

行政院國家科學委員會專題研究計畫 成果報告

製備合成氧化物在互補式金氧半閘極介電層及自旋電元件
應用之研究

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行政院國家科學委員會專題研究計畫成果報告

製備合成氧化物在互補式金氧半閘極介電層及自旋電元件應用之研究

Deposition and Characterization of Compound Oxide Films for High- κ CMOS Gate Dielectrics and Spintronics Applications

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ABSTRACT

In this study, we use metal-organic chemical vapour deposition (MOCVD) to fabricate hafnium oxides on silicon. An oxygen-free precursor, TDEAH (tetrakis diethylamido hafnium), was used in film deposition, with nitric oxide (NO) or oxygen (O_2) as oxidant gas. Nitrogen incorporation up to 11% in atomic ratio was obtained in NO oxidized films.

Hafnium silicate films were deposited using TDEAH and TDMAS (tetrakis dimethylamido silicon). Silane (SiH_4) was also examined to replace TDMAS as the silicon precursor. TDMAS needs higher temperature for surface decomposition, while SiH_4 can be used with lower temperature in deposition. When using SiH_4 , however, further study is required to enhance silicon incorporation and eliminate particular generation.

1. Introduction

Due to the needs of device scaling,

traditional gate-dielectric material, SiO_2 , was thinned to obtain higher coupling capacitance. However, with thinner and thinner oxide films, tunneling currents dominate the gate-leakage and SiO_2 loses its insulating property. Thus, the requirement turns to finding an alternative high dielectric constant (high- κ) material as the gate dielectric.

Materials with a higher dielectric constant than SiO_2 can be made thicker while preserving the same capacitance per unit area, thus reducing the leakage current significantly. The new high- κ material should have adequate band-gap energy and a high barrier height with a low interface-state density on silicon. Film morphology, CMOS-related process compatibility, and reliability are other important issues.^[1]

In this project, MOCVD was utilized to deposit hafnium oxide and hafnium silicate. For MOCVD, alkoxide precursors are often used. A recent review^[2] describing the latest precursors for ZrO_2 deposition points out that using

oxygen-containing precursors invariably results in a SiO₂-rich interfacial layer at the Si interface. This has been our experience with mixed alkoxide β-diketonate precursors for Zr and Si.^[3] Therefore, we decided to use precursors with amide ligands, which contain no oxygen. TDEAH, [(C₂H₅)₂N]₄Hf, and TDMAS, [(CH₃)₂N]₄Si, were used for Hf and Si precursors, respectively. In MOCVD process, oxidants are needed to form oxides or silicates; O₂ and NO were used for this purpose.

2. Experiments

After an HF-last RCA clean, 4-inch p-type (100) wafers were sent into the MOCVD chamber for film deposition. The chamber is equipped with a liquid injection system (ATMI LDS-300B) for introducing precursors (Fig.1). An *in-situ* ellipsometer (Rudolph 1000i) is added to the MOCVD chamber in order to monitor the growth rate of oxides or silicates.

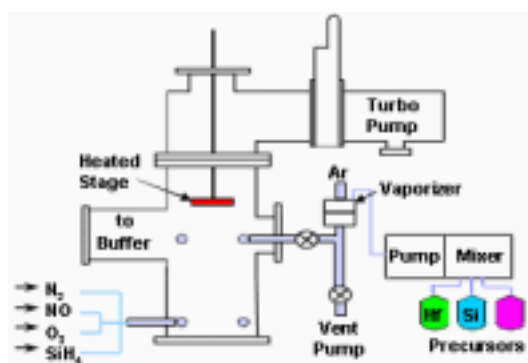


Fig.1 MOCVD chamber is equipped with a liquid injection system and a vaporizer. The sample wafer is face-down, sitting on a quartz ring, and heated by a set of halogen lamps.

During hafnium-oxide deposition, 0.1 M TDEAH solution was pumped at a rate of 0.2 ml/min and was vaporized while passing through the vaporizer, accompanied by a flow of 50 sccm Ar. The vaporizer was held at 150°C, as well as the lines into the deposition chamber and the gas distribution ring.

The oxidants, either O₂ or NO, were introduced into a separate gas distribution ring at a flow rate of 150 sccm. In the pulse-mode deposition we utilized, each deposition cycle consisted of 4 steps: a precursor (with Ar) introduction, a pump-down, an oxidant introduction, and another pump-down. A flow of 100 sccm N₂ was maintained throughout the deposition cycle. The total deposition pressure was in the range 3~11 mTorr where gas-phase collisions are rare. The sample stage temperature was controlled with a quartz-halogen heater-thermocouple combination. The base pressure of the MOCVD chamber was about 10⁻⁸ Torr. The deposition temperature was held at 400°C for the hafnium oxide deposition.

For the hafnium-silicate deposition, 0.1 M TDEAH and 0.3 M TDMAS solutions were mixed and then pumped through the vaporizer. The relative ratio of TDEAH versus TDMAS was tunable, and was held constant during film deposition. The vaporizer temperature was 150°C. Deposition temperature was set to be 500°C or 550°C when TDMAS was used.

Instead of TDMAS, SiH₄ was also

tested for hafnium-silicate deposition. In a pulse-mode deposition cycle, we introduced 10 sccm SiH₄ flow either in the TDEAH introduction step, or in the O₂ introduction step. When SiH₄ was used, the deposition temperature was held at 350°C, 375°C, or 400°C.

After film deposition, an *in-situ* rapid thermal anneal (RTA) was performed. The wafer was spike annealed at 800°C, while the chamber pressure was kept around 10⁻⁸ Torr.

Auger electron spectroscopy (AES) and *in-situ* X-ray photoelectron spectroscopy (XPS) were used to analyze the composition of hafnium oxide or hafnium silicate films. By proper calculation, atomic ratios of elements can be extracted from XPS results.

For micro-structural investigation, high resolution transmission electron microscopy (HRTEM) was utilized. The thermal stability of hafnium oxide or hafnium silicate was evaluated by investigating the crystallization behavior after RTA.

3. Results and Discussion

A. Hafnium oxinitride

Nitrogen incorporation was found in all hafnium oxide films, no matter oxidized by O₂ or NO during deposition. In those films deposited with O₂, the incorporated nitrogen can be attributed to the amide ligands in TDEAH. According to the calculation based on XPS results, the average nitrogen

composition was 4 at. % for films deposited with O₂ and 11 at. % for those deposited with NO. AES analysis in Fig.2 also provides evidence of nitrogen incorporation. In HRTEM images (Fig.3), retarded crystallization was observed in films with higher nitrogen incorporation.

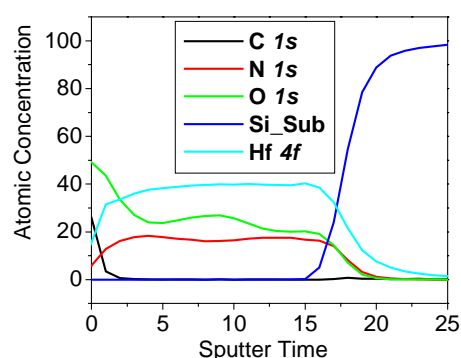


Fig.2 AES depth profile of a 15 nm HfO_xN_y film

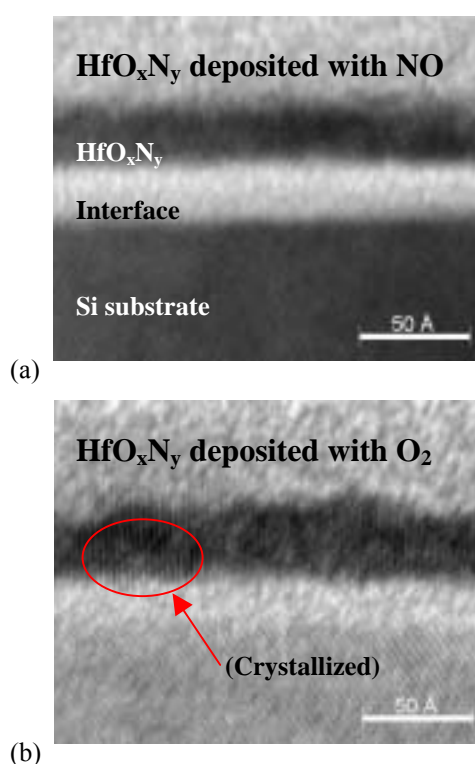


Fig.3 Cross-sectional HRTEM of HfO_xN_y films annealed at 600°C for 1 minute in oxygen ambient. Crystallized regions were found in films deposited with O₂.

B. Hafnium silicates (with TDMAS)

The composition $[Hf]/([Hf]+[Si])$ of the films is shown in Fig.4. At a substrate temperature of 500°C, the amount of hafnium in the films initially decreases as the TDMAS percentage in the precursor mixture increases but levels off at ~60% (*i.e.* silicon amount increases and levels off at ~40%). Increasing the Si precursor above 80% of the total precursor solution did not increase the silicon concentration further. Increasing the TDMAS percentage in the precursor mixture causes another drawback of lowering deposition rate, which is shown in Fig.5. The silicon concentration achieved in this study is much smaller than reported in reference [4], which is done at a much higher pressure (8 Torr). This suggests that the incorporation of silicon at high pressure is activated by gas-phase rather than surface reactions.

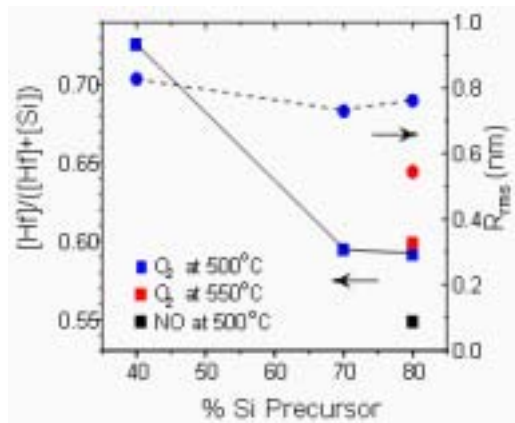


Fig.4 Composition (squares) obtained by in-situ XPS and root-mean-squared roughness (circles) obtained by AFM as a function of the fraction of TDMAS in the precursor mixture for silicate films deposited using TDMAS and TDEAH.

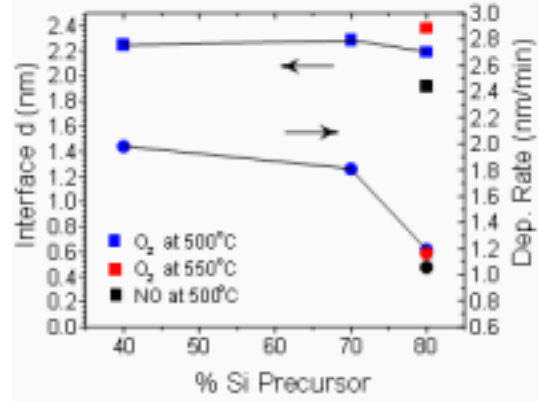


Fig.5 Interface layer thickness (squares) obtained by HRTEM and deposition rate (circles) as a function of the fraction of TDMAS in the precursor mixture for silicate films deposited using TDMAS and TDEAH.

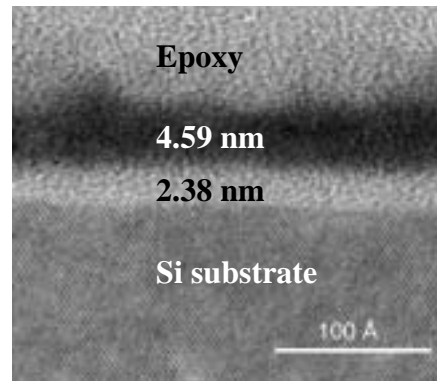


Fig.6 Cross-sectional HRTEM image of the $Hf_{0.6}Si_{0.4}O_2$ film deposited at 550°C using a precursor mixture of 20% TDEAH and 80% TDMAS, with O_2 as the oxidant.

C. Hafnium silicates (with SiH_4)

Table1 summarizes the silicon amount in hafnium silicate films deposited using TDEAH and SiH_4 with O_2 .

Table1: $[Si]/([Si]+[Hf])$ ratios in silicate films

SiH_4 was introduced	400°C	375°C	350°C
with O_2	0.12	0.19	0.16
with TDEAH	0.1	n/a	n/a
with dilute TDEAH	0.16	n/a	n/a

The silicon concentration could not be effectively increased. Higher silicon concentration was obtained when SiH₄ was introduced with dilute TDEAH (0.02 M TDEAH, diluted with octane). However, the deposition rate was dramatically decreased with dilute TDEAH precursor.

Although the silicon concentration in hafnium silicate films deposited with SiH₄ is low, the deposition temperature can be reduced to 400°C, as being used in hafnium oxide deposition with TDEAH. Tetra-ethoxy silane (TEOS) was reported to be used in MOCVD hafnium silicate.^[5] However, the temperature TEOS needs for surface decomposition is a concern.

4. Conclusions

Hafnium oxinitride films with 11 % nitrogen in atomic ratio were deposited using TDEAH with NO gas. TDEAH and NO gas were introduced in separate steps of a pulse-mode MOCVD process. With nitrogen incorporation, the films showed higher crystallization temperature, and were less likely to interface-layer growth in air-exposure tests.

MOCVD hafnium silicate films were deposited using TDEAH and TDMAS. The silicon versus hafnium concentration ratio was increased to 4:6 by increasing TDMAS percentage in the precursor mixture, with a drawback of lowered deposition rate. However, the higher temperature needed by TDMAS for surface decomposition limits its feasibility in MOCVD uses.

In order to decrease the substrate temperature during hafnium silicate deposition, SiH₄ was used as the silicon precursor in MOCVD, but the silicon concentration in deposited films was low. With SiH₄, further study is required to optimize [Si]/([Si]+[Hf]) ratio and eliminate particulate generation.

5. Publications

- [1] X. Wu, D. Landheer, M.J. Graham, H.-W. Chen, T.-Y. Huang, and T.-S. Chao, "Structure and thermal stability of MOCVD ZrO₂ films on Si(100)," *Journal of Crystal Growth*, 250, 479–485, 2003.
- [2] H.-W. Chen, T.-Y. Huang, D. Landheer, X. Wu, S. Moisa, G. I. Sproule, J. K. Kim, W. N. Lennard, and T.-S. Chao, "Ultrathin Zirconium Silicate Films Deposited on Si(100) Using Zr(Oⁱ-Pr)₂(thd)₂, Si(Oⁱ-Bu)₂(thd)₂, and Nitric Oxide," *Journal of The Electrochemical Society*, 150 (7), C465-C471, 2003.
- [3] X. Wu, J.-H. Chen, M.-S. Lee, S. Moisa, T.-F. Lei, T.-S. Chao, Z.-H. Lu, W.-T. Ng, and D. Landheer, "Analysis of Hafnium Silicate Films Deposited on Si (100) Using [(CH₃)₂N]₄Si or SiH₄ with O₂ and NO," 11th Canadian Semiconductor Technology Conference, 2003.

6. References

- [1] G.D. Wilk *et al.*, *J. Appl. Phys.*, **89**, 5243, 2001. (and references therein)
- [2] R.C. Smith *et al.*, *Adv. Mater. Opt. Electron.*, **10**, 105, 2000.
- [3] H.-W. Chen *et al.*, *J. Electrochem. Soc.*, **150**, C465, 2003.
- [4] B.C. Hendrix *et al.*, *Appl. Phys. Lett.*, **80**, 2362, 2002.
- [5] S. Inumiya *et al.*, Symp. on VLSI Tech. 2003