Mass Production Worthy HfO₂-Al₂O₃ Laminate Capacitor Technology using Hf Liquid Precursor for Sub-100nm DRAMs

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Abstract

For the first time, we successfully demonstrated MIS capacitor with ALD (Atomic Layer Deposition) grown $HfO_2-Al_2O_3$ laminate film using Hf liquid precursor (Hf(NEtMe)_4) with EOT of 22.5Å and acceptable leakage currents (1.0fA/cell at 1.65V) which is comparable to the smallest reported value. Advantages of Hf(NEtMe)_4 liquid precursor for DRAM capacitor dielectric are excellent step coverage (94% on high aspect ratio(>40:1)) and reasonable throughput (over two times higher than that of HfCl₄ solid precursor). This study will provide practical solution for chip-making industry in terms of mass production worthy process for sub-100nm DRAM capacitor.

Introduction

We have reported the characteristics of HfO2-Al2O3 laminate dielectric film using HfCl₄ solid precursor [1]. In spite of excellent electrical properties, there have been some potential problems such as poor step coverage and low throughput for HfO_2 deposition in the case of $HfCl_4$ [2]. To improve the step coverage of dielectric film on storage node with high aspect ratio, ALD precursors should have low sticking coefficient which is inversely related to diffusivity. In general, metal chlorides have relatively high sticking coefficient due to the strong ionic bonding characteristics. Previous study [3] reported that TaCl₅ has high sticking coefficient (k=0.02). The ionization potential of Hf (1.3eV) is similar to that of Ta (1.5eV), and besides, HfCl₄ has the same chlorine ligand as TaCl₅. Therefore, it can be assumed that HfCl₄ has high sticking coefficient. On the other hand, the sticking coefficient of Hf liquid precursors is expected to be lower than that of $HfCl_4$ on account of reduced ionic character by alkyl ligand.

Experimentals

 $HfO_2-Al_2O_3$ laminate dielectric film was deposited at 300°C by ALD using Genus Lynx2 tool for MIS capacitor evaluation. The thickness of each dielectric layer is 1nm and 2nm. Table 1 shows the vapor pressure and the decomposition temperature of various Hf liquid precursor candidates. Promising Hf liquid precursors for HfO₂ film deposition are Hf(NMe₂)₄ and Hf(NEtMe)₄ from the viewpoint of high surface reactivity. In this work, we have used Hf(NEtMe)₄ and Hf(NEt₂)₄ as Hf liquid precursors and HfCl₄ as Hf solid precursor. TMA and H₂O was also used to deposit laminate film.

Electrical Properties of MIS capacitor with HfO₂-Al₂O₃ laminate using HfCl₄ precursor

Fig. 1 shows the schematic diagram and the process flow to fabricate cylinder-type MIS capacitors. In previous study [1], the excellent leakage currents of $HfO_2-Al_2O_3$ laminate film (EOT=21Å) were shown (Fig. 2). These excellent leakage characteristics ensure superior device functionality which can be confirmed by Vp for generating solid "0" 10sec fail bit (Fig. 3). This Vp is increased by 0.4V for $HfO_2-Al_2O_3$ laminate compared to control Ta₂O₅. In the meantime, some recent study reported that the unacceptably high dielectric relaxation (DR) of HfO_2 may severely influence the performance of DRAM capacitor [4]. However, the estimated dielectric relaxation of $HfO_2-Al_2O_3$ laminate is comparable to currently used Ta₂O₅ film judging from the effective charge loss of Fig. 4.

Problems of HfCl₄ solid precursor

However, there are two major drawbacks using solid precursor (HfCl₄) for HfO₂ dielectric film deposition. First, fig. 5 shows the cross-sectional TEM view of MIS capacitor with HfO₂-Al₂O₃ laminate using HfCl₄ which has poor step coverage (about 42% on high aspect ratio (40:1)) in 1.3µm storage node height. Second, the saturation time (1.6sec) of the self-limiting reaction for HfCl₄ (Fig. 6) which is directly proportional to the process time (over 9.6sec/cycle) is longer than that (0.8sec) of Hf(NEtMe)₄ (Fig. 7). Therefore, we focused on Hf(NEtMe)₄ liquid precursor in order to find out the best solution for these problems. As mentioned above, Hf(NEtMe)₄ is one of the best candidates among Hf liquid precursors in terms of vapor pressure and the decomposition temperature, Although the vapor pressure of Hf(NEtMe)₄ is lower than that of Hf(NME₂)₄, it has higher decomposition temperature than Hf(NME₂)₄ precursor (Table 1).

Physical and electrical properties of HfO₂-Al₂O₃ laminate using Hf(NEtMe)₄ precursor

Fig. 8 shows the cross-sectional TEM view of MIS capacitor with HfO₂-Al₂O₃ laminate using Hf(NEtMe)₄ precursor as Hf source, which has good step coverage (about 94% on high aspect ratio (40:1)). In-film impurities such as carbon and nitrogen in HfO₂ films using Hf(NEtMe)₄ and H₂O as reactants are less than 1.0 at% and below detection limit, respectively, as shown in Fig. 9. However, TOF-SIMS analysis shows that carbon and nitrogen contents in HfO₂ dielectric films using Hf(NEtMe)₄ is about 1/3 and same level of those using $Hf(NME_2)_4$, respectively (Fig 10 and 11). For the first time, we fabricated MIS capacitor with HfO₂-Al₂O₃ laminate using Hf liquid precursor. Fig. 12 shows the leakage currents of MIS capacitor using HfCl₄, $Hf(NEtMe)_4$ and $Hf(NMe_2)_4$ precursors at the same EOT (22Å). Fig. 13 shows the comparison of temperature dependent leakage currents of MIS capacitor using $Hf(NEtMe)_4$ and $HfCl_4$ precursors at 1.2V. Leakage currents (1fA/cell at 1.65V) of MIS capacitor using Hf(NEtMe)₄ precursor are comparable to those of HfCl₄ (1fA/cell at 1.8V) (Fig. 14). EOT of 22.5 Å with acceptable leakage currents (1.0fA/cell at 1.65V) in the stack capacitor using Hf(NEtMe)₄, which is comparable to the smallest reported value, corresponds to 27.7fF/cell on the basis of Cmin at -0.9V. Cmin/Cmax ratio (88~91%) (Fig. 15) of HfO₂-Al₂O₃ laminate using Hf(NEtMe)₄ is similar to that of using HfCl₄ (87~92%). The leakage currents of MIS capacitor using Hf(NEtMe)₄ precursors are stable up to $125 \,^{\circ}$ (Fig. 16). This film also shows negligible frequency dispersion in the range of $20k\sim100$ kHz (Fig. 17). Fig. 18 shows TDDB lifetime projection of HfO₂-Al₂O₃ laminate capacitor using HfCl₄ and Hf(NEtMe)₄ precursors as a function of Vp(+). These data show that 10-year lifetime can be obtained at Vp=2.7V and Vp=2.9V for HfO₂-Al₂O₃ laminate capacitor using HfCl₄ (EOT=23.3Å) and Hf(NEtMe)₄ (EOT=22.5Å), respectively.

Conclusions

For the first time, we have successfully developed MIS capacitor with $HfO_2-Al_2O_3$ laminate using $Hf(NEtMe)_4$ liquid precursor. $HfO_2-Al_2O_3$ laminate dielectrics using $HfCl_4$ precursor show excellent leakage characteristics to ensure superior device functionality and negligible charge loss by dielectric relaxation (1.8%). However, low vapor pressure of $HfCl_4$ precursor gives rise to poor step coverage and low throughput. While, the ALD grown HfO_2 dielectric films using $Hf(NEtMe)_4$ liquid precursor show improved step coverage (94% for $Hf(NEtMe)_4$ compared to 42% for $HfCl_4$) and the reduced saturation time (0.8 sec. for $HfCl_4$) compared to 1.6 sec. for $HfCl_4$). Consequently, this study will sufficiently provide the mass production worthy process for next generation DRAM capacitor technology.

Acknowledgements

The authors would like to thank Professor R. Gordon, D. Hausmann at Harvard University for helpful discussions on alkylamide precursors.

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Top electrode formation TiN deposition

• Poly-Si deposition

Fig. 1 Schematic diagram and process flow of cylinder-type MIS capacitor with HfO_2 -Al₂O₃ laminate.



Fig. 4 Dielectric relaxation currents of HfO_2 - Al_2O_3 laminate compared to Ta_2O_5 film.



Table 1 Comparison of various Hf liquid precursors.

Compound	Temp.	Vapor Pressure [Torr]	Decomposition Temp.	M elting point
Hf(MMP) ₄	134 °C	0.6	-	Liquid
Hf(O-tBu) ₄	50°C	0.5	150℃	Liquid
Hf(NEt ₂) ₄	125 °C	1.0	150℃	Liquid
Hf(NEtMe)4	115 °C	1.0	140 °C	Liquid
$Hf(NMe_2)_4$	75℃	1.0	70~90℃	30℃



Fig. 2 Leakage currents of MIS capacitor with HfO_2 -Al₂O₃ laminate compared to $Ta_2O_5 at 85$ °C.



Fig. 3 Comparison of solid "0" 10sec fail bit counts as a function of Vp.



Fig. 5 Step coverage of HfO_2 -Al₂O₃ laminate on poly-Si storage node using solid precursor ($HfCl_4$).



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Fig. 8 Step coverage of HfO_2 -Al₂O₃ laminate on poly-Si storage node using liquid precursor $Hf(NEtMe)_4$ and H_2O ((a) top side of storage node, (b) bottom side of storage node).



Fig. 10 TOF-SIMS depth profiles of carbon in HfO_2 film using $Hf(NMe_2)_4$, $Hf(NEtMe)_4$



Fig. 13 Comparison of temperature dependent leakage currents of MIS capacitor using $Hf(NEtMe)_4$ and $HfCl_4$ at +1.2V.



Fig. 16 Frequency dispersions of MIS capacitor with HfO₂-Al₂O₃ laminate compared to control Ta₂O₅.



Fig. 11 TOF-SIMS depth profiles of nitrogen in HfO_2 film using $Hf(NMe_2)_4$, $Hf(NEtMe)_4$.



Fig. 14 Leakage currents of MIS capacitor with HfO_2 - Al_2O_3 laminate using $Hf(NEtMe)_4$ precursor at 25 °C.



Fig. 17 Temperature dependent leakage currents of MIS capacitor with HfO₂-Al₂O₃ laminate using Hf(NEtMe)₄.



Fig. 9 AES depth profiles of carbon and nitrogen in HfO_2 film using $Hf(NEtMe)_4$ precursor.



Fig. 12 Comparison of leakage current characteristics of MIS capacitor with $HfO_2-Al_2O_3$ laminate using solid Hf precursor and liquid precursor at the same EOT(22Å).



Fig. 15 C-V characteristics of MIS capacitor with HfO_2 -Al₂O₃ laminate and Cmin/Cmax ratio.



Fig. 18 Mean Time To Failure of HfO_2 - Al_2O_3 laminate capacitor using $Hf(NEtMe)_4$ and $HfCl_4$.

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