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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 source-carrying Ar (t_s), O_2 (t_o), and Ar purge gas (t_p) were important parameters, which were varied in these experiments. Total pressure in the reaction chamber during deposition was held at 1.5 Torr. The substrate temperature was maintained at 300 ^oC. *In situ* ellipsometry measurements were performed using a commercial ellipsometer which was attached to the reaction chamber. The time evolution of two different ellipsometry angles, Δ and Ψ, was recorded simultaneously during deposition. We focused on Δ only because the change of Ψ 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 Δ from the start to the end of the 4nm-thick film growth is shown in Fig. 1(a). The monotonic decrease of Δ with time is a result of the increase of film thickness. Oscillatory behavior observed in Δ is magnified in Fig.1(b). The period of oscillation was matched to the cycle of gas supply. Note that a rapid decrease of Δ occurred at the onset of the supply of the carrier gas. After that, Δ gradually increased while Ar purge gas was introduced. During the introduction of the O_2 gas and the following Ar purge gas, Δ did not change significantly until the carrier gas in the next cycle was supplied. As shown in Fig. 2, the time trajectory of Δ within any given cycle strongly depends on t_s, when t_o and t_p were held constant. Note that the initial rapid decrease of Δ in a cycle was essentially independent of t_s. Figure 3 shows the capacitance equivalent thickness (CET) and leakage current density, J_g, 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_s ~3 s can be identified, based on the shortest CET and the lowest J_g. One further notes that this optimum duration time coincides with the duration of the initial rapid decrease in Δ (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_s 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_s. However, interface morphology observed in the cross-sectional TEM (XTEM) image of the samples gets worse with decreasing t_s. The optimum period might be determined on the balance of these conditions. Similar optimizations were performed for t_o and t_p, and then the t_o ~ 40 s and the t_p ~ 20 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 HfO_2 films were obtained using growth conditions optimized through the help of *in situ* ellipsometry monitoring.

Acknowledgement

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References

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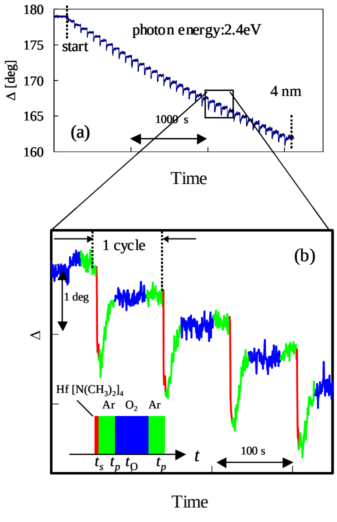

Fig. 1: (a) Typical time evolution of ellipsometry angle Δ during the pulsed-source MOCVD growth on the surface of Si substrate. (b) The oscillation of Δ during growth is magnified. Schematics of pulsed gas supply are shown as an inset.

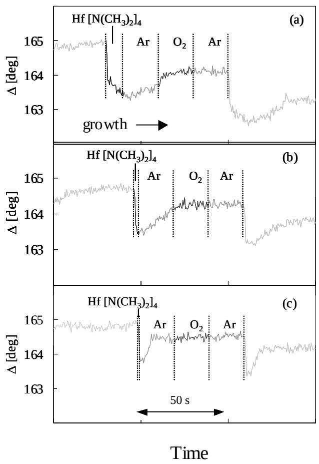

Fig. 2: Δ-t trajectories of one cycle for three samples with different duration times of the source gas supply, t_s = (a) 10 s, (b) 3 s, and (c) 1 s. t_o = 20 s and t_p = 20 s were fixed for all samples.

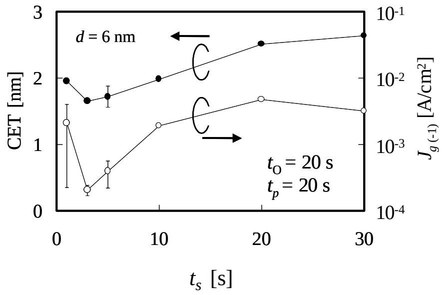

Fig. 3: CET and J_g of the samples with different t_s. The physical thicknesses, d, of all films were 6 nm. The film with the shortest CET and with the lowest J_g were manifested with t_s ~ 3 s.

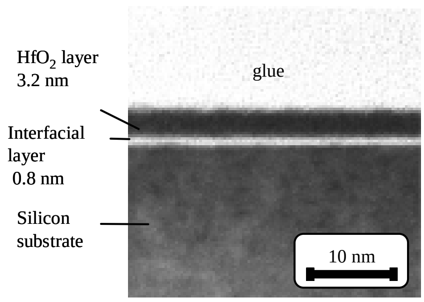

Fig. 4: XTEM image of the sample grown by using an optimized condition, where the t_s = 3 s, t_o = 40 s, and t_p = 20 s.

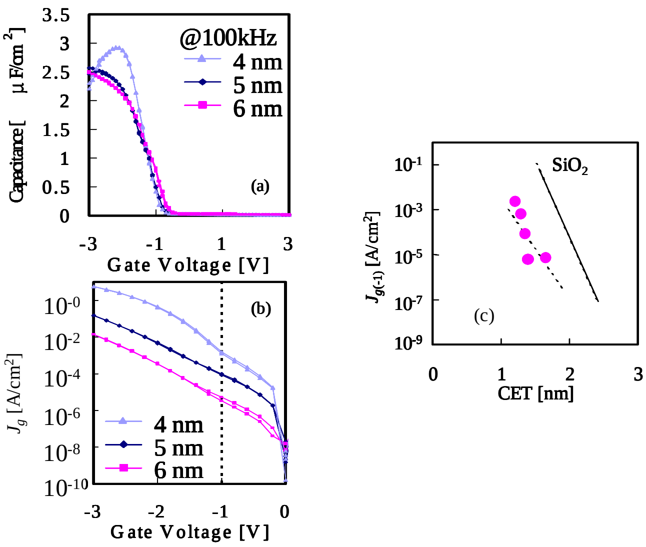

Fig. 5: Characteristics of the sample grown by using optimized conditions, where t_s = 3 s, t_o = 40 s, and t_p = 20 s: (a) *C-V*, (b) *J-V*, (c) J_g - CET plot; Each dot in (c) is correspondsto the data of samples with different physical thicknesses.