2O 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 N2 does not have a significant effect in the electrical properties of the films.

Initially, we compare the results for N2O vs. N2 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 N2O 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 N2 ambient for 45, 90 and 300 s. Even in this environment there is enough impurity O, probably in the form of O2 and H2O, 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. Equivalent oxide thickness (EOT) and flatband voltage VFB vs. oxidation time for 0.8 nm Hf-metal films oxidized in N2 (squares) and N2O (circles). Oxidation of Hf-metal on Si in N2O leads to growth of thick interfacial layers (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 N2 ambient for 45, 90 and 300 s. Even in this environment there is enough impurity O, probably in the form of O2 and H2O, 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. Equivalent oxide thickness (EOT) and flatband voltage VFB vs. oxidation time for 0.8 nm Hf-metal films oxidized in N2 (squares) and N2O (circles). Oxidation of Hf-metal on Si in N2O leads to growth of thick interfacial layers (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 N2 ambient for 45, 90 and 300 s. Even in this environment there is enough impurity O, probably in the form of O2 and H2O, 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.
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 N2O-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 (N2O-furnace vs. air-RTA) we plot (Fig. 4) the shift in the $V_{\text{FB}}$ ($\Delta V_{\text{FB}}$) vs. the increase in the interfacial layer thickness ($\Delta$EOT). We assume that the increase in the EOT and longer oxidation times reinforce this trend. At the same time the shift in the $V_{\text{FB}}$ becomes substantially more negative. So for the samples oxidized in N2O, 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) N2 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 SiO2 at the interface. From the Si 2p spectra, it is seen that the substrate peak Si0 can be detected for all samples. The peak at $\sim$ 102.5 eV is a mixture of SiO2 and HfSiOx bonding. For the samples (i) and (ii) oxidized in N2O for 30 and 90 s, respectively, the ratio of the HfSiOx/SiO2 to the Si0 peak areas is approximately the same and less than 1. However, for sample (iii) oxidized in N2O for 300 s a substantial increase in the HfSiOx/SiO2 peak area is observed, which is now larger than the Si0 peak. This increase in the HfSiOx/SiO2 peak area can be observed in the EOT and longer oxidation times reinforce this trend. At the same time the shift in the $V_{\text{FB}}$ becomes substantially more negative. So for the samples oxidized in N2O, 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) N2 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 SiO2 at the interface. From the Si 2p spectra, it is seen that the substrate peak Si0 can be detected for all samples. The peak at $\sim$ 102.5 eV is a mixture of SiO2 and HfSiOx bonding. For the samples (i) and (ii) oxidized in N2O for 30 and 90 s, respectively, the ratio of the HfSiOx/SiO2 to the Si0 peak areas is approximately the same and less than 1. However, for sample (iii) oxidized in N2O for 300 s a substantial increase in the HfSiOx/SiO2 peak area is observed, which is now larger than the Si0 peak. This increase in the HfSiOx/SiO2 peak area can be observed in the EOT and longer oxidation times reinforce this trend. At the same time the shift in the $V_{\text{FB}}$ becomes substantially more negative. So for the samples oxidized in N2O, 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) N2 oxidation point (square) is included in the graph.
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$_2$O, 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$_2$/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$_2$O 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$_2$O 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$_2$O 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 $\sim$1.6 nm of interfacial SiO$_2$ at 600 °C in N$_2$O in 300 s results in $\sim$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 $\sim$2.0 nm of additional interfacial SiO$_2$ in 120 s that is accompanied by a $\sim$$-0.6$ V shift of the flatband voltage (from $\sim$0.2 V to $\sim$0.8 V). The fact that this trend is reproducible both in the case of the furnace and the strictly controlled RTA oxidation demonstrates that the observed correlation is linked to some fundamental change in the quality of the interface and is not a side effect of poor film formation. Fig. 4 demonstrates that the charge generation mechanism is similar for the furnace (N$_2$O) and RTA (air) oxidations, and does not depend on the initial Hf metal film thickness. By comparison, very slow growth of 0.7 nm of interfacial SiO$_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$_2$O at 600 °C in the tube furnace for 20–60 min to produce $\sim$1.8–2.5 nm of SiO$_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 2 V, 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 ZrO$_2$/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$_2$O precursor [15]. Our process is H$_2$O free, and IR measurements on thick samples do not show any appreciable absorption of H$_2$O 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 photolelectrons have to transverse. For samples (i), (ii) and (iv) that exhibit comparable amounts of charge ($V_{FB}$ shifted by $\sim$−0.35 V) the substrate peak appears at $\sim$98.9 eV (Fig. 4) shifted by $\sim$−0.4 V from the nominal value of 99.3 eV. For sample (iii), which exhibits an additional $\sim$0.6 V shift in the $V_{FB}$, the Si$^0$ peak is shifted by $\sim$−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$_2$O. 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 $\sim-0.4$ 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.

Acknowledgements

The authors would like to thank Scott W. Burnside, and C. Franklin Goldsmith for assistance with the electrical data, and M. Jason Kelly for assistance with the Al deposition and helpful discussions. Financial support from SRC and NSF 00-72784 is gratefully acknowledged.

References