# Ultrathin Hafnium Oxide with Low Leakage and Excellent Reliability for Alternative Gate Dielectric Application

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## Abstract

Physical, electrical and reliability characteristics of ultra thin $HfO_2$ as an alternative gate dielectric were studied for the first time. Crucial process parameters of oxygen modulated dc magnetron sputtering were optimized to achieve an equivalent oxide thickness(EOT) of 11.5Å without deducting the quantum mechanical effect. Leakage current was $3x10^{-2}A/cm^2$ at +1V. Excellent dielectric properties such as high dielectric constant, low leakage current, good thermal stability, negligible dispersion and good reliability were demonstrated.

## Introduction

Gate dielectric materials having high dielectric constant, large band gap with a favorable band alignment, low interface state density and good thermal stability are needed for future gate dielectric application.

Unfortunately, many high-k materials such as $Ta_2O_5$, $TiO_2$, $SrTiO_3$, and $BaSrTiO_3$ are thermally unstable when directly contacted with silicon[1] and need an additional barrier layer which may add process complexity and impose thickness scaling limit.

Also, materials having too low or too high dielectric constant may not be adequate choice for alternative gate dielectric application. Ultra high-k materials such as STO or BST may cause fringing field induced barrier lowering effect[2]. Materials having relatively low dielectric constant such as $Al_2O_3$ and $Y_2O_3$ do not provide sufficient advantages over $SiO_2$ or $Si_3N_4$[3].

Among the medium-k materials compatible with silicon, oxides of Zr and Hf are attracting much attention recently. Especially, Hf forms the most stable oxide with the highest heat of formation($\Delta H_f$ = 271Kcal/mol) among the elements in IVA group of the periodic table(Ti,Zr,Hf). Hf can also reduce the native $SiO_2$ layer to form $HfO_2$. Unlike other silicides, the silicide of Hf can be easily oxidized[4]. The dielectric constant of $HfO_2$ is ~30 with the bandgap of 5.68eV[5]. $HfO_2$ is very resistive to impurity diffusion and intermixing at the interface because of it's high density ($9.68g/cm^3$)[5]. In addition, $HfO_2$ is compatible with $n^+$ polysilicon gate without any barrier materials[6]. These properties make $HfO_2$ one of the most promising candidates for alternative gate dielectric application.

In this paper, we present the process characteristics of reactive dc magnetron sputtering with oxygen modulation and the electrical characteristics and reliability aspects of ultra thin $HfO_2$.

## Experiments and material characterization

$HfO_2$ was deposited directly on p-type silicon substrate using two step reactive dc magnetron sputtering. At first, thin hafnium layer is deposited and annealed in vacuum. Then, thin $HfO_2$ layer was deposited in $Ar+O_2$ ambient. At this step, $O_2$ flow was modulated to control the interface quality and the growth of interfacial layer(Fig.1). Hf layer works as an oxidation barrier during $HfO_2$ deposition. Pt was used as a top electrode for metal-insulator-semiconductor (MIS). For comparison, metal-insulator-metal (MIM) devices were fabricated with Pt and Ir as top and bottom electrode respectively. Pt was patterned using aqua regia solution ($1HNO_3$:7HCl:$5H_2O$) at 80°C and the active area for MIS (Pt /$HfO_2$/Si) capacitor was $5x10^{-5}cm^2$.

Equivalent oxide thickness(EOT) was extracted from the accumulation capacitance at 1MHz and quantum mechanical correction was not applied. Leakage current was measured in ±3V range. Gate bias was swept from 0V to ±3V respectively for fresh device to reduce the initial stress. Reliability characteristics were studied under negative bias to avoid the current saturation problem. Various analysis methods such as XPS, XRD, and spectroscopic ellipsometry were used to analyze the physical properties of $HfO_2$ films.

Process parameters such as pressure, oxygen flow rate, and deposition temperature were optimized for the lowest EOT while maintaining low leakage current. Since excessive oxidation step causes growth of the interfacial layer and an increase of EOT(Fig.2), the control of oxygen amount is critical in this process. Thus, deposition times for Hf($t_1$) and $HfO_2$($t_2$) need to be optimized(Fig.3). The EOT of 45Å $HfO_2$ was reduced to 13.5Å by introducing oxygen flow stabilization period($t_s$) to avoid the initial oxygen burst effect(Fig.4). The EOT of $HfO_2$ film could be further decreased to 11.5Å when in-situ post deposition annealing was done in vacuum and Pt electrode was deposited immediately afterward. If quantum mechanical effect is deducted, the EOT of this thin $HfO_2$ is 9Å, the smallest value ever reported for $HfO_2$ dielectric.

When the process was properly optimized, the dielectric constant of $HfO_2$ layer deposited on silicon approached to the value obtained at the MIM(Pt/$HfO_2$/Ir) capacitor(~28) and the contribution of interfacial layer to the EOT was reduced to about 6Å(Fig.5). The effective dielectric constant of MIS capacitor including the interfacial layer varied in the range of 6-16 depending on the process condition and film thickness. Spectroscopic ellipsometry showed that the thickness of interfacial layer is around 20-22Å after annealing(Fig.6). Thus,



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based on the interfacial layer thickness extrapolated from Fig.5 and the observed thickness from spectroscopic ellipsometry, the dielectric constant of interfacial layer is found to be around 13-14.5. This implies that the composition of interfacial layer is rather close to that of hafnium silicate.

The EOT of $HfO_2$ was stable up to 700°C and even decreased for thick film(Fig.7). The thinnest sample showed a considerable increase in EOT after furnace annealing in $O_2$. This EOT increase is due to the excessive oxygen diffused into the interface through Pt electrode and thin $HfO_2$ film because such EOT increase could be suppressed by post metal rapid thermal annealing in nitrogen ambient(data not shown)[7]. Thick $HfO_2$ (185Å) film starts to be crystallized at 700°C (Fig.8). Thus, the EOT decrease for thick films appears to be due to the film densification and crystallization. Although crystallization can increase the leakage current for some metal oxides[8,9], the leakage current of $HfO_2$ was actually decreased as the annealing temperature increased. $HfO_2$ deposited at room temperature has a slightly oxygen rich composition and elemental Hf atoms still exist in the film(Fig.9). Elemental Hf atoms disappeared after 600°C annealing. The shift in silicon binding energy from Si to Si-O after annealing indicate the growth of interfacial layer after furnace annealing in $O_2$(Fig.9).

## Electrical and reliability characteristics

Normal CV characteristics was observed for $HfO_2$ capacitor even with an EOT <11.5Å(Fig.4). The leakage current of $HfO_2$ capacitor with the thinnest EOT(11.5Å) was $3x10^{-2}A/cm^2$ at Vg=+1V(Fig.10) and this leakage current is several orders of magnitude lower than that of $SiO_2$ at the same EOT(Fig.11). Note that J for negative polarity is about an order of magnitude lower than +Vg.

Since the charge trapping or detrapping at the gate dielectric causes the shift in flat band voltage, hysteresis of CV curve is an important indicator for threshold voltage controllability. When the gate bias was swept in ±3V, hysteresis due to the charge trapping was around 100-150mV for $HfO_2$ films annealed at 500°C in $N_2$ ambient. However, hysteresis can be reduced to even lower level by the proper post metal annealing(Fig.12). For ±1V operation, the hysteresis becomes negligible. There was no significant frequency dependence of capacitance(<1%/dec) for most process conditions(Fig.13).

As discussed above, the interfacial layer is hafnium silicate which contains Hf-Si-O bonds. Due to Si-O bonds in the interfacial layer, the interface state density of $HfO_2$ determined by Terman method was comparable to that of $SiO_2$(~$10^{11}$/$eVcm^2$)(Fig.14).

The leakage current of $HfO_2$ is determined by the combined effects of silicate interfacial layer and $HfO_2$ layer. As the physical thickness of $HfO_2$ layer decreased, leakage current showed more tunneling like behavior governed by the silicate layer(Fig.10). Thus, the temperature dependence of leakage was weaker for thin $HfO_2$(Fig.15).

The breakdown field of $HfO_2$ was inversely proportional to the physical thickness and increased to 11-13MV/cm(without $O_2$ stabilization) and ~7MV/cm(with $O_2$ stabilization) as the physical thickness decreased to 40-50Å(Fig.16). Lower breakdown field for $HfO_2$ films with thinner interfacial layer can be explained using simple series capacitor model[10,11].

Since the EOT of interfacial layer can be extrapolated from the curve in Fig.5, the electric field across the $HfO_2$ layer and interfacial layer at breakdown can be estimated. Interestingly, the calculated breakdown field for $HfO_2$ layer were all around 4MV/cm regardless of physical thickness and EOT(Fig.17). This value well matches with 2 - 4.5MV/cm reported for thick CVD $HfO_2$ films[5]. This result indicates that the breakdown process probably occurs at the $HfO_2$ layer rather than the interfacial layer. Also, the model suggests that the reliability of $HfO_2$ film will converge to that of bulk film as the EOT is further reduced by the scaling of interfacial silicate layer. Thus, for good reliability and interface properties, the presence of minimal interfacial silicate layer is necessary.

TDDB measurement showed that there was no considerable charge trapping for most process conditions (Fig.18). Also, no significant stress induced leakage current(SILC) current was observed(Fig.19). Due to the excellent reliability characteristics as shown above, the lifetime longer than 10 years was achieved for $HfO_2$ with an EOT of 13.5 Å even at $V_{DD}$=2V(Fig.20).

## Conclusion

For the first time, various aspects of ultra thin $HfO_2$ as an alternative gate dielectric were studied. Key process parameters of oxygen modulated dc magnetron sputtering were found and optimized to obtain EOT less than 11.5Å(~9Å if deducting the quantum mechanical effect). Excellent dielectric properties such as high dielectric constant, low leakage current, good thermal stability, negligible dispersion and excellent reliability were demonstrated. These results suggest that $HfO_2$ is a promising material for the future gate dielectric application.


## Acknowledgement

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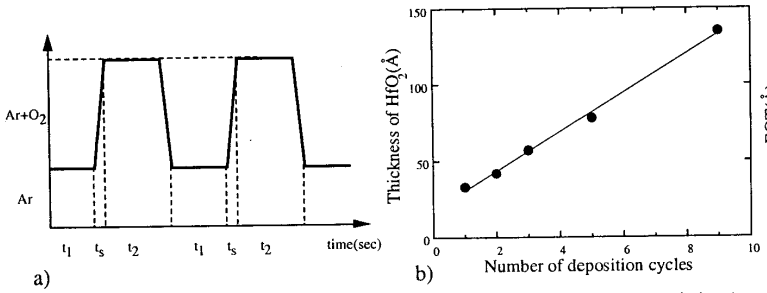


Fig.1 Reactive dc magnetron sputtering process; a) Schematic diagram of process($t_1$ period = Ar ambient,$t_2$ = Ar+$O_2$ ambient, $t_s$ = $O_2$ flow stabilization period), b) Film thickness is linearly proportional to the process cycles.

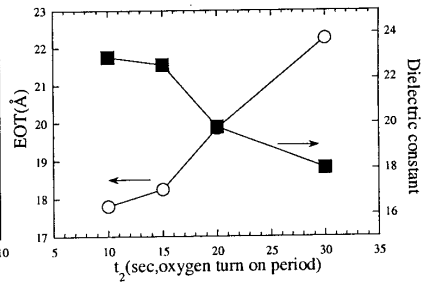


Fig.2 The effect of oxidation time $t_2$ on EOT with a fixed $t_1$. Dielectric constant of $HfO_2$ layer drops when oxidation time $t_2$ is excessive.

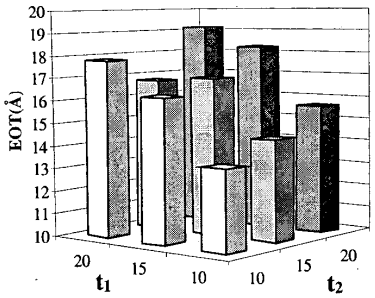


Fig.3 13.5Å of EOT is obtained by optimizing $t_1$ and $t_2$.

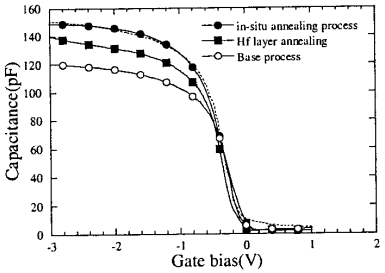


Fig.4 Typical CV curve of $HfO_2$ capacitor showing the effect of oxygen supply control. Dashed line is a modified curve accounting quantum mechanical effect.

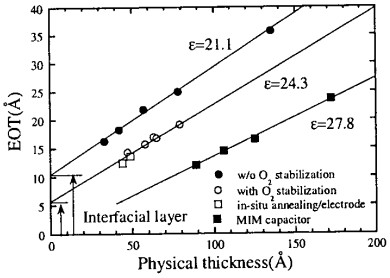


Fig.5 Extrapolation of EOT vs physical thickness curve shows the thickness of interfacial layer. Inverse of slope is the relative dielectric constant.

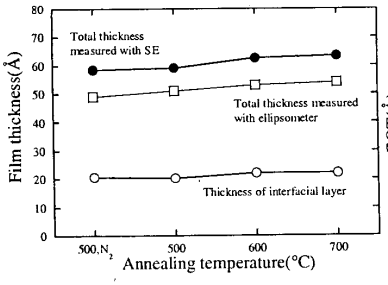


Fig.6 Interfacial layer thickness measured with spectroscopic ellipsometer.

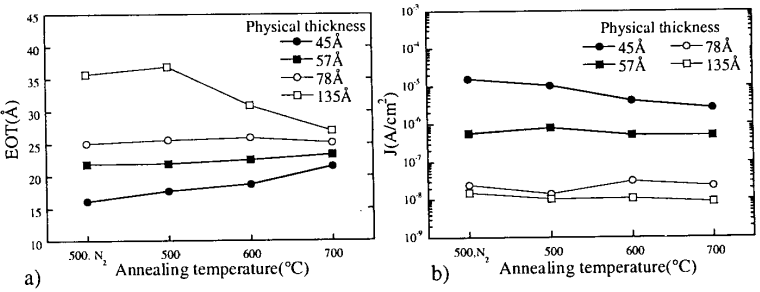


Fig.7 The effect of annealing in oxygen ambient on a) EOT and b) Leakage current at Vg=+1V.

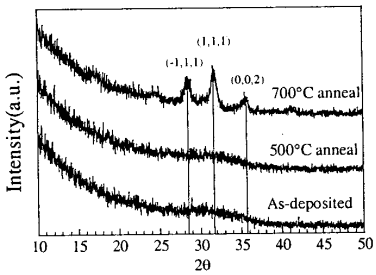


Fig.8 XRD peak of 185Å $HfO_2$ films showing that the film is crystallized after 700°C anneal.

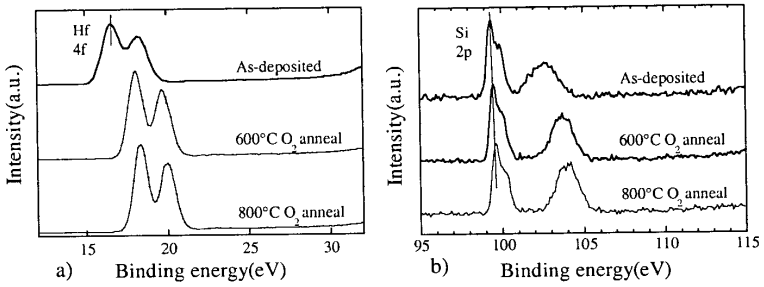


Fig.9 Binding energy shift of 45Å $HfO_2$ after annealing; a) Hafnium peak, b) Silicon peak.



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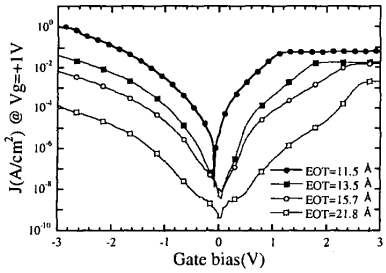



Fig.10 Typical J-V curve of $HfO_2$ capacitors for various film thickness.

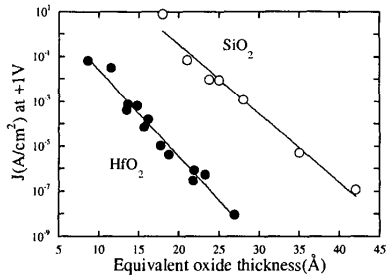



Fig.11 At the same EOT, $HfO_2$ films show lower leakage current than conventional $SiO_2$.

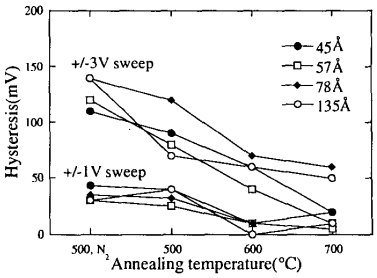



Fig.12 Hysteresis of $HfO_2$ decreases as the annealing temperature increases.

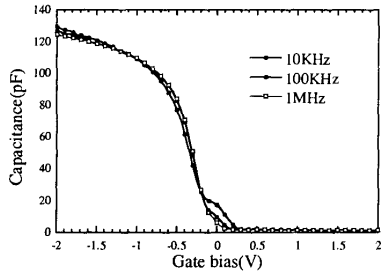



Fig.13 $HfO_2$ film has a negligible frequency dispersion at the frequency range of 10kHz – 1MHz.

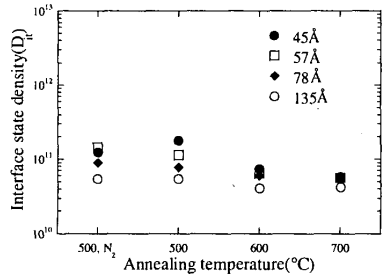



Fig.14 Interface state density determined by Terman method.

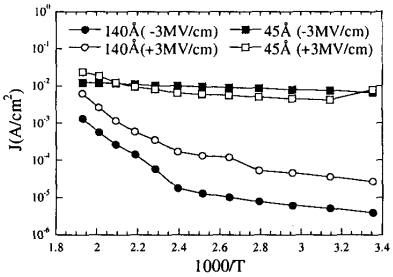



Fig.15 The temperature dependence of leakage current for thick and thin $HfO_2$.

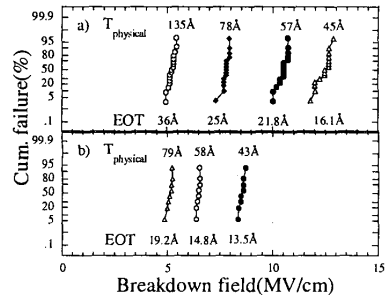



Fig.16 Breakdown field under –Vg increases as the physical thickness of $HfO_2$ film decreases; a) w/o $O_2$ flow stabilization, b) with $O_2$ flow stabilization.

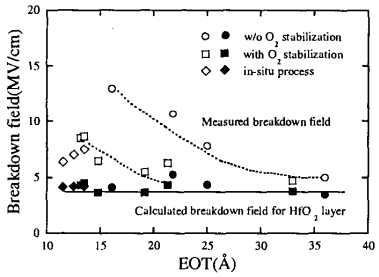



Fig.17 Modeled breakdown field for $HfO_2$ layer showing that the actual breakdown field is around -4MV/cm.

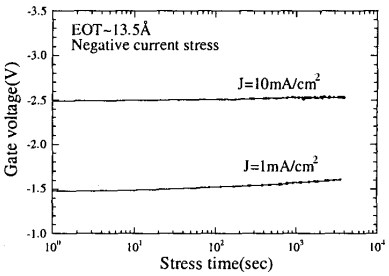



Fig.18 Time dependence of gate voltage shows that there is no significant charge trapping.

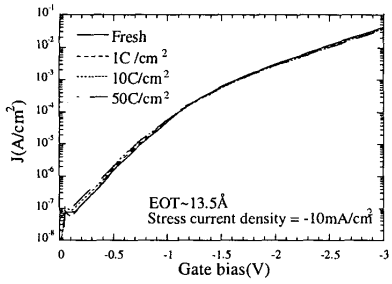
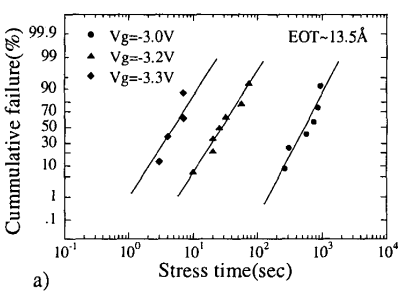



Fig.19 Stress induced leakage current (SILC) characteristic of thin $HfO_2$.



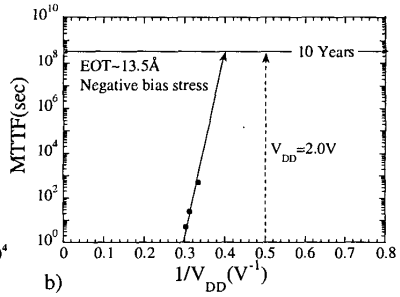




Fig.20 Reliability characteristics of 45Å $HfO_2$ ; a) Cumulative breakdown distribution under negative bias stress, b) Lifetime extrapolation.



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