Advanced Studies of High-k Gate Dielectrics toward Future Generation with Equivalent Gate Oxide Thickness of Less Than 1 nm

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1. Introduction

The technological needs for overcoming the leakage current issue of ultra-thin gate SiO_2 have been accelerating the research into alternative high-k materials [1]. HfO_2 and related compounds have been considered as promising materials for the next generation, however, exploring new gate insulator materials with a higher dielectric constant is also important towards further device scaling. Lanthanide oxides are attractive candidates for the post HfO_2 era [2]. In Ref. [3], a high dielectric constant (~31) is reported for the epitaxially grown Pr_2O_3 films on the Si substrate, and the result indicates that praseodymium oxide and related composites are potential materials. We have been investigating praseodymium silicate (Pr-silicate) as a possible candidate for the post Hf-composites generation [4, 5]. Structural and electrical properties of Pr-silicate grown by using metal-organic chemical vapor deposition (MOCVD) are reported in the following section. Another important issue in the era with the equivalent gate oxide thickness of less than 1 nm is to establish a reliable technique for fabricating and controlling such ultrathin films with atomic-scale precision. Pulsed-source (PS-) MOCVD is a potential technique for deposition of the ultrathin films with good surface coverage as well as large area uniformity. Furthermore, *in situ* optical growth monitoring technique was chosen for good reproducibility and throughput [6,7]. From these points of view, the preparation of HfO_2 thin films by using PS-MOCVD, combined with *in situ* ellipsometry monitoring of film growth, is discussed in section 3. The last section is dedicated to the summary.

2. Structural and electrical properties of Pr-silicate

P-type Si (100) wafers were used as a substrate. A lateral flow-type deposition chamber was used for our Pr-silicate fabrication process. $Pr(DPM)_3$ was used as the source of praseodymium and introduced to the chamber by Ar carrier gas. Since oxygen atoms are contained in this precursor, we did not use any oxidizing agent in this deposition, and the source was continuously supplied to the chamber. Total pressure in the reaction chamber during deposition was held at 1.5 Torr. Films were grown at various substrate temperatures of 460, 600, and 770 °C.

The chemical structure and the band energy profile at the Si/Pr-silicate interface were studied using the high-resolution x-ray photoelectron spectroscopy (HRXPS). Photoelectrons were excited by the monochromatic AlK radiation with an acceptance angle of 3.3°, using ESCA-300 (Scienta Instruments AB). Capacitance-Voltage (C-V) characteristics and the leakage current densities (J_gs), were studied for the Au/Pr-silicate/Si/Al MIS diode structure.

Angle-resolved O 1s spectra for the7.5-nm-thick film deposited at 770 °C are shown in Fig. 1(a). Two peaks around 530 eV and 533 eV in the spectra with the take-off angles (TOAs) of 8° and 15° can be attributed to the Si-O or H-O, and Pr-O bonds, respectively. Note that a peak between the above two peaks develops in the spectrum with the TOA of 90°, and the origin of the peak can be the Si-O-Pr bonds, implying the formation of Pr-silicate. In the spectra for a thinner (5.5 nm) film (Fig. 1(b)), the Pr-silicate peak is clearly observed even in

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the spectrum with the lowest TOA, while the peak at 530 eV is not identified. A cross-sectional TEM image of the 5.5-nm-thick film is shown in Fig. 2. A thin Pr-silicate layer maintains amorphous structures in spite of the growth at rather high temperature of 770 °C.

From the analysis of O1s energy loss spectrum and angle-resolved valence band spectra, the band gap of Pr-silicate is estimated to be 6.3 eV and the valence band offset at the Pr-silicate/Si interface to be 2.3 eV and 2.9 eV. Assuming that the band gap of Si is 1.1 eV, the conduction band offset is estimated to be 2.9 eV immediately. The band energy parameters of the films deposited at various temperatures are summarized in Table 1. A decrease in the valence band offsets with decreasing deposition temperatures corresponds to the change in the Pr-Si ratio of the film, which is consistent with the analysis of Si 2p spectra of the same samples.

The *C-V* and J_g-*V* curves for the MIS diode are shown in Fig. 3. The film with a capacitance equivalent thickness (CET) of ~1.5 nm and J_g of ~ 9.6×10^{-6} A/cm^2 at -1 V of gate voltage is obtained.

3. PS-MOCVD of HfO_2 with *in situ* ellipsometry monitoring of film growth

Next we report on applying *in situ* ellipsometry monitoring to the PS-MOCVD HfO_2 film growth [8]. Especially the time evolution of ellipsometry angles measured through deposition at single wavelength is focused on because of its advantage for time resolution. P-type Si (100) wafers were used as substrates. Schematic diagram of our deposition chamber was shown in Fig. 4. Hf $[N(CH_3)_2]_4$ was used as a precursor, and O_2 gas was used as the oxidizing agent. The precursor and O_2 were supplied alternatively, and Ar purge gas was supplied between these supplies. 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 was held at 1.5 Torr during deposition. The substrate temperature was maintained at 300 °C. *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 $\triangle$ and Φ, was recorded simultaneously during deposition. We focused only on $\triangle$ because the change of during a deposition was negligible. Metal-Insulator-Semiconductor (MIS) diode structure using Al electrodes was fabricated for measurements of *C-V* and *J-V* characteristics.

Typical time evolution of from the start to the end of the 4-nm-thick film growth is shown in Fig. 5(a). The monotonic decrease of with time is a result of the increase of film thickness. The blowup of the oscillatory behavior observed for is shown in Fig. 5(b). The period of oscillation agrees with the cycle of gas supply. Note that a rapid decrease in occurred at the onset of the supply of the carrier gas. After that, gradually increased while Ar purge gas was introduced. During introducing the O_2 gas and the following Ar purge gas, did not change significantly until the carrier gas in the next cycle was supplied. As shown in Fig. 6, the time trajectory of within any given cycle strongly depends on t_s, when t_o and t_p were held constant. Note that the initial rapid decrease in in a cycle was essentially independent of t_s. Figure 7 shows the CET and J_g at -1 V of gate voltage of HfO_2 films with a constant film thickness (6 nm), but fabricated using different supply durations of source-carrying gas. An optimum duration time of t_s ~3 s can be found, based on the smallest CET and the lowest J_g. One further notes that this optimum duration time coincides with the duration of the initial rapid decrease in (Fig. 6). 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 for obtaining films with higher quality. Carbon concentration in the film obtained from the secondary ion mass spectroscopy analysis decreases with decreasing t_s. However, interface morphology observed in the cross-sectional transmission electron microscope (TEM) image for 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 ~ 40 s and t_p ~ 20 s. The TEM image of the sample fabricated with the optimized condition is shown in Fig. 8. Thickness of interfacial layer is 0.8 nm, which is consistent with the result from *ex situ* spectroscopic ellipsometry measurement. The band gap of the HfO_2 film and the valence band offset at the interface with Si estimated from

HRXPS are 5.1 and 2.5 eV, respectively. The C-V and J_g-V characteristics of MIS diode are shown in Fig. 9. The 4-nm-thick film with a CET of ~1.2 nm and J_g at -1 V of ~ 2.5×10^{-3} A/cm^2 is obtained.

4. Summary

The Praseodymium silicate ultrathin films formed on the Si (100) substrate by MOCVD were studied by using the HRXPS measurement. Both the valence and conduction band offsets at the Pr-silicate/Si interface are larger than 1 eV, which meets a general criterion for deciding whether the material can be used as a gate dielectric for reducing the leakage current.

In situ single-wavelength ellipsometry observation of the PS-MOCVD process of HfO_2 ultrathin films revealed a relationship between the ellipsometry signal during growth and the electrical properties of the film. High quality HfO_2 films were obtained using the growth conditions optimized through the help of *in situ* ellipsometry monitoring.

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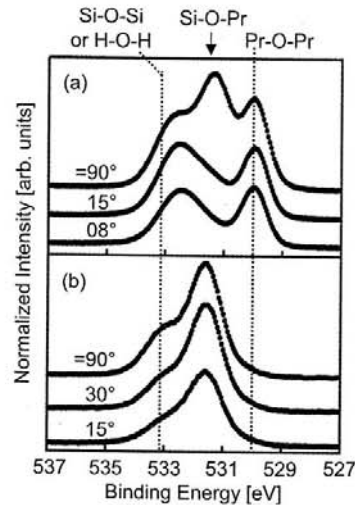

Fig. 1: Angle-resolved XPS spectra of the film deposited at 770 °C with the thickness of (a) 7.5 nm, and (b) 5.5 nm.

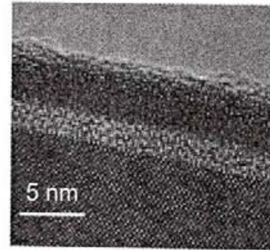

Fig. 2: A cross-sectional TEM image of the Pr-silicate thin film.

Deposition Temperature [°C]	770	600	460
Band Gap [eV]	6.3	5.8	4.9
Valence Band Offset [eV]	2.2	1.9	1.7
Conduction Band Offset [eV]	3.0	2.8	2.3

Table 1: Band energy parameters of the films deposited at various temperatures.

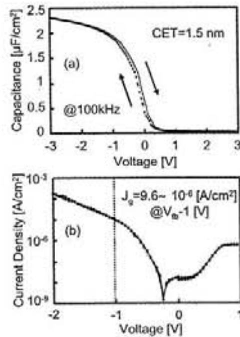

Fig. 4 Electrical properties of the sample: (a) *C-V* curve; (b) $J_g - V$ curve.

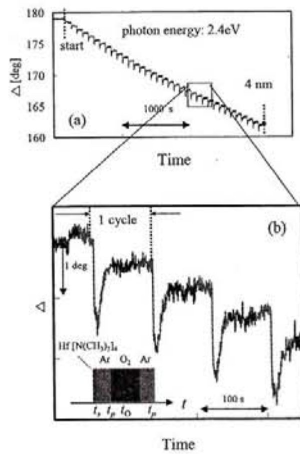

Fig. 5: (a) Typical time evolution of ellipsometry angle during the PS-MOCVD growth of HfO_2 on the Si substrate. (b) The oscillation of during growth is magnified.

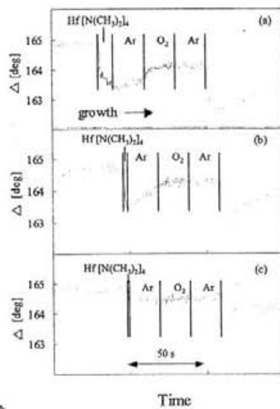

Fig. 6: -*t* trajectories of one cycle for three samples with different duration times of the source gas supply, t_s = (a) 10 s, (b) 3 s, and (c) 1 s. t_o = 20 s and t_p = 20 s were fixed.

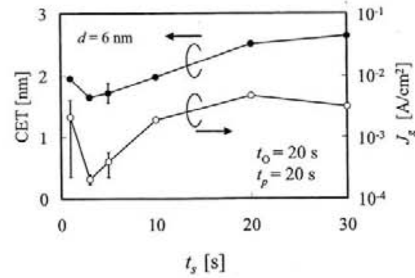

Fig. 7: Capacitance equivalent thickness (CET) and current density, J_g, at -1 V of the samples with various source gas pulse duration, t_s. The physical thickness, *d*, of all films is 6 nm. The film with the smallest CET and with the lowest J_g were manifested with $t_s \sim 3$ s.

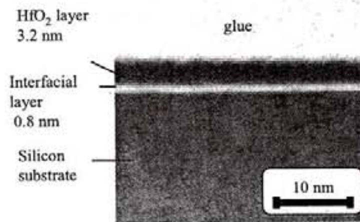

Fig. 8: Cross-sectional TEM image of the sample grown by using an optimized condition, where the $t_s = 3$ s, $t_o = 40$ s, and $t_p = 20$ s.

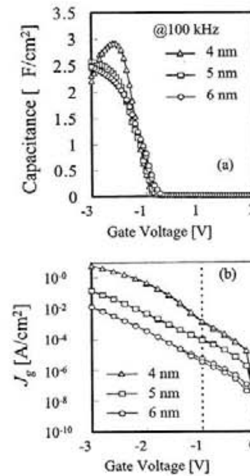

Fig. 9: Characteristics of the sample grown by using optimized conditions, where $t_s = 3$ s, $t_o = 40$ s, and $t_p = 20$ s: (a) *C-V*, (b) *J-V*.