

Reduction of Electrical Defects in Atomic Layer Deposited HfO₂ Films by Al Doping

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The gate leakage current density (J_g) of ultrathin (~ 3 nm) Al-doped HfO₂ (Al:HfO₂) films with an Al concentration of $\sim 11\%$ was lower than that of the control HfO₂ film by 2 orders of magnitude at an equivalent oxide thickness of ~ 1 nm. The permittivity of the Al:HfO₂ film was similar to that of the control HfO₂ film. Al doping of HfO₂ films reduced the concentration of the oxygen vacancies and carbon in the film, which act as electrical defects (traps). It also increased the band gap of the film, resulting in a reduced J_g . Although the crystalline structure of a ~ 12 nm-thick Al:HfO₂ film contained both tetragonal and monoclinic phases after high temperature annealing, the ~ 3 nm thick Al:HfO₂ film showed a monoclinic structure, which is the same as the control HfO₂ film. Therefore, there was no modification of the crystalline structure of the Al:HfO₂ film in the ultrathin film case that would increase the permittivity. However, Si diffusion into the film and interfacial layer growth during annealing were suppressed significantly, which improved the thermal stability of the Al:HfO₂ films.

Introduction

Recently, post high- k gate dielectric materials with superior properties over that of the conventional high- k materials (HfO₂, ZrO₂, etc.) have been studied extensively to be used in advanced gate-stack structures in further-scaled metal-oxide-semiconductor field effect transistors (MOSFETs).^{1,2} Most methods for improving the electrical properties of high- k films are based on the incorporation of small concentrations of another material (doping)

into conventional binary oxide high- k films.^{3–20} In several experiments reporting the improved properties in doped high- k films, the increased permittivity was mainly attributed to the change in the crystalline structure of the film.^{14–20} It was reported that the k values of HfO₂ and ZrO₂ are enhanced by doping with Y₂O₃, Al₂O₃, SiO₂, etc. The crystalline structures of HfO₂ and ZrO₂ were modified by doping from monoclinic to tetragonal or cubic phases, which have a higher permittivity.^{21–24} Therefore, a systematic understanding of the improved properties of doped high- k film from the other viewpoints

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is insufficient. In addition, the improved properties of doped high- k films with an amorphous structure are difficult to explain using the crystalline structure model at present. In addition, the crystallization of high- k films is affected not only by doping but also by other factors, such as the film thickness, stress from the substrate, and the diffusion of substrate elements. Therefore, it is important to examine the parameters that affect the crystalline structure of doped high- k films.

In this study, Al-doped HfO_2 (Al:HfO₂) films with various Al concentrations were grown by atomic layer deposition (ALD). The electrical and chemical properties as well as the thermal stability of the films were evaluated. The origins of the improved electrical properties were examined systematically by analyzing the following: (i) the chemical structure, (ii) the state of electrical defects, (iii) the electronic structures, (iv) the crystalline structures, and (v) the interfacial reactions of the Al:HfO₂ films with the Si substrate.

Experimental Section

Sample Preparations. The control HfO₂ and Al-doped HfO₂ thin films were grown to a thickness of ~ 3 to ~ 20 nm at 280 °C on 4 in. diameter p-type (100) Si substrates by thermal ALD using $\text{Hf}[\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)]_4$ (TEMAH) and $\text{Al}(\text{CH}_3)_3$ (TMA) as the Hf and Al precursors, respectively. O₃ at a concentration of 165 g/m³ was used as the oxygen source. An Al–O layer was inserted discretely into the film by substituting one Hf–O cycle with one Al–O cycle among a total of 30 ALD cycles to allow the incorporation of Al ions into the films. Accordingly, to grow the control HfO₂ and Al-doped HfO₂ films with different Al concentrations, we controlled the number of ALD cycles to 30 (TEMAH) for the control HfO₂ film, 15(TEMAH)/1(TMA)/14 (TEMAH) for the HAO1 film, 10/1/9/1/9 for the HAO2 film, and 7/1/7/1/7/1/6 for the HAO3 film. PDA was performed by rapid thermal annealing at 850 °C for 30 s under a N₂ atmosphere. Sputtered Pt as the top electrode was deposited through a shadow mask to fabricate the metal–insulator–semiconductor capacitors. Forming gas annealing was performed at 400 °C for 10 min in a 95% N₂/5% H₂ atmosphere after the formation of a Pt top electrode.

Analyses and Measurements. The depth profiles of the chemical compositions in the control HfO₂ and Al:HfO₂ films were examined by time-of-flight SIMS. The quantitative chemical compositions of the control HfO₂ and Al:HfO₂ films were estimated by a STEM-EDS and RBS under an oxygen resonance condition (He⁺ ion acceleration energy of 3.04 MeV) to observe the oxygen concentration precisely. The chemical binding status and valence band spectra of the film was examined by high resolution XPS using Al K α as the X-ray source. The binding energies of the XP spectra were calibrated using the Si–Si binding energy in the Si 2p XP spectra from the Si substrate (99.0 eV). The thicknesses and microstructures of the films were observed by HRTEM equipped with a field emission electron gun. The physical thicknesses of the films were also measured by ellipsometry. The typical capacitance–voltage (C – V) and J_g – V measurements were performed using an HP 4194 impedance analyzer and HP 4140B picoammeter/dc voltage source, respectively. The EOT was calculated from the accumulation capacitance using the two frequency method²⁵ considering the quantum mechanical effect. The frequencies of the C – V measurement were 500 kHz and 1 MHz. The V_{FB} value was

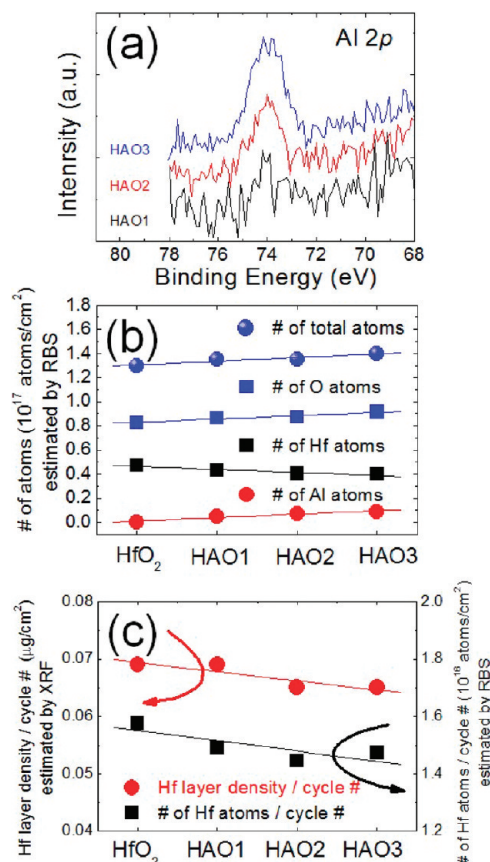


Figure 1. (a) Al 2p core level XP spectra of the Al:HfO₂ films, (b) number of O, Hf, Al, and total ions measured by RBS for the control HfO₂ and Al:HfO₂ films, and (c) Hf layer density and number of Hf ions per ALD cycle of Hf–O estimated by XRF and RBS.

determined from the calculated flatband capacitance values using the measured C – V curve. The size of the top electrodes was measured carefully by optical microscopy. For an analysis of the J_g mechanism, the J_g – V characteristics were collected at several different temperatures (from 75 to 135 °C) using an HP 4145B semiconductor parameter analyzer.

Theoretical Calculations. Theoretical investigations were performed based on density functional theory. The optimized atomic and electronic structure were examined using a Vienna ab initio simulation package.^{26,27} The generalized gradient approximation was used for exchange–correlation potential, and projector-augmented wave method was employed to describe the electron–ion interaction. The k-points were sampled with $2 \times 2 \times 2$ uniform grids. Plane waves up to an energy cutoff of 500 eV were used to expand the electronic wave functions. The forces on the atoms and stress on the cell were reduced to below 0.02 eV/Å and 1 kb, respectively.

Results and Discussion

Chemical and Physical Structures of Al:HfO₂ Thin Films. ~ 3 – 20 nm thick Al:HfO₂ films with three different Al concentrations (HAO1, HAO2, and HAO3, where HAO3 has the highest Al concentration) were prepared (see the Experimental Section). The Al 2p core level X-ray photoelectron (XP) spectra of Al:HfO₂ films in Figure 1(a) shows an increase in the Al concentration in the films with

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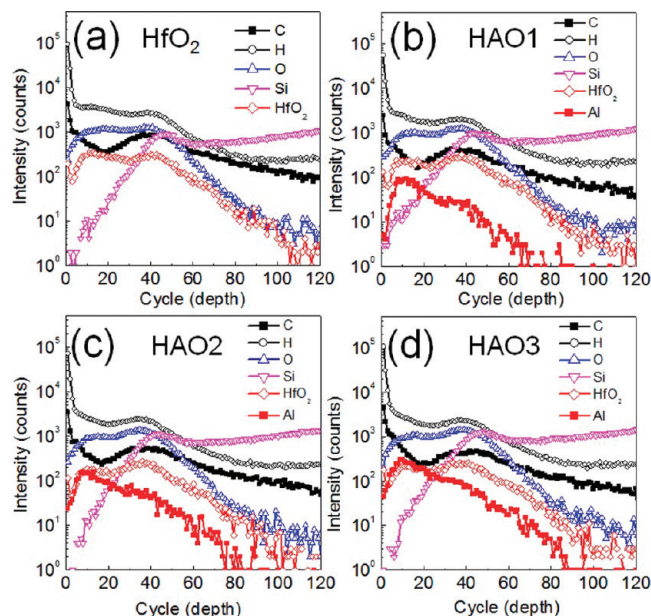
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Table 1. Al Concentrations in the Al:HfO₂ Films Estimated by XPS, RBS, STEM EDS, and Calculation Using the Bulk Atomic Density of HfO₂ and Al₂O₃

	methods	HAO1	HAO2	HAO3
Al/(Hf + Al) (%)	by RBS (~20 nm)	10.8	15.3	18
	by XPS (~20 nm)	6.5	11.5	17.4
	by STEM EDS (~3 nm)		11.4	
	ideal	5.5	10.8	15.8

increasing ALD cycle number of Al–O. The thickness of the Al:HfO₂ films used for XP spectroscopy (XPS) analysis in Figure 1a was controlled to ~20 nm by repeating the unit 30 ALD cycles to remove the interface effects at the interface with the Si substrate on Al incorporation into the film. Figure 1b shows the atomic number density (number of atoms per volume) of each element in the control HfO₂ and Al:HfO₂ films, which was estimated by Rutherford back-scattering spectroscopy (RBS) under the oxygen resonance condition. The film thickness was the same (~20 nm) as those used for XPS analysis in Figure 1a. The atomic density of Hf and Al respectively decreased and increased with increasing number of ALD cycles of Al–O. The growth rates of the ALD HfO₂ and Al₂O₃ films were similar, ~0.09 nm/cycle. This means that the combined volume of HfO₂ and Al₂O₃ molecules deposited per ALD cycle is similar. The bulk atomic density of HfO₂ and Al₂O₃ films was ~0.046 and ~0.039 mol/cm³, respectively. Therefore, the amount of Hf and O ions (for HfO₂) deposited per an ALD cycle of Hf–O is proportional to the bulk atomic density of HfO₂, ~0.046 and ~0.092 mol/cm³ (0.046 mol/cm³ × 2), respectively, because the number of Hf and O ions per a single HfO₂ molecule is one and two, respectively. In the same respect, the amount of Al and O ions (for Al₂O₃) deposited per an ALD cycle of Al–O is also proportional to the bulk atomic density of Al₂O₃, ~0.078 (≈ 0.039 × 2) and ~0.117 mol/cm³ (≈ 0.039 × 3), respectively, because the number of Al and O ions per a single Al₂O₃ molecule is two and three, respectively. As a result, when one Hf–O cycle is substituted with one Al–O cycle, the number of O ions and anions (Hf+Al) increased compared to that of the control HfO₂ film, because Al₂O₃ generated by one Al–O cycle has more O ions than HfO₂ generated by one Hf–O cycle (3 and 2 O ions for Al₂O₃ and HfO₂, respectively). This is supported by the increased number of O and total ions with increasing number of ALD cycles of Al–O, as shown in Figure 1b.

The Al concentrations in the Al:HfO₂ films were examined by XPS, RBS and scanning transmission electron microscopy - energy dispersive X-ray spectroscopy (STEM-EDS), as summarized in Table 1. The values for the “ideal”, which were calculated using the bulk atomic density of HfO₂ and Al₂O₃, as mentioned above, were also included. The “ideal” Al concentration in the film corresponds to the case where the incorporation rate of each layer (Al–O and Hf–O) into the film was not influenced by the presence of other layer. Figure 1c shows the Hf layer density and number of Hf ions deposited per ALD cycle of Hf–O estimated by X-ray fluorescence (XRF) and RBS, respectively. Both XRF and RBS results showed that the growth of the HfO₂ layer was retarded further with increasing number of ALD cycles of

**Figure 2.** SIMS depth profiles for the (a) control HfO₂ and (b–d) Al:HfO₂ films.

Al–O. Therefore, the measured Al concentration in the Al:HfO₂ films was slightly larger than the “ideal” values, as shown in Table 1.

Although the film thickness used for STEM-EDS was much smaller (~3 nm) than that of the films used for RBS and XPS analyses (~20 nm), the Al concentration in Al:HfO₂ films estimated by STEM-EDS was similar to those of other analyses. Therefore, the effects of the film thickness or interface on the Al concentration in the Al:HfO₂ films appear to be insignificant. To confirm this, the spatial distribution of Al along the vertical direction in the Al:HfO₂ films with a thickness of ~3 nm was traced by the secondary ion mass spectroscopy (SIMS) depth profiles, as shown in Figure 2b–d for HAO1, HAO2, and HAO3, respectively. It is generally difficult to quantify the SIMS signal due to the matrix effect and inaccurate etching rate of the film during the analysis. Therefore, the relative change in the Al signal with respect to the HfO₂ signal was considered. The Al and HfO₂ signals in the upper layer (UL, 0 to ~30 SIMS cycle (depth)) showed similar trends in all Al:HfO₂ films. Both HfO₂ and Al signals increased between SIMS cycle (depth) 0 through 10 and decreased between SIMS cycle (depth) ~10 and ~30 in all Al:HfO₂ films. This suggests that the Al concentration was almost constant along the thickness direction in the UL of Al:HfO₂ films. However, the metal-silicate phase constituting the interfacial layer (IL, ~30 to ~50 SIMS cycle (depth)) contained a smaller Al signal than that in the UL. This is because Hf-silicate formation is more likely than Al-silicate formation in the IL.

The signals of C and H impurities in the Al:HfO₂ films were much lower than those of the control HfO₂ film in the SIM spectra in Figure 2. This became obvious when they were compared with the O signal, which is almost independent of Al doping. In particular, the C concentration in the films was decreased significantly by Al doping. Although the

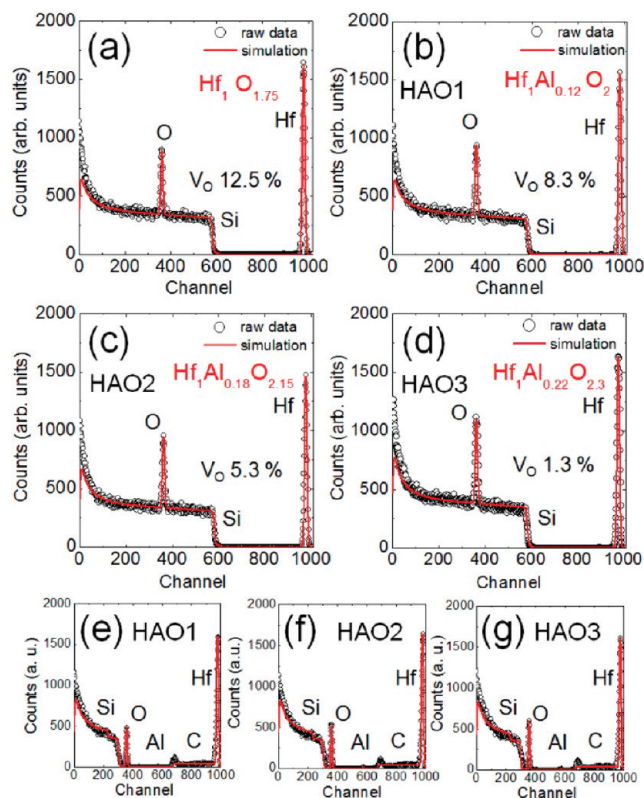


Figure 3. RBS results with the oxygen resonance condition for (a) control HfO_2 and (b–d) Al:HfO_2 films on Si substrates and (e–g) diamond substrates.

origin of the reduced impurities in the Al:HfO_2 films is unclear,²⁸ this appears to have a close relationship with the concentration of oxygen vacancies (V_O) in the Al:HfO_2 films. When a molecule of TEMAH and TMA precursor contains twelve and three C atoms, respectively, it is also possible that the reduced supply of C atoms from the precursor ligands decreased the C concentration in the Al:HfO_2 films. However, the difference in C concentration between the control HfO_2 and the Al:HfO_2 films is much larger than what is expected based on the difference in the supplied amount of C atoms from the precursor ligands. Although the difference in the supplied amount of C atoms between the control HfO_2 and the Al:HfO_2 films [TEMAH/TMA ratios of 29/1 (HAO1), 28/2 (HAO2), and 27/3 (HAO3)] is ~ 2.5 – 7.5% , SIMS results showed that the difference in C concentration between the control HfO_2 and the Al:HfO_2 films is much larger.

The V_O concentration in the Al:HfO_2 films was estimated from the RBS results. Figure 3a–d shows the RBS spectra under the oxygen resonance condition for the control HfO_2 and Al:HfO_2 films with a thickness of ~ 20 nm on Si substrates, as mentioned above. Figure 3e–g show the RBS results for the Al:HfO_2 films on chemical vapor deposited diamond/Si substrates. This substrate provides information (concentrations) of Al in the Al:HfO_2 films without any interference of the overlapped Si signal from the substrate. The Al concentrations are also summarized in Table 1. The

V_O concentration of $\sim 12.5\%$ for the control HfO_2 film decreased to ~ 8.3 , ~ 5.3 , and $\sim 1.3\%$ with increasing Al concentration in the Al:HfO_2 films. Here, the V_O concentration was determined by comparing the measured O stoichiometry and the ideal stoichiometric value calculated from the measured cation stoichiometry. For example, the stoichiometric HAO2 film ($\text{Hf:Al} = 1:0.18$, see Figure 3c), requires 2.27 O atoms per molecule ($2\text{ O for 1 Hf} + 0.27\text{ O} (= 0.18 \times 3/2)$ for 0.18 Al). Considering the measured O stoichiometry is 2.15, the V_O concentration of the HAO2 is $\sim 5.3\%$. $[(2.27 - 2.15)/2.27] \times 100$ This is not because of the simple replacement of oxygen-deficient $\text{HfO}_{1.75}$ with stoichiometric Al_2O_3 . If this were the case, the oxygen stoichiometry of HAO1, HAO2, and HAO3 would be 1.93 ($= 1.75 + (0.12 - 3/2) = 1.93$), 2.02 ($= 1.75 + (0.18(3/2)) = 2.02$), and 2.08 ($= 1.75 + (0.22(3/2)) = 2.08$), respectively, which is lower than the estimated values of 2.00, 2.15, and 2.30, respectively. This suggests that the V_O concentration in the HfO_2 material is decreased by Al doping. This is consistent with the first-principles calculations by X. F. Wang et al., who reported that the presence of Al in HfO_2 led to the passivation of defect states induced by V_O in the film.²⁹ N. Umezawa et al. also reported that that doping materials, such as Ba and La, reduced the V_O concentrations in HfO_2 films considerably.^{30,31} These changes in the V_O concentration in the film as a function of the Al concentration are consistent with the electrical defect status estimated by the electrical measurements, which will be discussed in detail later.

The low concentrations of C and H in the Al:HfO_2 films are closely related to the low V_O concentration. Dutta et al. recently reported, based on first-principles calculations, that the ZrO_2 film with V_O is more stable when there is a similar level of substitution or interstitial C atoms in the film.³² Suzuki et al. also reported that the reduction of V_O (addition of more oxygen) in the HfO_2 eliminated the C-related defect states in the band gap.³³ Therefore, the lower V_O concentration in the Al:HfO_2 films could reduce the concentrations of C and H in the films. It is also likely that the high reactivity of the Al precursor [TMA, $\text{Al}(\text{CH}_3)_3$] removed the residual C and H impurities in the film more efficiently.³⁴ J. Kwon et al. also reported that TMA pulse decreased the residual surface ligands, resulting in the reduction of C impurity in the film.³⁵

The microstructures of the as-deposited control HfO_2 with 30 and 33 ALD cycles, and Al:HfO_2 film (HAO2) with 30 ALD cycles were observed by cross-sectional high resolution transmission electron microscopy (HRTEM), as shown in

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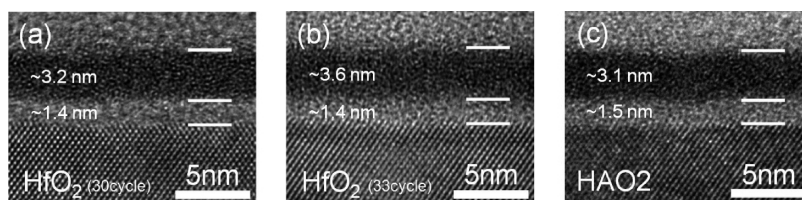


Figure 4. Cross-sectional HRTEM images of the as-deposited control HfO_2 with 30 and 33 ALD cycles, and Al:HfO_2 film (HAO2) with 30 ALD cycles.

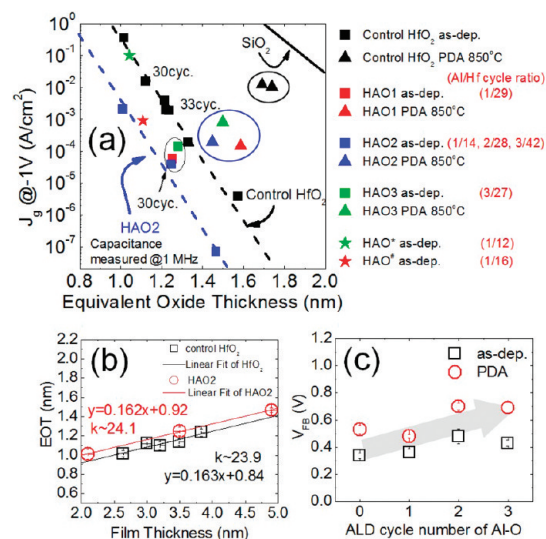


Figure 5. (a) Plot of EOT vs J_g for control HfO_2 and Al:HfO_2 films (HAO1, HAO2, and HAO3); (b) EOT as a function of physical film thickness for control HfO_2 and Al:HfO_2 film (HAO2); and (c) V_{FB} variations for the control HfO_2 and Al:HfO_2 films.

Figure 4. All the films had amorphous structures. The thickness of each layer is the average value calculated from more than 15 HRTEM images taken from different regions of the film. The UL and IL thicknesses of the control HfO_2 film with 30 ALD cycles was ~ 3.2 and ~ 1.4 nm, respectively. When the number of ALD cycles was increased to 33, the UL thickness of the control HfO_2 film increased to ~ 3.6 nm with no notable increase in the IL thickness. The UL and IL thickness of the Al:HfO_2 (HAO2) film was ~ 3.1 and ~ 1.5 nm, respectively. Since the silicate reaction is suppressed during ALD because of the Al_2O_3 phase, the UL of the HAO2 film (~ 3.1 nm) is slightly thinner than that of the control HfO_2 film (~ 3.2 nm) with the same (30) ALD cycles. Although HAO2 film was physically thinner than the control HfO_2 film produced from 33 ALD cycles, the equivalent oxide thickness (EOT) of HAO2 was similar to that of the control HfO_2 film. This is because the HAO2 film has a thicker IL than the control HfO_2 film. The electrical properties of the films are discussed in detail below.

Electrical Properties of the Al:HfO_2 Thin Films. Figure 5a shows a plot of the EOT versus the gate leakage current density (J_g) for the control HfO_2 , and Al:HfO_2 films (HAO1, HAO2, and HAO3). The black squares indicate the results for the as-deposited control HfO_2 films with different thicknesses, which are aligned on the black dashed line. The appropriate Al concentrations ($\sim 10.8\%$ of HAO2 based on the ‘ideal’ value, blue squares and a blue dashed line) in the films reduced the J_g value by 2 orders of magnitude compared to the control HfO_2 films. The three HAO2 films

on the blue dashed line were produced from 1/14, 2/28, and 3/42 Al–O/Hf–O ALD cycles (with the same Al–O/Hf–O ALD cycle ratio of 1/14), respectively. The red and green squares indicate the result for the as-deposited HAO1 and HAO3 films (Al concentrations of ~ 5.5 and $\sim 15.8\%$), respectively, of which the dielectric properties were slightly better than those of the control HfO_2 films but worse than those of the HAO2 films. The red stars and green star indicate the result for the film grown with 1/12 and 1/16 Al/Hf cycles, respectively. These films have a slightly higher and lower Al concentration in the film (Al concentrations of ~ 12.5 and $\sim 9.5\%$), respectively, than the HAO2 film. These Al concentrations in the film degraded the dielectric properties of the films compared to the HAO2 film. Therefore, the dielectric properties of the Al:HfO_2 films improved with increasing Al concentration in the film until a certain optimal point ($\sim 10.8\%$ in this study, the HAO2 film has the optimized Al concentration for the best electrical properties), then became rapidly worse beyond that optimization point. In Figure 5a the flat band (V_{FB}) shift by the different Al-doping concentrations was not considered. When this was considered (i.e., J_g at $V_{FB} - 1$ V), the HAO2 films showed an even better dielectric performance than that shown in Figure 5a.

The permittivity of the films can be calculated using the inverse slope of the EOT vs physical thickness plot, as shown in Figure 5b. Even though the film thickness range may not be wide enough to achieve the permittivity accurately, the thickness range should be limited to the ultrathin region because the main purpose of this study is to examine the film properties in the ultrathin region. Thicker films might be crystallized during ALD, which could induce changes in the permittivity. Interestingly, the permittivity of the HAO2 film (~ 24) was similar to that of the control HfO_2 film in this thickness region. However, it is expected that the lower permittivity of Al_2O_3 began to decrease the permittivity of the Al:HfO_2 film beyond a certain optimization point ($\sim 10.8\%$ in this study).^{36,37} The permittivity of the IL in the control HfO_2 and HAO2 is also similar, being ~ 6.5 and ~ 6.4 , respectively. (EOT and thickness of the IL provides the information needed to extract the permittivity of the IL). Therefore, the superior electrical properties of Al:HfO_2 films to that of HfO_2 were due to the reduced J_g not the enhanced permittivity of the films. S. Jeon et al. reported that ultrathin lanthanide-doped HfO_2 films grown by e-beam evaporation showed a reduced J_g without any significant changes in permittivity.³⁷

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The reduced J_g of the Al:HfO₂ films is believed to originate from the lower concentrations of V_O and impurities, such as C and H in the films, as discussed above, which were verified by the electrical measurements and analysis in next section. Although the concentrations of V_O and impurities in the film were reduced further, the HAO3 film showed degraded properties compared to the HAO2 film. This might be because the decrease in the permittivity of the Al:HfO₂ film by Al₂O₃ ($k \approx 8$) in the film dominated the advantages from the lower concentrations of V_O and impurities in the film.^{36,37}

The smaller EOT of the control HfO₂ film than that of the HAO2 film with the same thickness (30 cycle, ~ 4.6 nm) was induced by the thicker IL of the HAO2 film, as shown in Figure 4. This is also supported by the results in Figure 5b, which show that the electrical thickness of the IL (y -intercept) of HAO2 film (~ 0.92 nm) is larger than that of the control HfO₂ film (~ 0.84 nm). The reason for the slightly thicker IL in the Al:HfO₂ film is unclear.

The V_{FB} increased with increasing Al concentration in the Al:HfO₂ film before and after PDA, as shown in Figure 5c, because the Al ions in the HfO₂ films act as the negative fixed charges.^{38,39} This provides advantages for a lower J_g at a lower threshold voltage in the operation of p-MOSFET devices. The annealed Al:HfO₂ films also have superior dielectric properties than the annealed control HfO₂ films. There was not only a decrease in J_g of approximately 2 orders of magnitude but also an ~ 0.3 nm decrease in the EOT in the case of the HAO2 film. The electrical properties of the annealed Al:HfO₂ films will be discussed later in terms of the chemical and crystalline structures.

Electronic Band Structure and Defects of Al:HfO₂ Thin Films. The temperature dependent J_g - V characteristics of the control HfO₂ and HAO2 films were examined to confirm the effects of the reduced V_O and impurities by Al-doping on the energy band structure and electrical defects state of the Al:HfO₂ films. The control HfO₂ film with 33 ALD cycles and the HAO2 film with 30 ALD cycles were compared because the two films have a similar EOT, as discussed above. Panels a and b in Figure 6 show the typical J_g - V curves of the control HfO₂ and the HAO2 films measured at various temperatures ranging from 75 to 135 °C with a negative bias applied to the Pt gate. For a detailed analysis of the conduction mechanism, it is important to know the electric field distribution across the dielectric layer (UL and IL). The electric field across the dielectric film was calculated on the basis of the following formula

$$E = \frac{V_g - V_{FB} - \phi_s}{t} \quad (1)$$

where t is the physical thickness of the dielectric film, and ϕ_s indicates silicon band-bending. The electric field distribution across the dielectric layer (UL and IL) was considered with

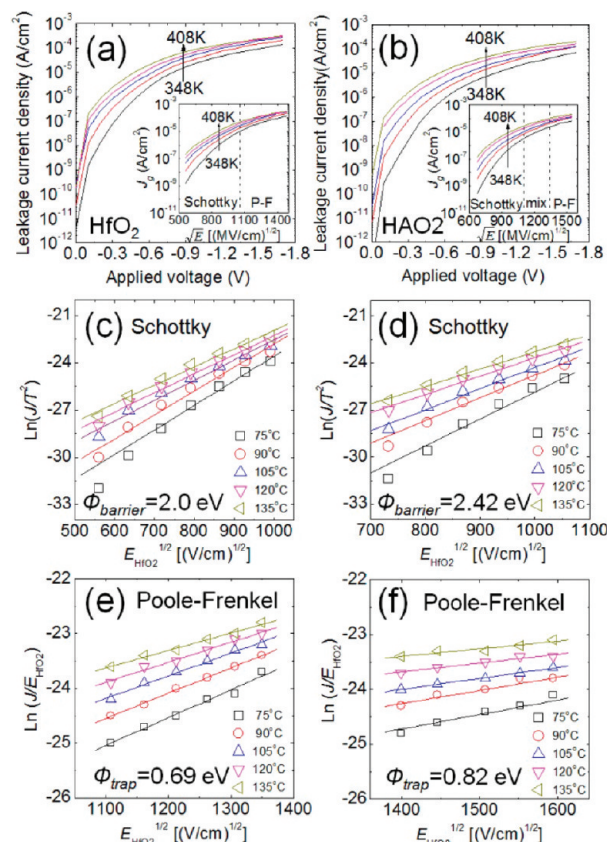


Figure 6. (a, b) Typical J_g - V and J_g - E curves measured at various temperatures ranging from 75 to 135 °C, respectively, (c, d) electric-field-dependent Schottky emission plots and (e, f) Poole-Frenkel emission plots for the control HfO₂ and Al:HfO₂ (HAO2) films, respectively.

the dielectric constants and physical thicknesses of each layer. The dielectric constants of the UL for both of the control HfO₂ and HAO2 film used to calculate the electric field distribution were 24, which were calculated from the slope of the graph in Figure 5b. The dielectric constants of the IL were assumed to be 6.5 considering the physical thicknesses of the ILs (see Figure 4) and their electrical thickness (see Figure 5b), which is consistent with the values reported elsewhere.⁴⁰ The IL thickness of ~ 1.4 – 1.5 nm for the control HfO₂ and HAO2 film are so thin that it must show direct tunneling behavior of electrons, of which the leakage current should be much higher than the observed leakage current through the entire film. Therefore, the leakage current through the entire film would be determined by the UL, so that electric field of the UL was taken to fit the electric field dependent J_g in the subsequent analyses of the conduction mechanism.

The appropriate electrical conduction mechanisms of the films were dependent on the electric field region, as shown in the insets in panels a and b in Figure 6. The applied electric field of the control HfO₂ and HAO2 film could be divided into two regions corresponding to Schottky and Poole-Frenkel emission (conduction) regions. There was a third region with mixed conduction behavior of the HAO2 film. In the graph of $\ln(J_g/T^2)$ vs $E^{1/2}$ for the control HfO₂ and HAO2 films (Figure 6c, d), the well-fitted straight lines could be

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obtained in the low-field regions from ~ 0.31 to ~ 0.98 MV/cm, which corresponds to the applied voltage from approximately -0.1 to approximately -0.7 V for the control HfO₂ film, and from ~ 0.45 to ~ 1.11 MV/cm, which corresponds to the applied voltage from approximately -0.1 to approximately -0.7 V for the HAO2 films. In these E regions, Schottky emission was found to be the dominant conduction mechanism. Schottky emission can be described as follows

$$J = A^* T^2 \exp\left[\frac{-q(\phi_B - \sqrt{qE/4\epsilon\pi})}{kT}\right] \quad (2)$$

where A^* is the effective Richardson constant, and ϵ and k are the dynamic dielectric constant and the Boltzmann constant, respectively. The ϵ value obtained from a fit of Schottky emission ranged from ~ 4.03 and ~ 4.82 , which is similar to the theoretical value ($n^2 \approx 4.0$, n is the refractive index). The zero-field Schottky barrier height (ϕ_B) extracted by extrapolating the plot of $E^{1/2}$ vs ϕ_B under each specific electric field to the zero electric field from the temperature-dependent Schottky emission fitting in panels a and b in Figure 7 was ~ 2.00 and ~ 2.42 eV for the control HfO₂ and HAO2 film, respectively, as shown in panels e and f in Figure 7. Therefore, Al doping in a HfO₂ film increased the ϕ_B by ~ 0.42 eV, which is one of the main causes for the decrease in J_g of the Al:HfO₂ films.

On the other hand, Poole–Frenkel emission was the dominant conduction mechanism in the high field region from ~ 1.22 to ~ 2.22 MV/cm for the control HfO₂ film, which corresponds to the applied voltage from approximately -0.9 to approximately -1.7 V, and from ~ 1.95 to ~ 2.54 MV/cm for the HAO2 film, which corresponds to the applied voltage from approximately -1.4 to approximately -1.8 V. The $\ln(J_g/E)$ vs $E^{1/2}$ plots (Poole–Frenkel plots) showed straight lines, as shown in panels e and f in Figure 6 for the control HfO₂ and HAO2 film, respectively. P–F conduction can be described as follows

$$J = CE \exp\left[\frac{-q(\phi_t - \sqrt{qE/\epsilon\pi})}{kT}\right] \quad (3)$$

The obtained dynamic dielectric constants were reasonable (3.80–4.61). Poole–Frenkel conduction is controlled by the trapping and activation of trapped carriers from bulk traps. The trap energy depth (ϕ_t) under each specific electric field can be obtained from the slope of the $\ln(J_g/E)$ vs $1/T$ plot in panels c and d in Figure 7. Therefore, the intrinsic ϕ_t value without the field effect can be extracted by extrapolating the curve to zero electric field, as shown in panels g and h in Figure 7. The extracted ϕ_t value for the control HfO₂ and HAO2 film was ~ 0.69 and ~ 0.82 eV, respectively.⁴¹ It was reported that V_O in the HfO₂ film produced shallow trap level of ~ 0.5 eV beneath the conduction band edge.⁴² Therefore, the higher estimated ϕ_t value suggests that Al doping removed these shallow defect states. This also contributed to the decrease in J_g of the Al:HfO₂ films.

In the middle field region from ~ 1.11 to ~ 1.95 MV/cm, which corresponds to the applied voltage from approximately -0.7 to approximately -1.4 V, the HAO2 film

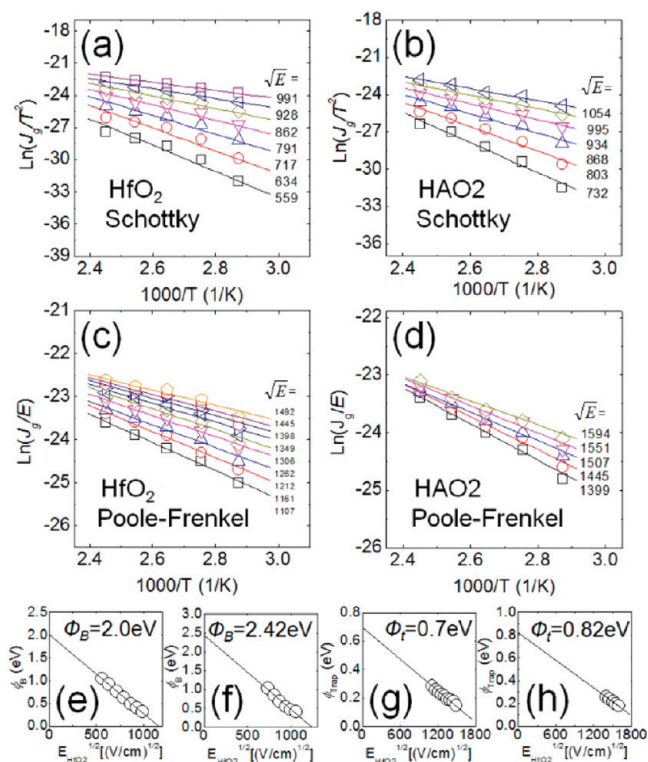


Figure 7. (a, b) Temperature-dependent Schottky emission plots, (c, d) Poole–Frenkel emission plots, (e, f) Schottky barrier height (ϕ_B) under each specific electric field from the temperature-dependent Schottky plot, (g, h) trap energy depth (ϕ_t) under each specific electric field from the temperature-dependent Poole–Frenkel plot for the control HfO₂ and Al:HfO₂ (HAO2) films, respectively.

showed a mixed conduction mechanism, as indicated in the inset figure of Figure 6b, where the conduction behavior is difficult to be defined by only one mechanism; either Schottky or Poole–Frenkel emission.

With increasing electric field over the UL, the electrons transport to the traps through a more tunneling-like mechanism rather than by thermionic emission. Therefore, with increasing voltage, the films show a transition from Schottky emission to Poole–Frenkel behavior.

Even though the lower J_g of HAO2 in the Poole–Frenkel conduction region can be explained by its lower trap concentration, the J_g in the Schottky region, where the plot of EOT– J_g measured at -1 V in Figure 5 was taken, is mostly dominated by the band structure (band offset) of the film. Therefore, the energy band structures of the Pt-gated control HfO₂ and HAO2 film on Si were examined by XPS, and the electrical measurement results. The band gap energy of the control HfO₂ and HAO2 films was estimated from the O 1s loss spectra, as shown in Figure 8a. The band gap energy of the film was determined by the energy separation between the peak energy and threshold energy of the loss spectrum because a photoelectron loses its kinetic energy by a Plasmon and band to band excitation.⁴³ The estimated band gap energy of the control HfO₂ and HAO2 films was ~ 5.05 and ~ 5.40 eV, respectively. The XPS valence band spectra provide information on the energy distance between the Fermi energy level (E_F) and upper edges of the valence band

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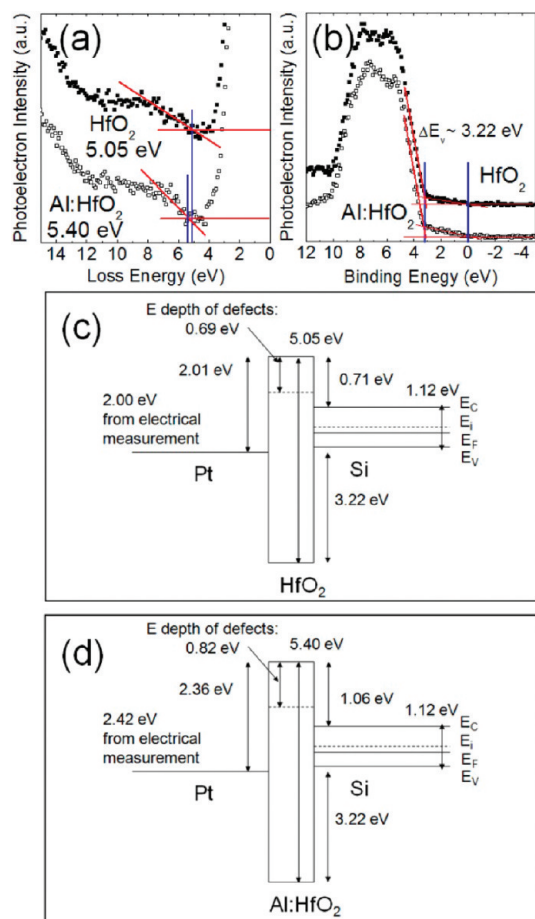


Figure 8. (a) O 1s loss spectra, (b) valence band spectra, and (c, d) reconstructed band structures based on the XPS results and electrical measurements of the control HfO₂ and Al:HfO₂ (HAO2) film on Si, respectively.

(E_V) of the films and Si substrate. Therefore, the valence band offset with a Si substrate can be obtained from the XPS valence band spectra, as shown in Figure 8b. The estimated valence band offset with a Si substrate of both films was the same, ~ 3.22 eV. Similar results were reported by M. Komatsu et al., where the valence band offset of HfO₂/Si was almost unchanged by Y-doping.⁴⁴ The band gap energy of Si is ~ 1.12 eV. The work function of Pt was ~ 5.25 eV,⁴⁵ which was obtained experimentally from y-intercept value in the V_{FB} vs EOT plot of the films with various thickness (data not shown). As a result, the band structures of the Pt-gated control HfO₂ and Al:HfO₂ films on a Si substrate could be reconstructed, as shown in panels c and d in Figure 8. The ϕ_B values between Pt and the films (~ 2.01 and ~ 2.36 eV for the control HfO₂ and Al:HfO₂ film, respectively) in the reconstructed band structures are consistent with the ϕ_B values (~ 2.00 and ~ 2.42 eV for the control HfO₂ and Al:HfO₂ film, respectively) estimated from the Schottky emission fitting shown in Figure 6. The larger ϕ_B for the HAO2 films in the Schottky emission simulation originated from the increased band-gap energy.

Panels a and b in Figure 9 show the density of states (DOS) for the control HfO₂ and Al:HfO₂ films (Al concentration of ~ 3 atomic %), respectively, extracted by first-principles calculations based on density functional methods. Here, V_O and C impurities were not considered. The top of the valence band was set to zero in all cases. Although the materials have an amorphous structure, a crystalline structure must be assumed for first principle calculations because a regular atomic structure of the material is needed. Therefore, the crystalline structures of the films were assumed to be a monoclinic phase, which is closest to the amorphous phase. A supercell containing 96 atoms was used and an Al atom was substituted for the Hf site. The supercell was obtained by doubling the unitcell of monoclinic HfO₂ along each axis. The calculated band gap energies of the control HfO₂ and Al:HfO₂ film were similar (~ 4.0 eV). Considering the well-known underestimation of the band gap in the density functional method, this suggests that Al₂O₃ itself in Al:HfO₂ film is not the main cause of the increased band-gap energy of the Al:HfO₂ film.

X. F. Wang et al. also reported that Al in the HfO₂ had little effect on the band gap energy of HfO₂.²⁹ G. Dutta et al. recently reported a first-principles study of the effect of V_O and C doping on the dielectric properties of ZrO₂. They showed that the band gap energy of a ZrO₂ film was increased by the reduction of V_O and C impurities in the film.³² Suzuki et al. also reported that stoichiometric HfO₂ has a larger band gap energy than HfO₂ with C impurities.³³ Therefore, the band gap energy of the Al:HfO₂ film may have increased as the concentration of V_O and C is reduced. Although the band gap energies of the thin ILs are hard to determine, it is believed that they are similar in both films because the ILs are mostly composed of SiO₂ and have similar dielectric constants as mentioned above.

Thermal Stability of Al:HfO₂ Thin Films. PDA at a high temperatures generally degrades the dielectric properties of the high- k gate dielectric films because Si diffuses from the substrate into the films (Hf-silicate reaction) and oxidation of the Si substrate at the interface with the film (IL growth) during PDA increases the EOT of the film. In addition, the degraded interfacial properties and crystallization of the film by PDA at a high temperature increases the J_g of the film.^{46–49} These adverse interfacial and structural effects eventually degrade the MOSFET performance. Therefore, the dielectric properties of both the control HfO₂ and Al:HfO₂ film were degraded after PDA at 850 °C, as shown in Figure 5a. Although J_g increased by an order of magnitude for both the control HfO₂ and Al:HfO₂ films, the differences in J_g (~ 2 orders of magnitude for HAO2) was maintained even after PDA. The increase in the EOT after PDA was also suppressed in

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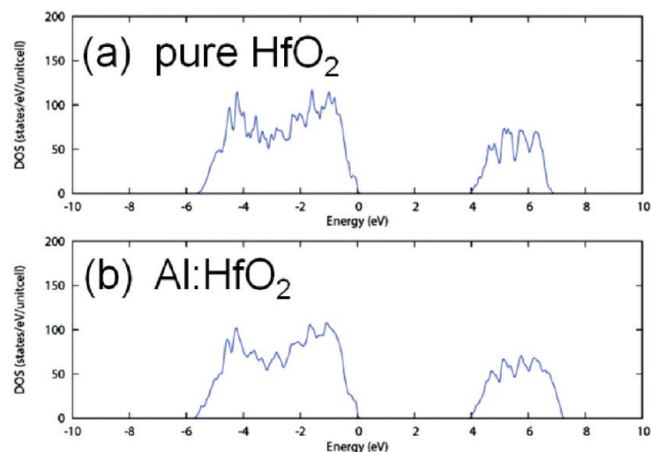


Figure 9. Density of state plots of (a) control HfO₂ and (b) Al:HfO₂ film.

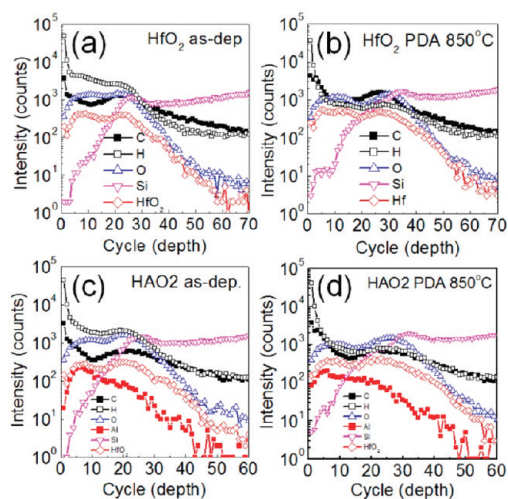


Figure 10. SIMS depth profiles of the control HfO₂ and Al:HfO₂ (HAO2) film (a,c) before and (b,d) after PDA.

case of the Al:HfO₂ films (~ 0.2 nm) compared to the control HfO₂ film (~ 0.5 nm) as shown in Figure 5a.

The crystalline and chemical structures of the Al:HfO₂ films were analyzed to explain the improvement in thermal stability of electrical properties against degradation by PDA. The chemical structures of the films were examined by SIMS depth profiling for the control HfO₂ and HAO2 film before and after PDA, as shown in Figure 10. PDA reduced the concentration of H impurity in both films. However, the control HfO₂ and HAO2 film showed similar chemical structural changes after PDA. The change in the Al profile in the film after PDA was also negligible. Considering that the J_g level of the film was determined mainly by the C and V_O concentration in the film, the lack of a difference in the chemical structural changes by PDA is consistent with the fact that the differences in J_g (~ 2 orders of magnitude for HAO2) between the control HfO₂ and HAO2 film had been preserved, even after PDA.

The EOT increase during the PDA is suppressed by the increased permittivity of the film or the suppressed Hf-silicate reaction and IL growth. It was reported that doped HfO₂ and ZrO₂ films have a tetragonal or cubic phase, which has a larger permittivity (≥ 30) than a monoclinic phase

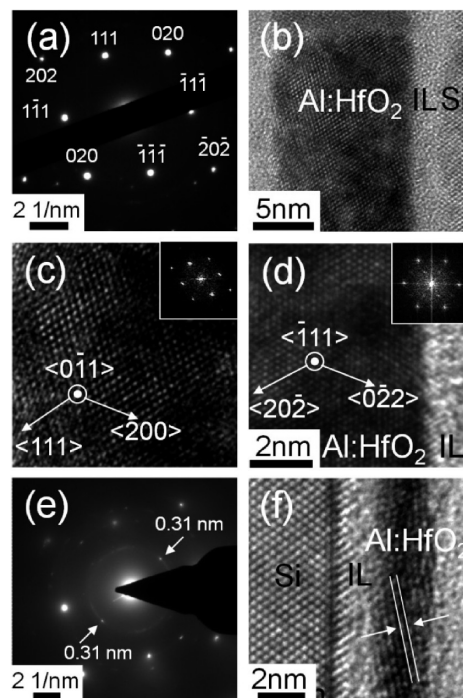


Figure 11. (a) SADP, (b–d) cross-sectional HRTEM images, (insets of c and d) FFT images for ~ 12 nm-thick Al:HfO₂ (HAO2) film, and (e, f) plan-view DP and cross-sectional HRTEM image of ~ 3 nm-thick Al:HfO₂ (HAO2) film, respectively.

(≈ 20).^{21–24} The diffraction patterns (DP) and HRTEM images of the annealed Al:HfO₂ films were examined to confirm the crystalline structure, as shown in Figure 11. Although the increased permittivity of the annealed Al:HfO₂ films with a large thickness (≥ 10 nm) was reported,²⁰ there are no results reported for ultrathin Al:HfO₂ films, ≤ 5 nm in thickness. There is no guarantee that thinner films would show the same crystallization as thicker films. Therefore, a rather thick Al:HfO₂ (HAO2) film, ~ 12 nm in thickness, and an ~ 3 nm thick Al:HfO₂ (HAO2) film were examined. Images a and b in Figure 11 show the selected area DP (SADP) and cross-sectional HRTEM image of the ~ 12 nm-thick HAO2 film, respectively. The zone axis was identified as tetragonal HfO₂ corresponding to $[10\bar{1}]$ in Figure 11a.²¹ The tetragonal HfO₂ with the zone axis of $[0\bar{1}\bar{1}]$ and $[\bar{1}11]$ was also observed in the ~ 12 nm thick Al:HfO₂ film, as shown in panels c and d in Figure 10, which was confirmed by the fast Fourier transform (FFT) images in the insets of panels c and d in Figure 10. On the other hand, the ~ 12 nm thick HAO2 film also contained a proportion of monoclinic structure (data not shown). Therefore, the ~ 12 nm thick HAO2 film has a tetragonal and monoclinic structure, which is consistent with previous reports.^{14–20}

However, the results from the ~ 3 nm thick HAO2 film were quite different. Images e and f in Figure 11 show the plan-view DP and cross-sectional HRTEM image of an ~ 3 nm thick HAO2 film, respectively. In SADP, the matrix spots are from the Si substrate with a zone axis of $[100]$. There is a ring pattern and spots with a strong intensity indicated by the white arrows. This originated

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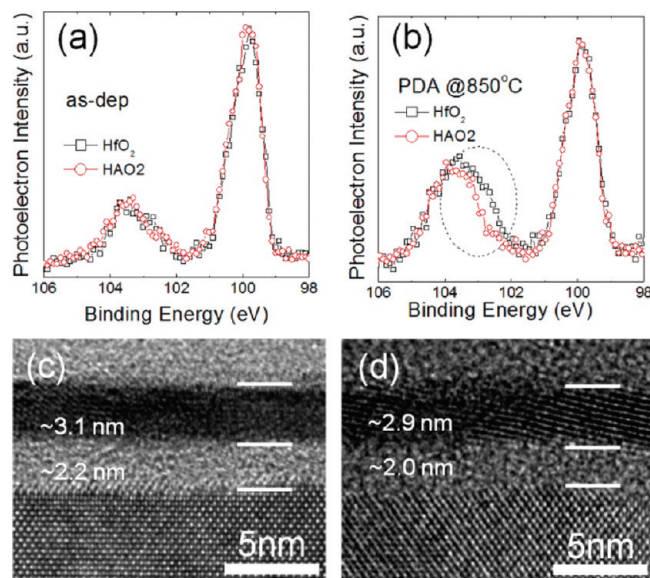


Figure 12. (a, b) Si 2p core level XP spectra for the control HfO₂ and Al:HfO₂ (HAO2) film before and after PDA, respectively, (c, d) HRTEM image of the control HfO₂ film and Al:HfO₂ (HAO2) film after PDA, respectively.

from the lattice-space of 0.31 nm, which corresponds to the ($\bar{1}11$) plane of a monoclinic HfO₂.⁵⁰ A 0.31 nm lattice fringe was also observed in the HRTEM image of the ~3 nm-thick HAO2 film, as shown in Figure 11f. As the plan-view SADP covers a large area (40 μ m in diameter), this strongly suggests that most of the ~3 nm thick HfO₂ film remained in the monoclinic structure even after Al doping. This might be because the ultrathin HAO2 film is influenced mainly by the Si substrate, such as Si diffusion into the film and the stress field from the Si substrate. Hence, the superior electrical properties of the ultrathin HAO2 films after PDA cannot be explained by the increased permittivity of the films.

Therefore, the suppressed increases in the EOT of Al:HfO₂ films after PDA must be due to the other reasons mentioned above, suppressed silicate reaction and IL growth. Panels a and b in Figure 12 show Si 2p core level XP spectra of the control HfO₂ and HAO2 films before and after PDA, respectively. Although the intensity of the peaks corresponding to Si–O bonding (near the binding energy of 102–104 eV) were similar in both cases of the control HfO₂ and HAO2 film before PDA (Figure 12a),

the increase in the peak intensity after PDA was suppressed in the case of the HAO2 film. This suggests that the Al₂O₃ in the film suppressed the silicate reaction and IL growth.⁵¹ Hf-aluminate suppresses Hf-silicate formation. Images c and d in Figure 12 show HRTEM images of the control HfO₂ and HAO2 film with 30 ALD cycles after PDA, respectively. The IL thickness of the control HfO₂ and HAO2 film after PDA was ~2.2 and ~2.0 nm, respectively. IL growth during PDA was significantly suppressed in case of the HAO2 film (~0.5 vs ~0.8 nm) because the IL thickness of the control HfO₂ and Al:HfO₂ films before PDA were ~1.4 and ~1.5 nm, respectively. Therefore, the silicate reaction and IL growth during PDA could be suppressed even by a small quantity of Al doping in the film. This can explain the improved thermal stability of the Al:HfO₂ films.

Conclusions

This study examined the effects of Al doping in HfO₂ thin films (~3–12 nm) on their electrical, structural, and chemical properties. An appropriate Al concentration of ~11% in the HfO₂ film significantly improved the electrical properties. The leakage current density of the Al:HfO₂ film with the optimized Al concentration was reduced by ~2 orders of magnitude compared to that of the control HfO₂ film, even at a given EOT of ~1 nm. The permittivity of HfO₂ film in the thickness range near ~3 nm was not increased by Al-doping, suggesting that the crystalline structure of the film had not transformed to a tetragonal or cubic structure. This is in contrast to thicker films. Al doping largely decreased the oxygen vacancy and C impurity concentrations, which increased the energy gap of the film. This is despite the fact that Al doping itself had little influence on the band gap. The reduced vacancy and impurity concentration also removes the shallow traps. These effects, increased band gap and removal of shallow traps, decreased the leakage current both before and after PDA. The thermal stability of the HfO₂ films was also improved by Al doping because Si diffusion into the film and the oxidation of Si at the interface during annealing were suppressed significantly.

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