

## B-1-3

# Study on Densification and Oxidation Mechanism during PDA for Minimum EOT of Ultrathin CVD HfO<sub>2</sub>

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## 1. Introduction

CVD HfO<sub>2</sub> has received much attention as gate dielectrics for sub-100nm technology owing to its compatibility with conventional self-aligned poly-Si gate. Equivalent oxide thickness (EOT) of HfO<sub>2</sub> with poly-Si gate has been saturated at ~10Å according to previous reports [1-4]. In terms of the process dependent limitation, high-k gate structures including upper and lower diffusion barrier layers are proposed to obtain smaller EOT.

In this work, we clarify the relation between the deposition temperature and the film density as well as an additional oxidation during PDA (Post deposition Anneal). A real-time investigation about the oxidation of Si substrate as well as the diffusion of Hf elements into the interfacial layer is performed in this experiment by means of *in-situ real-time heating observation* by cross-sectional TEM(XTEM). Our theoretical comprehension implies the existence of the minimum EOT due to the oxidation and the diffusion mechanisms in CVD-HfO<sub>2</sub>.

## 2. Experimental

After the RCA cleaning and diluted HF dip, the CVD-HfO<sub>2</sub> gate stacks were formed using Hf(OC(CH<sub>3</sub>)<sub>3</sub>)<sub>4</sub> [Hf "t-butoxide"] at 200~500°C in O<sub>2</sub>. These samples were subjected to the PDA at 800°C 30sec in N<sub>2</sub>, followed by poly-Si deposition. The poly Si was formed by phosphorus implantation and activation annealing at 900°C in N<sub>2</sub>. EOT of the MOS with the poly-Si gate was estimated by eliminating quantum mechanical and poly-depletion effects. And *in-situ real-time* observation by XTEM after CVD deposition was performed within the temperature range from 25 to 850°C in UHV.

## 3. Results and Discussion

### Densification and Oxidation Factors during PDA

Comparisons of ellipsometric Tox before and after the PDA for several deposition temperatures are shown in Fig. 1. The densification of film and the oxidation at an interface with Si substrate were observed. The slope denoted as a densification factor "De" of the films during the PDA became steeper with increasing of the deposition temperature. The intercepts across the vertical axis in Fig. 1 are related to the additional oxidation thickness denoted as an additional oxidation factor, "ΔT". Samples deposited at higher deposition temperature indicate thinner additional oxide thickness. The "De" and the "ΔT" are plotted as a function of 1/K<sub>b</sub>/T(depo.) in Fig. 2. These results can be explained by theoretical formulas which are concerned about a surface diffusion coefficient "Di" of Hf molecules from a CVD source, a deposition temperature "T(depo.)", a surface diffusion length "Λ" of Hf molecules in CVD, and a ratio of porosity part to total film (1-"De") defined by the surface diffusion length "Λ". As the "Di" is ruled by a surface activation energy "Es", these theoretical equations are expressed as follows.

$$Di = Di_0 \exp \{- Es/K_b/T(depo.)\} \quad (1),$$

$$\Lambda = 2(Di t)^{0.5} \quad (2),$$

$$[Porosity] = 1-De = \exp(-\Lambda_0 \Lambda) \quad (3),$$

$$De = 1 - \exp \{-2 \Lambda_0 [Di_0 \exp \{- Es/K_b/T(depo.)\} t]^{0.5}\} \quad (4).$$

The surface diffusion coefficient "Di" controlled by the "T(depo.)" determines the densification factor "De". The simulated "De" is plotted in Fig. 2. Based on the Deal-Grove oxidation model, the mechanism for the additional oxidation denoted as the oxidation factor "ΔT" are explained by a diffusion coefficient of oxygen "D(oxygen)" enhanced by a ratio of porosity (1-"De") inside HfO<sub>2</sub> film.

$$D(oxygen) = n_c \lambda^2 v (1-De) \quad (5),$$

$$B = 2 D(oxygen) C^* / N_1 \quad (6),$$

$$\Delta T = (T_0^2 + B t)^{0.5} - T_0 + \Delta T(offset) \quad (7).$$

Considering from both theoretical and experimental standpoints, the "ΔT" decrease with increasing the "De" as shown in Fig. 3. The porosity in as deposited film should be eliminated by selecting the higher deposition temperature, in addition, which leads to a thinner additional Si oxidized layer during PDA, hence thinner EOT.

### Additional Oxidation and Hf diffusion during PDA

The diffusion of Hf into interfacial layer was clarified by the *in-situ* XTEM as shown in Fig. 4, where a new "inter-diffusion layer" was generated as a result of Hf diffusion into interfacial layer and out-diffusion of Si toward the surface. Because the hydrogen is supplied from a CVD source of Hf(OC(CH<sub>3</sub>)<sub>3</sub>)<sub>4</sub>, the hydrogen is desorbed from inside of the films at ~700°C resulting in the inter-diffusion layer (ID) as shown in Fig. 4. Hf and Si inter-diffusion was enhanced by the vacancy evolution after the hydrogen desorption during PDA. The total physical thickness, the interfacial layer (IL) and the inter-diffusion layer (ID) are plotted as shown in Fig. 5 according to the *In-situ real-time* observation by XTEM (Fig. 4). Furthermore, these increasing tendencies can be explained by an experimental activation energy for D(oxygen) according to the fitting. These are modeled by the following equations.

$$D(oxy.) = D_0(oxy.) \exp \{- Ea(oxy.)/K_b/T(anneal)\} \quad (8),$$

$$D(Hf) = D_0(Hf) \exp \{- Ea(Hf)/K_b/T(anneal)\} \quad (9),$$

$$\Delta T(Hf) = 2\{D(Hf) t\}^{0.5} \quad (10).$$

Diffusion coefficients estimated from Fig.5 and these equations were applied to a real thermal budget effect under the PDA at 800°C for 30sec as shown in Fig. 6. The calculated result from the initial 7 Å of SiN and 23 Å of HfO<sub>2</sub> leads to an increment of the total physical thickness from 30 Å to 36 Å. This thickness increment corresponds to the additional oxidized Si layer, the consequent inter-diffusion layer of 10 Å, and the thinning of the

interfacial layer from 7 Å to 3 Å. Compared with XTEM image of the SiN/HfO<sub>2</sub> treated by the PDA at 800°C for 30sec, the interfacial layer thickness (<5Å) shown in Fig. 7 is in good agreement with the simulated result (3 Å). This interfacial layer thinning due to the consequent Hf inter-diffusion significantly reduces the EOT.

#### Minimum EOT of CVD HfO<sub>2</sub>

The minimum EOT can be evaluated from the oxidation of Si substrate and the Hf diffusion into the interfacial layer. Along with the experimental results with poly-Si, the calculated results indicate that the minimum EOT of 11~12 Å exists at 30 Å of physical thickness of CVD HfO<sub>2</sub> as shown in Fig. 8. This implies that even though the physical thickness is thinned, it is difficult to reduce EOT due to the oxygen diffusion and the additional oxidation during the conventional process. In other words, a partial pressure of the residual oxygen should be controlled

rigidly to obtain smaller minimum EOT during fabrication.

#### 4. Conclusion

The higher deposition temperature results in the higher density film during deposition and the thinner additional oxidation at Si substrate during PDA. Hf diffusion into the interfacial layer takes place during PDA and this mechanism is responsible for thinner EOT. In addition, based on the comprehensive theoretical study related to the oxidation and the diffusion in CVD-HfO<sub>2</sub>, the existence of the minimum EOT was ascertained. Our study may give the useful insight into smaller EOT for high-k gate dielectrics.

#### References

- [1] B. H. Lee et al., IEDM Tech. Dig., p39, 2000.
- [2] S. J. Lee, et al., IEDM Tech. Dig., p.31, 2000.
- [3] A. Shanware, et al., IEDM Tech. Dig., 137, 2001.
- [4] E. P. Gusev, et al., IEDM Tech. Dig., p. 451, 2001

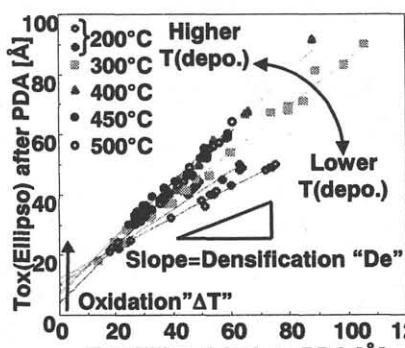


Fig.1 Comparison of ellipsometric Tox before and after PDA. Slope and intercept indicate a densification "De" and an additional oxidation "ΔT" factors during PDA.

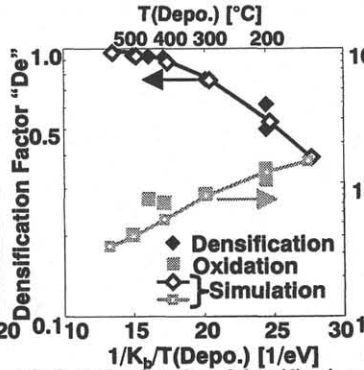


Fig.2 Arrhenius plot of densification "De" and oxidation "ΔT" factors.

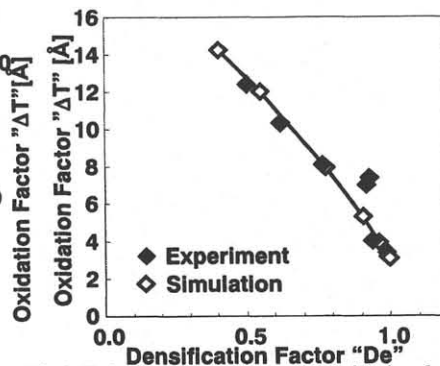


Fig.3 Relationships between the oxidation factor "ΔT" and the densification factor "De". Dense film effectively prevents oxidation during PDA.

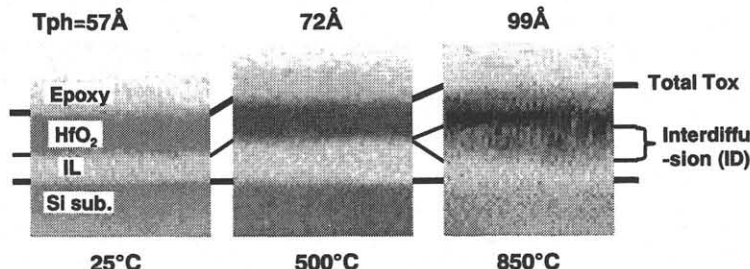


Fig. 4 In-situ XTEM images of HfO<sub>2</sub> deposited at 500 °C on 7Å-Si<sub>3</sub>N<sub>4</sub> from "t-butoxide" as a function of annealing temperature in UHV. Oxidation of Si is observable at even low temperature (25~ 500°C). Inter-diffusion layer between HfO<sub>2</sub> and interfacial layer (IL) at 850°C means a remarkable diffusion of Hf toward IL.

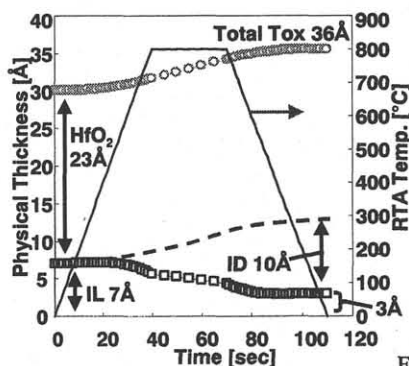


Fig.6 Diffusion coefficient estimated from Fig.5 can be applied to the real thermal budget during PDA at 800 °C for 30sec in N<sub>2</sub>.

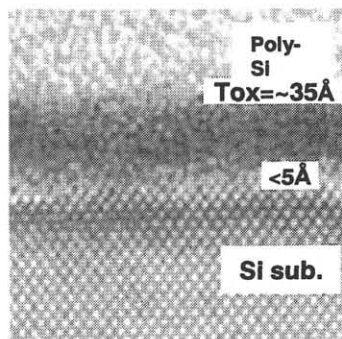


Fig. 7 XTEM images of HfO<sub>2</sub> formed as MOS capacitor. The interfacial thickness (<5Å) and Tox (~35Å) are consistent with the simulation (IL~3Å, Tox~36Å) in Fig. 6.

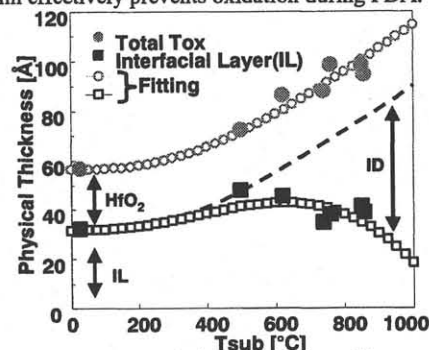


Fig.5 Total Tox, interfacial layer (IL), and inter-diffusion layer (ID) observed by XTEM in Fig. 4 are fitted by the theoretical model.

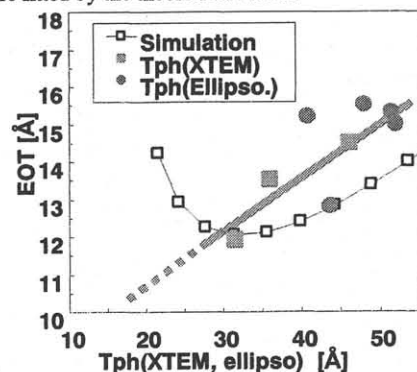


Fig.8 Relationships of EOT and physical thickness as an experiment with poly-Si gate. Minimum EOT of 12 Å is found to exist at around 30Å of physical thickness.