

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 11.5\AA without deducting the quantum mechanical effect. Leakage current was $3 \times 10^{-2} \text{A/cm}^2$ at $+1\text{V}$. 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($\Delta H_f = 271\text{Kcal/mol}$) 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 its 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 $\text{Ar}+\text{O}_2$ 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 ($1\text{HNO}_3:7\text{HCl}:5\text{H}_2\text{O}$) at 80°C and the active area for MIS (Pt/ HfO_2 /Si) capacitor was $5 \times 10^{-5} \text{cm}^2$.

Equivalent oxide thickness(EOT) was extracted from the accumulation capacitance at 1MHz and quantum mechanical correction was not applied. Leakage current was measured in $\pm 3\text{V}$ range. Gate bias was swept from 0V to $\pm 3\text{V}$ 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 45\AA HfO_2 was reduced to 13.5\AA 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 11.5\AA 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 9\AA , 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 6\AA (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 $20\text{-}22\text{\AA}$ 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 HfO₂ 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 O₂. This EOT increase is due to the excessive oxygen diffused into the interface through Pt electrode and thin HfO₂ film because such EOT increase could be suppressed by post metal rapid thermal annealing in nitrogen ambient(data not shown)[7]. Thick HfO₂ (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 HfO₂ was actually decreased as the annealing temperature increased. HfO₂ 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 O₂(Fig.9).

Electrical and reliability characteristics

Normal CV characteristics was observed for HfO₂ capacitor even with an EOT <11.5Å(Fig.4). The leakage current of HfO₂ capacitor with the thinnest EOT(11.5Å) was $3 \times 10^{-2} \text{A/cm}^2$ at $V_g = +1\text{V}$ (Fig.10) and this leakage current is several orders of magnitude lower than that of SiO₂ at the same EOT(Fig.11). Note that J for negative polarity is about an order of magnitude lower than +V_g.

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 $\pm 3\text{V}$, hysteresis due to the charge trapping was around 100-150mV for HfO₂ films annealed at 500°C in N₂ ambient. However, hysteresis can be reduced to even lower level by the proper post metal annealing(Fig.12). For $\pm 1\text{V}$ 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 HfO₂ determined by Terman method was comparable to that of SiO₂($\sim 10^{11} \text{eVcm}^{-2}$)(Fig.14).

The leakage current of HfO₂ is determined by the combined effects of silicate interfacial layer and HfO₂ layer. As the physical thickness of HfO₂ 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 HfO₂(Fig.15).

The breakdown field of HfO₂ was inversely proportional to the physical thickness and increased to 11-13MV/cm(without O₂ stabilization) and $\sim 7\text{MV/cm}$ (with O₂ stabilization) as the physical thickness decreased to 40-50Å(Fig.16). Lower breakdown field for HfO₂ 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 HfO₂ layer and interfacial layer at breakdown can be estimated. Interestingly, the calculated breakdown field for HfO₂ 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 HfO₂ films[5]. This result indicates that the breakdown process probably occurs at the HfO₂ layer rather than the interfacial layer. Also, the model suggests that the reliability of HfO₂ 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 HfO₂ with an EOT of 13.5 Å even at $V_{DD} = 2\text{V}$ (Fig.20).

Conclusion

For the first time, various aspects of ultra thin HfO₂ 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($\sim 9\text{Å}$ 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 HfO₂ is a promising material for the future gate dielectric application.

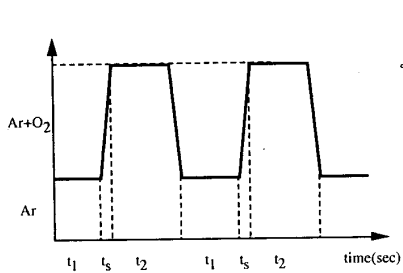
Acknowledgement

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References

- [1] K.J.Hubbard and D.G.Schlom, *J. Mater. Res.* **11**, 2757 (1996).
- [2] B.Cheng et al, *IEEE Tran. Electron Device*, **46**, 1537, (1999).
- [3] C.T.Liu, *Tech. Dig. Of IEDM*, p.747, (1999).
- [4] S.P.Muraka and C.C.Chang, *Appl. Phys. Lett.* **37**, 639 (1980).
- [5] M.Balog et al, *Thin Solid Films*, vol.**41**, 247 (1977).
- [6] Y.Jeon et al, submitted to the late news of IEDM, (1999).
- [7] In preparation.
- [8] S.Ezhilvalavan and Tseung-Yuen Tseng, *J. Appl. Phys.* **83**, 4797 (1998).
- [9] G.D.Wilk and R.M.Wallace, *Appl. Phys. Lett.* **74**, 2854 (1999).
- [10] Y.Nishioka, H.Shinriki, and K.Mukai, *J.Appl.Phys.* **15**, 2335 (1987).
- [11] Byoung Hun Lee et al, *Appl. Phys. Lett.* **74**, 3143 (1999).

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a) Fig. 1 Reactive dc magnetron sputtering process; a) Schematic diagram of process (t_1 period = Ar ambient, t_2 = Ar+O₂ ambient, t_s = O₂ flow stabilization period), b) Film thickness is linearly proportional to the process cycles.

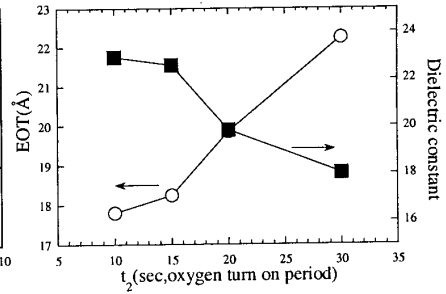
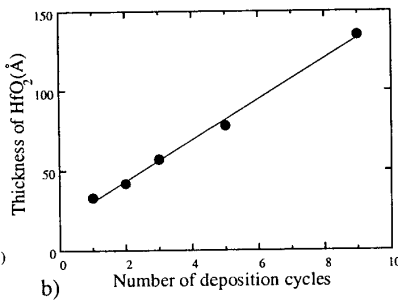


Fig. 2 The effect of oxidation time t_2 on EOT with a fixed t_1 . Dielectric constant of HfO₂ layer drops when oxidation time t_2 is excessive.

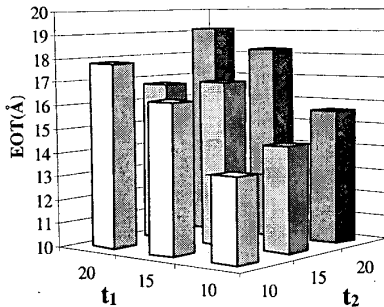


Fig. 3 13.5 Å of EOT is obtained by optimizing t_1 and t_2 .

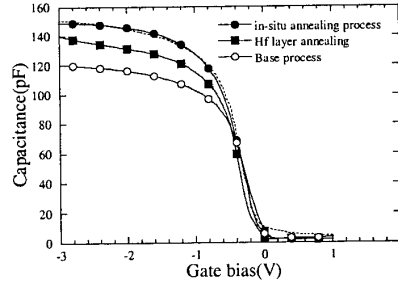


Fig. 4 Typical CV curve of HfO₂ capacitor showing the effect of oxygen supply control. Dashed line is a modified curve accounting quantum mechanical effect.

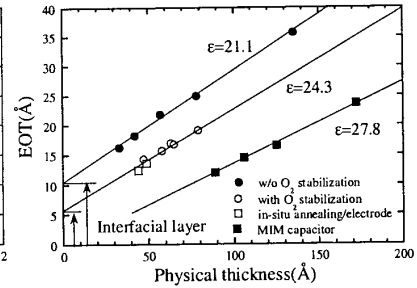


Fig. 5 Extrapolation of EOT vs physical thickness curve shows the thickness of interfacial layer. Inverse of slope is the relative dielectric constant.

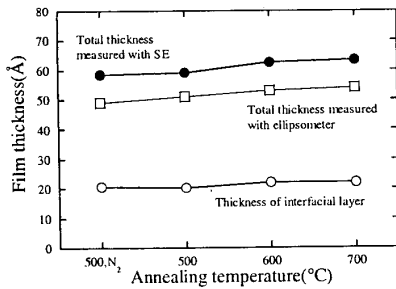


Fig. 6 Interfacial layer thickness measured with spectroscopic ellipsometer.

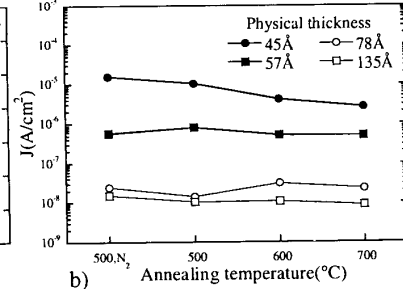
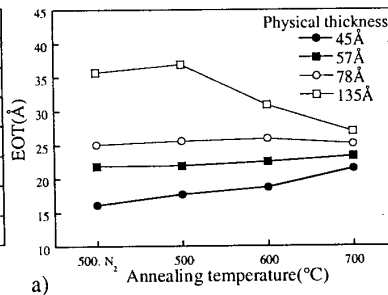


Fig. 7 The effect of annealing in oxygen ambient on a) EOT and b) Leakage current at $V_g=+1V$.

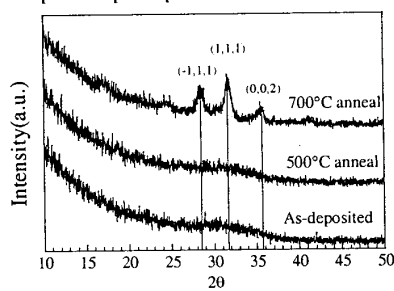


Fig. 8 XRD peak of 185 Å HfO₂ films showing that the film is crystallized after 700°C anneal.

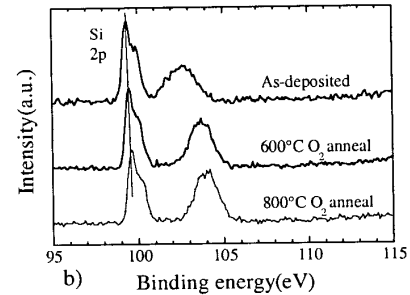
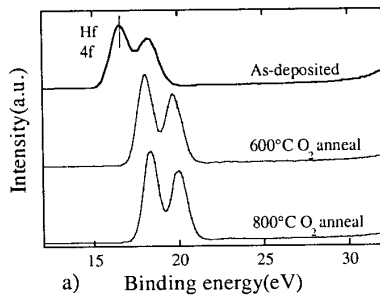


Fig. 9 Binding energy shift of 45 Å HfO₂ after annealing; a) Hafnium peak, b) Silicon peak.

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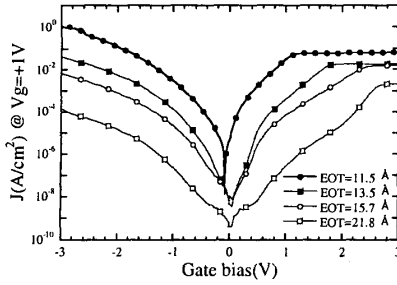


Fig. 10 Typical J-V curve of HfO₂ capacitors for various film thickness.

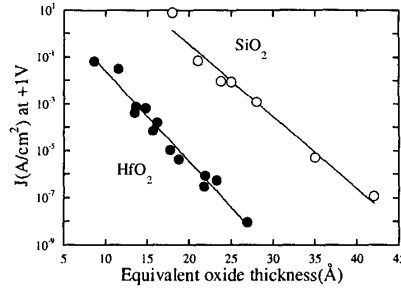


Fig. 11 At the same EOT, HfO₂ films show lower leakage current than conventional SiO₂.

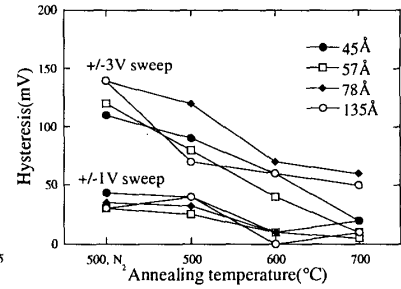


Fig. 12 Hysteresis of HfO₂ decreases as the annealing temperature increases.

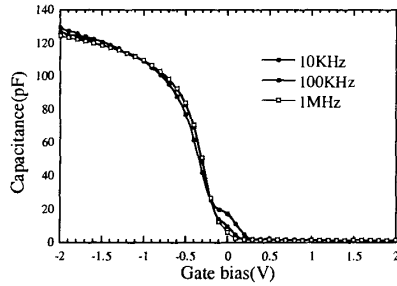


Fig. 13 HfO₂ film has a negligible frequency dispersion at the frequency range of 10kHz – 1MHz.

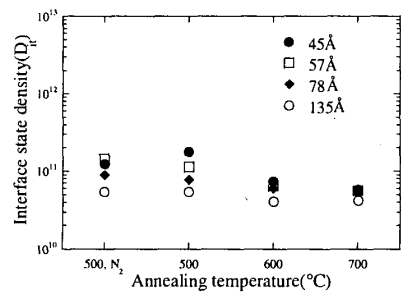


Fig. 14 Interface state density determined by Terman method.

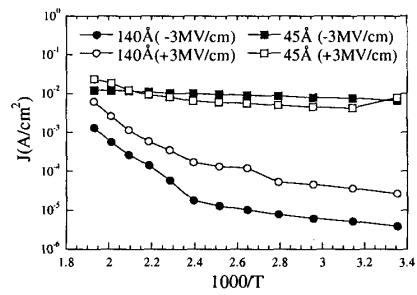


Fig. 15 The temperature dependence of leakage current for thick and thin HfO₂.

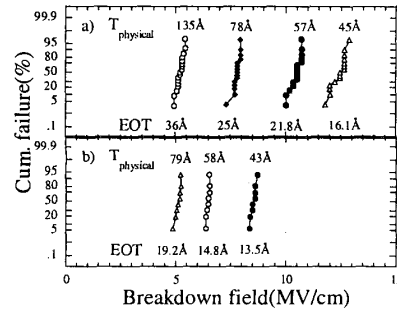


Fig. 16 Breakdown field under $-V_g$ increases as the physical thickness of HfO₂ film decreases; a) w/o O₂ flow stabilization, b) with O₂ flow stabilization.

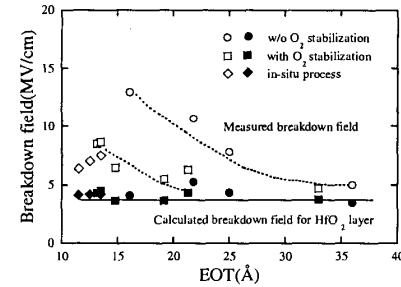


Fig. 17 Modeled breakdown field for HfO₂ layer showing that the actual breakdown field is around -4MV/cm.

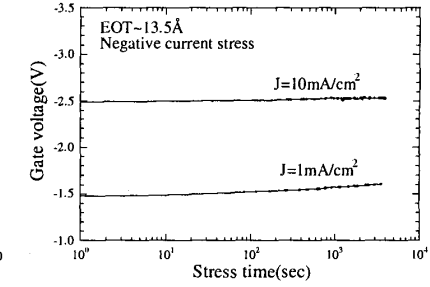


Fig. 18 Time dependence of gate voltage shows that there is no significant charge trapping.

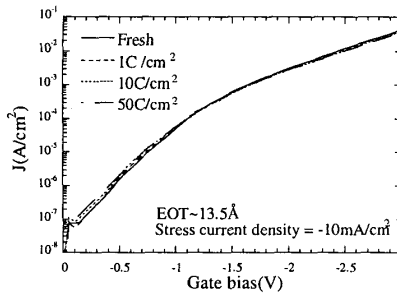


Fig. 19 Stress induced leakage current (SILC) characteristic of thin HfO₂.

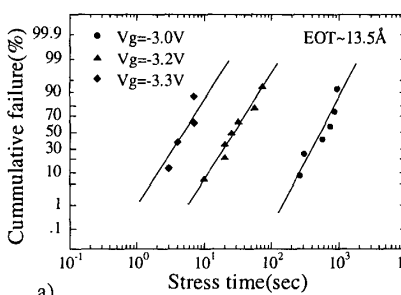
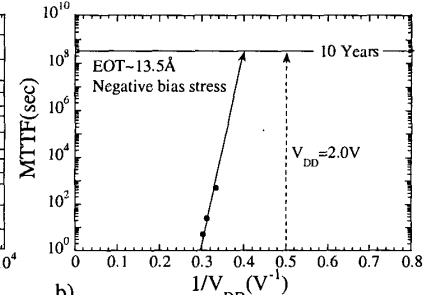


Fig. 20 Reliability characteristics of 45 Å HfO₂; a) Cumulative breakdown distribution under negative bias stress, b) Lifetime extrapolation.



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