Atomic layer deposition of HfO$_2$ for gate dielectrics

Yuichi Yokoyama, Hiroyuki Ishii and Anri Nakajima

Research Center for Nanodevices and Systems, Hiroshima University
1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
Phone: +81-824-24-6274, Fax: +81-824-22-7185, E-mail: nakajima@sxsys.hiroshima-u.ac.jp

1. Introduction

Recently, the substitution of conventional SiO$_2$ with a high-dielectric-constant thin film as the gate dielectrics for sub-0.1 μ m MOSFETs has received extensive attention from the viewpoint of gate leakage current. One of the most promising candidates for the replacement of SiO$_2$ is HfO$_2$ [1].

Recently, in view of film uniformity, thickness control capability and low thermal budget, the application of self-limiting atomic-layer deposition (ALD) is accelerating in the fabrication of various gate dielectrics [2,3]. For the ALD of HfO$_2$ gate dielectrics, the alternating exposure of HfCl$_4$ and H$_2$O gases has most commonly been applied to date [1]. However, in the ALD using the source gases, HfO$_2$ has a risk of Cl contamination and particle adhesion to the substrate surface. Tetrakis(hexafluoroacetylacetone) hafnium [Hf(HFAcAc)$_4$] is one of the candidates of alternative Hf precursors with the highest vapor pressure, allowing evaporation at low temperatures. As to the ALD of HfO$_2$ using Hf(HFAcAc)$_4$, no report has been published to date. Therefore, in this study, we study the possiblity of ALD of HfO$_2$ for a future gate dielectrics using Hf(HFAcAc)$_4$ and H$_2$O as source gases.

2. Experiments

The possibility of ALD of HfO$_2$ was examined by carring out the altyernate supply of Hf(HFAcAc)$_4$ [Central Glass Company] and H$_2$O gases on p-type Si (100) wafers (~10 Ω ・ cm). The Si surfaces were terminated with hydrogen in a 0.5 % HF solution to suppress native oxidation before the deposition. Hf(HFAcAc)$_4$ exposure followed by H$_2$O exposure was cyclically repeated 5-15 times at the substrate temperature (T$_{sub}$) of 200-500 ¡C. The H$_2$O exposure time was 60-180 s. The vapor pressures of Hf(HFAcAc)$_4$ and H$_2$O during the deposition were controlled to 0.01 and 0.70 kPa, respectively.

3. Results

Figure 1 shows the dependence of the HfO$_2$ film thickness on Hf(HFAcAc)$_4$ exposure time after five deposition cycles at T$_{sub}$ of 350 ¡C and 400 ¡C. At T$_{sub}$ of 350 ¡C, the film growth seems to have a self-limiting properties with Hf(HFAcAc)$_4$ exposure time (over 60 s).

A saturated film thickness of about 2.0 nm was achieved at five deposition cycles with H$_2$O exposure time from 60 s to 180 s at T$_{sub}$ of 350 ¡C (Fig. 2), which is consistent with the result for Hf(HFAcAc)$_4$ exposure time of 60 s at T$_{sub}$ of 350 ¡C shown in Fig.1.

The deposited thickness is in linear relation with the number of deposition cycles though some offset thickness occurred (Fig.3). This offset thickness is about 1 nm and is considered to be due to the presence of the interfacial oxidized Si layer. From the slope of the linear line in the figure, the growth rate is estimated to be about 0.2 nm/cycle.

Figure 4 shows the dependence of HfO$_2$ film thickness on substrate temperature after five deposition cycles. In the temperature regions from 350-450 ¡C, the increase in deposition rate with temperature is smaller than that in the other T$_{sub}$ region.

Figure 5 shows a high-resolution cross-sectional TEM micrograph of the deposited HfO$_2$ film. The HfO$_2$ deposited at T$_{sub}$ of 350 ¡C has an amorphous structure. Uniform thickness of deposited HfO$_2$ is observed. The thickness of the interfacial layer is observed to be ~1.5 nm by TEM.

Figure 6 is the composition of the deposited HfO$_2$ film obtained from Rutherhord backscattering (RBS) spectra. The large concentration of the carbon atom are observed throughout the deposited film. Fluorine atoms are also observed throughout the film. It is necessary to reduce these carbon and fluorine for the use of this film as gate dielectrics.

4. Conclusions

In summary, the possiblity of ALD of HfO$_2$ for the future gate dielectrics have been examined using Hf(HFAcAc)$_4$ and H$_2$O as source gases. Self-limiting properties of film growth with Hf(HFAcAc)$_4$ and H$_2$O exposure time were achieved at the growth temperature of 350 ûC. Carbon and fluorine atom are observed by throughout the film. Fluorine atoms are also observed by RBS spectra throughout the film. It is necessary to reduce these carbon and fluorine for the use of this film as gate dielectrics.

Acknowledgements

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References

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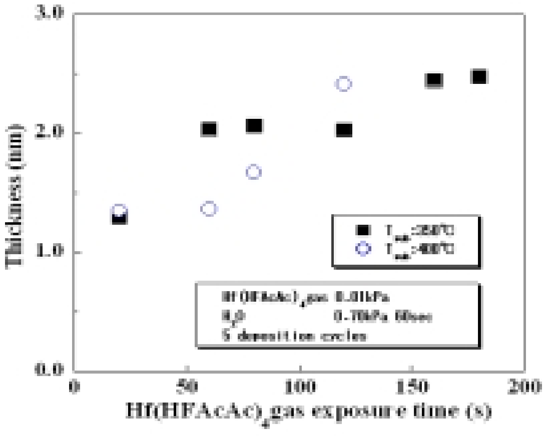

Figure 1 Dependence of HfO_2 film thickness on the $Hf(HFAcAc)_4$ gas exposure times after five deposition cycles. Vapor pressure of $Hf(HFAcAc)_4$ and H_2O was 0.01 and 0.70 KPa.

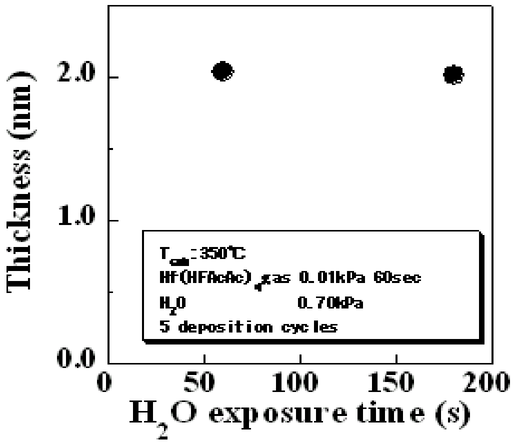

Figure 2 Dependence of HfO_2 film thickness on the H_2O exposure time after five deposition cycles. The vapor pressure of $Hf(HFAcAc)_4$ and H_2O was 0.01 and 0.70 KPa.

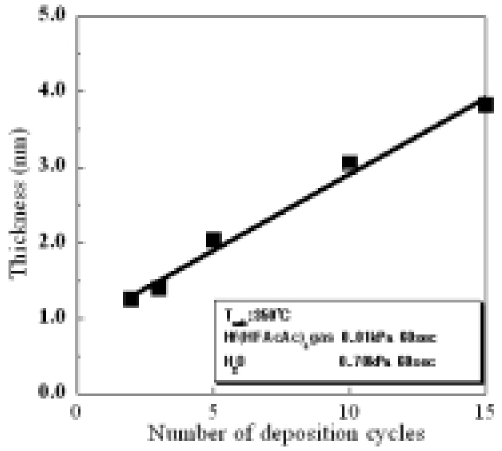

Figure 3 Thickness of HfO_2 versus number of deposition cycles. The thickness of HfO_2 was measured by ellipsometry. Exposure time was 60 s for both $Hf(HFAcAc)_4$ and H_2O. Vapor pressures was 0.01 and 0.70 kPa for $Hf(HFAcAc)_4$ and H_2O, respectively.

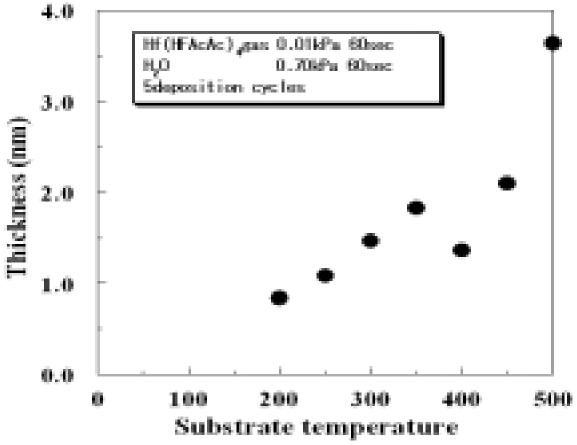

Figure 4 Dependence of HfO_2 film thickness on substrate temperature after five deposition cycles. Exposure time was 60 s for both $Hf(HFAcAc)_4$ and H_2O. Vapor pressures was 0.01 and 0.70 kPa for $Hf(HFAcAc)_4$ and H_2O, respectively.

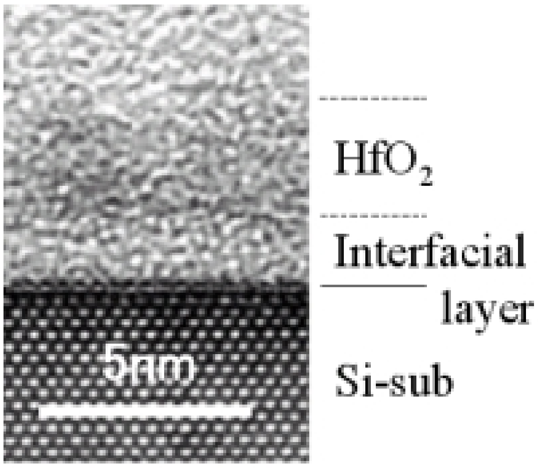

Figure 5 High-resolution cross-sectional TEM micrograph of HfO_2 deposited at T_{sub} of 350 ¡C. Exposure time was 60 s for both $Hf(HFAcAc)_4$ and H_2O. Vapor pressures was 0.01 and 0.70 kPa for $Hf(HFAcAc)_4$ and H_2O, respectively. Number of deposition cycles was 15.

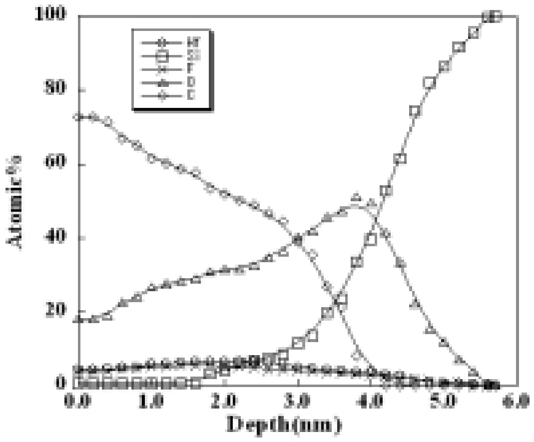

Figure 6 Composition of HfO_2 film obtained from Rutherhord backscattering spectra. The film was grown on Si. The film is the same in Fig. 5.