

**Dichlorobis[bis(trimethylamido)]hafnium과 물을 이용한
Hafnium Silicate의 단원자층 화학증착**

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**FT-IR Diagnostics and Atomic Layer Deposition Study of Hafnium Silicate
Using Dichlorobis[bis(trimethylsilyl)amido]hafnium and Water**

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Introduction

Silicon dioxide (SiO₂) has been used as a primary gate dielectric material in metal-oxide-semiconductor field effect transistors (MOSFETs) for more than 30 years. However, as the dimensions of MOSFET devices are scaled down to sub-0.1μm, higher dielectric constant materials is needed to allow the use of physically thicker gate dielectric with electrically equivalent oxide thickness (EOT).

Among many high-k materials, ZrO₂, HfO₂, and their silicates have been considered as alternative gate dielectrics. Various techniques have been applied to deposit high-k thin films including sputtering and chemical vapor deposition method (CVD). Recently, atomic layer deposition (ALD) has attracted intensive attention for the deposition of nanoscale thin films. In this work, we studied a new ALD precursor, HfCl₂[N(SiMe₃)₂]₂, which has two chlorines and two methylsilazanes. This new precursor has high reactivity, lower process temperature, liquid phase over 50°C, and possibility of Si and N incorporation. Water was used as an oxidant.

Experimental

HfCl₂[N(SiMe₃)₂]₂ was synthesized with a modification of published procedure, from the reaction of anhydrous HfCl₄ and Na[N(SiMe₃)] in toluene. The films were grown in a cold-wall flow-type ALD reactor on (100) oriented p-Si single crystal substrates. Prior to deposition, the Si substrate was cleaned using the modified RCA method. Argon was used as a carrier and purging gas. The valve on/off time was varied to control source injection and purge time. HfCl₂[N(SiMe₃)₂]₂ was evaporated at 100°C. Feed lines and shower head are all heated to prevent condensation.

The FT-IR spectroscopy experiments were performed to study the surface reaction mechanism in the ALD process. High surface area metal oxide powder was used to achieve sufficient surface sensitivity for FT-IR investigations. High surface area metal oxide powder was pressed into a tungsten photoetched grid. This tungsten grid has 100 lines per inch. This sample could be resistively heated to about 1000 K by controlling the current. The thermocouple spot-welded to the grid provides accurate sample temperature measurement. IR spectrum transmitted through the oxide surface on the grid gives the information about the adsorbed species on the surface.

The film thickness and optical properties were calculated using spectroscopic ellipsometry (SE, JA Woolam). Chemical composition of the deposited films was measured by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 220iXL) and Auger electron spectroscopy (AES, PHI680) as a function of the process parameters. Secondary ion mass spectroscopy (SIMS, CAMECA IMS 6F) was used to examine the presence of residual impurities. Crystallinity and crystallite orientations of the as-deposited film and the post-annealed films were examined by X-ray diffraction (XRD, Rigaku D-max 1400) using Cu Kα radiation. For electrical characterization, metal-insulator-

semiconductor (MIS) capacitors were fabricated with deposited dielectric thin films. The capacitance-voltage (C-V) characteristics and the current-voltage (I-V) characteristics were analyzed with an electrical probe station.

Results and Discussion

In order to verify the self-limiting growth, the pulse time of $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ and water was varied respectively. As the $\text{HfCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ pulse time increased, the growth rate was saturated above 3s. Varying the water pulse time between 0.5s and 2s had no effect on the growth rate. Ideal linear dependence of the film thickness on the number of ALD cycles was confirmed at optimized pulse time and the constant growth rate was $1.2\text{\AA}/\text{cycle}$ at 200°C .

Figure 1 shows the dependence of the film growth rate on the substrate temperature. Maximum growth rate of $1.3\text{\AA}/\text{cycle}$ was obtained at 250°C and the growth rate rapidly decreased with increasing temperature. The analysis shows that the composition ratio of $\text{Si}/(\text{Hf}+\text{Si})$ linearly increased from 0.15 to 0.3 as the deposition temperature increased as shown in Figure 1 (b). Other impurity levels, such as carbon, nitrogen and chlorine, were measured below the detection limit (<1 at.%) of XPS or AES. In addition, the refractive index calculated at $\lambda=632.8\text{nm}$ decreased from 1.77 to 1.63 with the increase of the silicon content in the film.

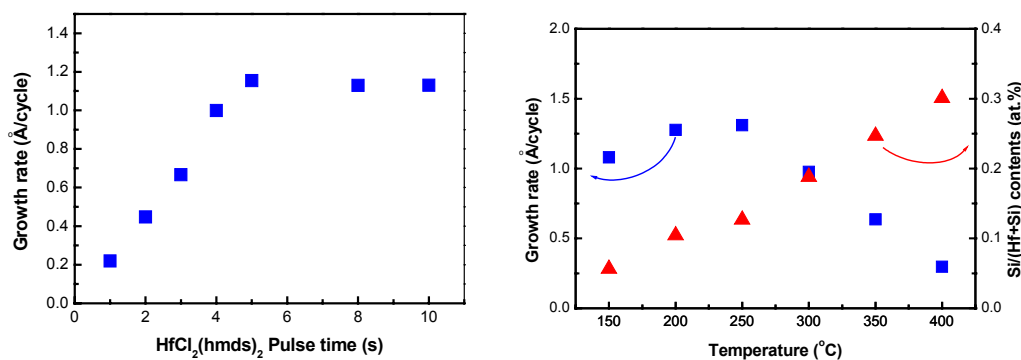


Figure 1. Growth rate per cycle as a function of (a) precursor injection time and (b) deposition temperature along with $\text{Si}/(\text{Hf}+\text{Si})$ ratio in the film.

ALD process using water proceeds by successive exchange reactions between hydroxyl groups formed after water dose and the ligands of the precursor. In our ALD process, it is believed that hydroxyl group in water replaces bis(trimethylsilyl)amido ligand and chlorine, releasing hydrogen chloride (HCl) and hexamethyldisilazane (HMDS, $(\text{Me}_3\text{Si})_2\text{NH}$) as by-products. At low deposition temperature below 250°C , all the ligands will almost completely react with water, producing almost pure HfO_2 with low silicon content. However, at high deposition temperature above 250°C , the Si-containing bis(trimethylsilyl)amido ligand seems to be decomposed on the surface and hafnium silicate film will be formed instead of Hf oxide.

Figure 2 shows the FT-IR peaks of -OH on the oxide surface after dosing of H_2O and successive change in peak intensity of -OH and -CH after each $\text{HfCl}_2(\text{HMDS})_2$ dosing. To study the decomposition of the precursor on the oxide surface with -OH, we dosed the precursor at 150°C until the peaks were saturated. It is clearly seen that -OH disappears through the surface reaction with the precursor and -CH peak becomes dominant due to the absorption of the precursor. After the experiment, IR cell was flushed at 1000°K to remove the information of the previous step and the impurities on the surface.

Figure 3 shows the FT-IR spectra from the surface and the normalized integrated absorbance of -OH after water dosing and -CH peaks after precursor dosing, respectively. We increased the surface temperature step by step and at each step, we waited for 3min to take a spectrum. This experiment was repeated up to 725°C . The -OH peak did not decrease appreciably up to 250°C and this is the reason why the deposition rate per cycle increased slightly up to this temperature as shown

in Figure 1. The growth rate was decreased with the increasing deposition temperature due to the decrease of $-OH$ on the surface. Also the precursor was dissociated as the surface temperature was increased and $-CH$ peak intensity was decreased. Figure 4 shows the surface IR measurement after the precursor was introduced up to saturation on the $-OH$ saturated surface from water dosing at given temperature. $Si-(CH_3)_n$ related peaks were observed at 3 different locations and the ones around 1250-1270 shows the dissociation of this bonding as the temperature was increased ($Si-(CH_3)_3$ at 1250, $Si-(CH_3)_2$ at 1260, $Si-(CH_3)$ at 1270). Also the peaks around 1000-1200 correspond to $Si-O-Si$ or $Si-O-R$ and it is believed that silicon oxide and alkoxide were formed from the precursor dissociation and reaction with $-OH$.

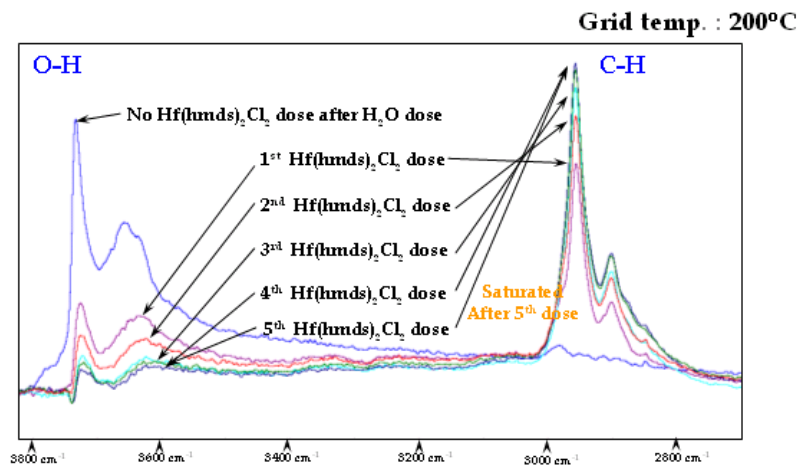


Figure 2. The FT-IR absorption spectra transmitted through the oxide surface after H_2O dosing and subsequent dosing of $HfCl_2(hmds)_2$.

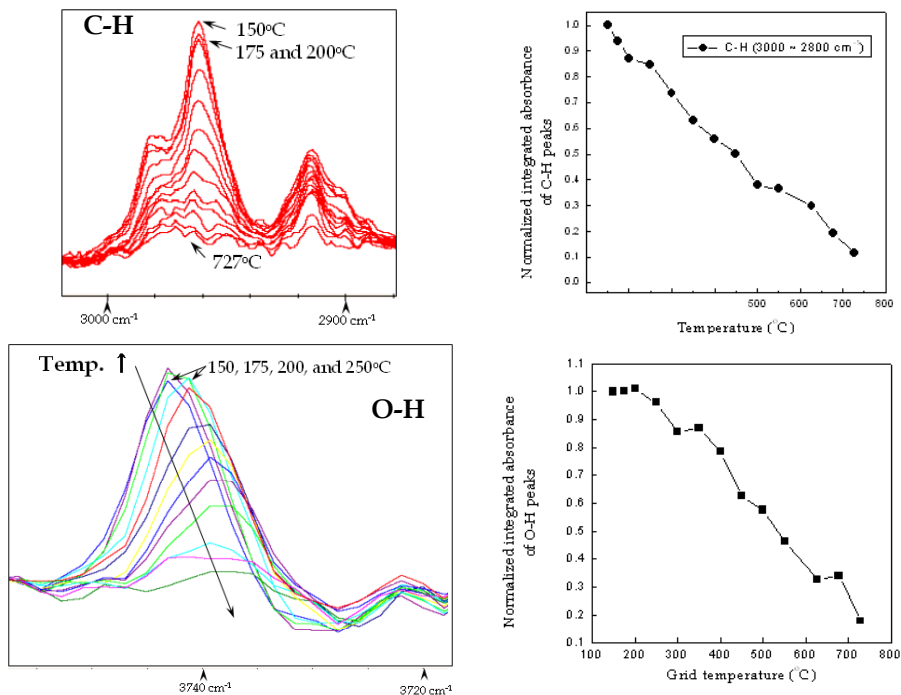


Figure 3. The change of peaks of O-H after water dosing and C-H peak after precursor dosing as a function of the grid temperatures.

Figure 5 shows the IR spectrum when water was introduced on the precursor saturated surface. It is clearly seen that as we introduced water, the number of methyl group on silicon was decreased and the Si-(CH₃)_n peak shifted towards larger wave number. It is believed that water also breaks Si-C bonding. The whole mechanism of the ALD reaction is not clearly identified with IR measurement but we could see some of the reactions involved in the ALD process.

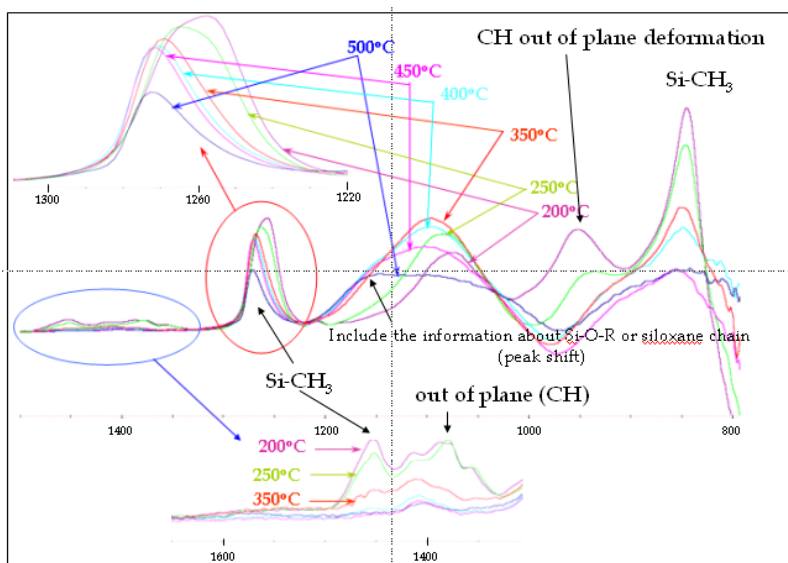


Figure 4. The peaks of Si-(CH₃)_x and Si-O-R when the precursor was dosed on -OH saturated surface as a function of the grid temperature.

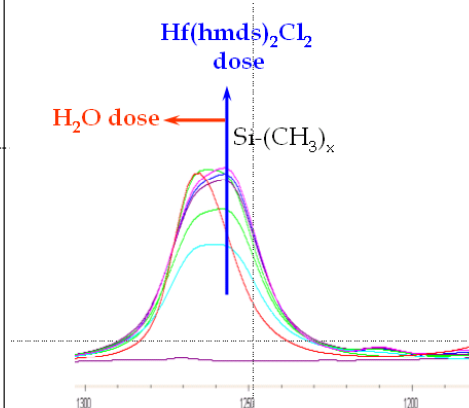


Figure 5. The peak change of Si-(CH₃)_x as H₂O was dosed. (200°C)

SIMS analysis was used to examine the composition profile and carbon, nitrogen and chlorine exist uniformly throughout the film. From the uniform distribution of silicon in the film, it is evident that Si was not outdiffused from the substrate into the film, but was incorporated into the film during ALD process. The content of carbon and chlorine in the film decreased with the increase of the deposition temperature.

Conclusions

A new single precursor, HfCl₂[N(SiMe₃)₂]₂, and water were used to deposit hafnium silicate thin films by ALD in the temperature range of 150-400°C. Also FT-IR diagnostic experiment was carried out to study the surface mechanism of the ALD process. As the deposition temperature increased, the growth rate decreased but the Si content in the film increased. It was shown that we could obtain hafnium dioxide at low temperature (150°C) and hafnium silicate with the composition ratio of Si/(Hf+Si)=0.3 at high temperature (400°C). FT-IR analysis could explain the deposition behavior of the ALD process.

References

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