Pulsed-source MOCVD HfO$_2$ ultrathin film growth optimized by in situ ellipsometry monitoring

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1. Introduction
Among several potential materials, HfO$_2$ is a promising candidate as an alternative gate dielectric for future CMOS devices in terms of its thermodynamic stability on Si and high dielectric constant (~25) [1]. Since the required equivalent oxide thickness after the 65 nm node era will be less than 1 nm, it is important to establish a reliable technique to fabricate and control such ultrathin films with atomic-scale precision. Pulsed-source metal-organic chemical vapor deposition (PS-MOCVD) is a potential technique to deposit the ultrathin films with good surface coverage and with large area uniformity. Furthermore, in situ optical growth monitoring technique was chosen for good reproducibility and good throughput [2]. In this paper, the preparation of HfO$_2$ thin films by PS-MOCVD, combined with in situ ellipsometry monitoring of film growth, is discussed.

2. Experimental
P-type Si (100) wafers were used as substrates. Hf[N(CH$_3$)$_2$]$_4$ was used as the source for hafnium and was introduced to the chamber by Ar carrier gas. O$_2$ gas was used as the oxidizing agent. The hafnium compound and oxygen were supplied alternatively. Ar purge gas was supplied between Hf source and O$_2$. The supply durations of oxygen were supplied alternatively. Ar purge gas was used as the oxidizing agent. The hafnium compound and oxygen were supplied alternatively. Ar purge gas was introduced to the chamber by Ar carrier gas. O$_2$ gas was supplied between Hf source and O$_2$. The supply durations of oxygen were supplied alternatively. Ar purge gas was used as the oxidizing agent.

The time evolution of two different ellipsometry angles, $\Delta$ and $\Psi$, was recorded simultaneously during deposition. We focused on $\Delta$ only because the change of $\Psi$ during a deposition was negligible. MIS diode structure using Al electrodes was fabricated for measurements of C-V and J-V characteristics.

3. Results and Discussion
Typical time evolution of $\Delta$ from the start to the end of the 4nm-thick film growth is shown in Fig. 1(a). The monotonic decrease of $\Delta$ with time is a result of the increase of film thickness. Oscillatory behavior observed in $\Delta$ is magnified in Fig. 1(b). The period of oscillation was matched to the cycle of gas supply. Note that a rapid decrease of $\Delta$ occurred at the onset of the supply of the carrier gas. After that, $\Delta$ gradually increased while Ar purge gas was introduced. During the introduction of the O$_2$ gas and the following Ar purge gas, $\Delta$ did not change significantly until the carrier gas in the next cycle was supplied. As shown in Fig. 2, the time trajectory of $\Delta$ within any given cycle strongly depends on $t_p$, when $t_p$ and $t_s$ were held constant. Note that the initial rapid decrease of $\Delta$ in a cycle was essentially independent of $t_p$. Figure 3 shows the capacitance equivalent thickness (CET) and leakage current density, $J_p$, at -1 V of gate voltage of HfO$_2$ films with a constant film thickness (6 nm), but fabricated using different $t_s$’s. An optimum duration time of $t_p\sim3$ s can be identified, based on the shortest CET and the lowest $J_p$. One further notes that this optimum duration time coincides with the duration of the initial rapid decrease in $\Delta$ (Fig. 3). These results indicate the existence of a characteristic time for adsorption of the Hf precursor on the growing surface and suggest that the matching of $t_p$ to this characteristic period is a key to obtaining films with higher qualities. C concentration in the film obtained from SIMS analysis decreases with decreasing $t_p$. However, interface morphology observed in the cross-sectional TEM (XTEM) image of the samples gets worse with decreasing $t_p$. The optimum period might be determined on the balance of these conditions. Similar optimizations were performed for $t_s$ and $t_p$, and then the $t_s\sim40$ s and the $t_p\sim20$ s were estimated as optimum periods. An XTEM image of the sample fabricated with the optimized condition is shown in Fig. 4. Thickness of interfacial layer is 0.8 nm, which is consistent with the results from XPS and spectroscopic ellipsometry measurements. The band gap of the HfO$_2$ film and the valence band offset at the interface with Si estimated from XPS are 5.1 and 2.5 eV, respectively. The C-V and J-V characteristics of MIS diode are shown in Fig. 5, together with the $J_g$ - CET plot. The 4nm-thick film with a CET of ~1.2 nm and $J_g$ at -1 V of ~2.5 $\times 10^{-3}$ A/cm$^2$ is obtained.

4. Conclusions
In situ ellipsometry monitoring of the PS-MOCVD process of HfO$_2$ ultrathin films demonstrated a relationship between the ellipsometry signal during growth and the...
electrical properties of the film. High quality HfO₂ films were obtained using growth conditions optimized through the help of in situ ellipsometry monitoring.

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**References**

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Fig. 1: (a) Typical time evolution of ellipsometry angle Δ during the pulsed-source MOCVD growth on the surface of Si substrate. (b) The oscillation of Δ during growth is magnified. Schematics of pulsed gas supply are shown as an inset.

Fig. 2: Δ-t trajectories of one cycle for three samples with different duration times of the source gas supply. t₀ = (a) 10 s, (b) 3 s, and (c) 1 s, t₀ = 20 s and t₀ = 20 s were fixed for all samples.

![Graph showing Δ-t trajectories](image)

Fig. 3: CET and Jₓ of the samples with different t₀. The physical thicknesses, d, of all films were 6 nm. The film with the shortest CET and with the lowest Jₓ were manifested with t₀ ~ 3 s.

![CET and Jₓ graph](image)

Fig. 4: XTEM image of the sample grown by using an optimized condition, where the t₀ = 3 s, t₀ = 40 s, and t₀ = 20 s.

![XTEM image](image)

Fig. 5: Characteristics of the sample grown by using optimized conditions, where t₀ = 3 s, t₀ = 40 s, and t₀ = 20 s: (a) C-V, (b) J-V, (c) Jₓ - CET plot; Each dot in (c) is correspondsto the data of samples with different physical thicknesses.