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Impact of Hf metal pre-deposition in CVD- and PVD-HfO_2 dielectrics

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1. Introduction

High-κ gate dielectrics have been extensively studied with much attention focused on HfO_2 and ZrO_2[1,2]. However, there have been some difficulties in preparing these thin films by chemical vapor deposition (CVD) and physical vapor deposition (PVD). A post -deposition annealing (PDA) is required to densify CVD-HfO_2 removing impurities (Cl, hydrogen, carbon and H_2O)[3,4]. CVD growth in oxidizing ambient and PDA process cause the thick interfacial layer growth. Although PVD-HfO_2 is no contaminated with impurities like CVD-HfO_2, energetic species are likely to react with Si substrates, leading to a thick interfacial layer [5-8]. Both deposition techniques will make the thick interfacial layers with low permittivity, leading to increase an effective oxide thickness. In this paper, we will demonstrate the EOT reduction of CVD- and PVD-HfO_2 capacitors with acceptable lower leakage current by means of pre-deposition of Hf metal layer.

2. Experimental procedure

Figure 1 shows the fabrication process of MOS capacitor with TiN/HfO_2/Hf/RTN-SiN/p-type Si stack. PVD-Hf metal pre-deposition on nitrided (<1nm) Si substrates prior to CVD- or PVD-HfO_2 deposition (0-2nm) was performed by sputtering Hf target in Ar. CVD-HfO_2 was grown by metal organic CVD using tetrakis(1-1-dimethyl-2-methoxy-Hf)(Hf[$OC(CH_3)_2CH_2OCH_3]_4$) and plasma-oxygen. PVD- HfO_2 was prepared by reactive sputtering from Hf metal target in Ar/O_2. PDA of the HfO_2/Hf was performed at 650 °C for 15 min in N_2. After the HfO_2/Hf deposition, TiN layer was grown by CVD at 650 °C and were defined by photolithography and etching to form gate electrode of MOS capacitor. The capacitance equivalent thickness (CET) of HfO_2 was obtained from capacitance value at Vg = –3 V.

3. Results and Discussion

A. CVD-HfO_2

Figure 2 shows the CET and leakage current density at –1V (Jg) dependence of CVD-HfO_2/PVD-Hf stack capacitors on the pre-deposited Hf metal thickness. The CVD-HfO_2 thickness is fixed to 3.4 nm. With decreasing the Hf metal thickness, the CET decreases due to the thinning of physical thickness. However, the CET reduction is deteriorated to approximately 1.6 nm for thinner Hf metal thickness regime (<~0.5 nm). Jg of the CVD-HfO_2 without Hf metal layer is three-orders of magnitude larger than that of Hf metal pre-deposited samples. To illustrate the effect of Hf metal pre-deposition, the CET plots are compared in Fig. 3. The solid triangles represent the CET for CVD-HfO_2 films without Hf metal layer. In the case of CVD-HfO_2 on Hf metal layer, total thickness is calculated as $T_{total} = T_{Hf} \times 1.62 + 3.4$ (nm), owing to the assumption that the thickness of HfO_2 increases by 1.62 times from that of Hf metal layer when Hf metal is completely oxidized. As can be expected from the intersection in the y axis, the interfacial layer thickness of HfO_2/Hf stack capacitors is smaller than that samples without Hf metal layer. Note that HfO_2/Hf capacitors grown at lower temperatures revealed much smaller CET. We speculate that the difference of slope, permittivy, reflects the film quality. Figure 4 shows the CET versus Jg at Vg = -1 V of CVD-HfO_2/Hf capacitors. Jg of HfO_2/Hf stack capacitors at the same CET value is smaller than that of samples without Hf metal layer. These results indicate that Hf metal pre-deposition suppresses the increase of the interfacial layer thickness (hence reduces the CET) and improves the film quality with low leakage current.

B. PVD-HfO_2

Figure 5 shows the CET and Jg dependence of PVD-HfO_2/PVD-Hf capacitors on the pre-deposited Hf metal thickness. The sputtering conditions of HfO_2 films are the same for all samples, where the HfO_2 thickness is fixed to 1.3 nm. When HfO_2 film is directly deposited on Si (0nm), the CET is around 2.6 nm, which is thicker than the HfO_2 thickness (1.3 nm), implying the growth of a relatively thick interfacial layer like SiO_2 during sputtering. It is interesting to note that the CET tends to decrease dramatically with increasing the Hf metal layer thickness and reveals minimum CET value (~1.3 nm) at an approximately 1.3 nm of pre-deposited Hf metal layer prior to the HfO_2 deposition, indicating that permittivity of HfO_2 with Hf metal is higher than that without Hf metal. In contrast, lower Jg is obtained for both thin and thick regime of Hf metal layer due to the thick interfacial layer and the thick physical thickness of HfO_2, respectively.

Figure 6 shows the TEM images for as-sputtered HfO_2 films on Hf metal thickness, (a) 0nm, (b) 1.3nm, and (c) 3.9nm. As seen in (a), it is clearly observed a 2.8 nm thick interfacial layer is present between the HfO_2 layer and the substrate after sputtering of an 1.3 nm thick HfO_2 layer. The thick interfacial layer is likely formed due to the sputtering in an Ar/O_2 gas mixture. When the Hf metal layer is thin enough, the excess oxidizing species such as radical, ion, and molecule in plasma result in this interfacial layer growth by diffusing into Si substrate to form SiO_2 layer. Then the total CET starts to increase again with further increase of Hf metal layer thickness. In contrast, the growth of the interfacial layer is prevented by consuming the pre-deposited Hf metal into HfO_2 and its silicate. This leads to a significant

reduction in the SiO_2 like interfacial layer thickness. Note that the HfO_2 film on thick Hf metal (c) is crystallized although that on thin Hf metal (a, b) remained as an amorphous phase. From this, the simple oxidation of Hf metal was found to make the films to be crystallized, leading to the leaky films.

Figure 7 shows the CET versus Jg at Vg = -1 V of PVD-HfO_2/Hf capacitors. Different slopes in Jg vs CET indicate different conduction mechanism due to the change of stack structures.

From above experiments, the pre-deposited Hf metal layer is found to be effective to block the diffusion of oxygen into Si due to the oxidation of Hf metal for both CVD and PVD growth. In PVD, oxygen radical in plasma has much oxidative than that in CVD, resulting in the thicker CET than that without Hf metal.

4. Conclusions

The Hf metal pre-deposition prior to Hf oxide deposition was used to modify the structure of interfacial layer to achieve a thin CET for both CVD and PVD techniques. During the growth, the oxidation of Si substrate was inhibited because the excess oxygen species are used for the oxidation of Hf metal, resulting in a thin interfacial layer with higher Hf composition. This pre-deposition technique can be applicable to most high-k materials and deposition methods.

References

[1] E. P. Gusev et.al. , IEDM Tech. Dig. p.451, 2001.
[2] Y. Kim et.al. , IEDM Tech. Dig. p. 455, 2001.
[3] S. J. Lee, H. F. Luan, W. P. Bai, C. H. Lee, T. S. Jeon, Y. Senzaki, D. Roberts, and D. L. Kwong, IEDM Tech. Dig. p31, 2000.
[4] Z. Zao, T. P. Ma, E. Cartier, M. Copel, and T.Tamagawa, Symp. VLSI Tech. Dig. ,pp. 135, 2001.
[5] A. Callegani, E. Cartier, M. Gribelyuk, H. F. Okorn-Schmidt, and T. Zabel. J. Appl. Phys. 90, 6466, 2001.
[6] R. Choi, C. S. Kang, B. H. Lee, K. Onishi, R. Nieh, S. Gopalan, E. Dharmarajan, and J. C. Lee, Symp. VLSI Tech. Dig.,pp. 15, 2001.
[7] B. H. Lee, L. Kang, W. Qi, R. Nieh, Y. Jeon, K. Onishi, and J. C. Lee, IEDM Tech. Dig. 133, 1999.
[8] S-H. Su, and M. Yokoyama, ECS Let. , 4, F18, 2001.

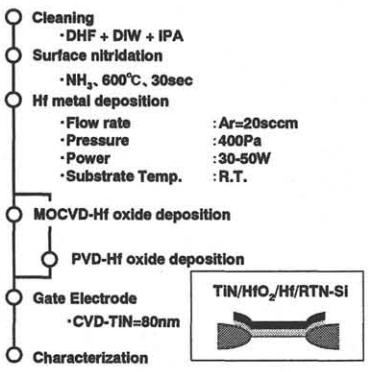

Fig. 1 Process flow of MOS capacitors

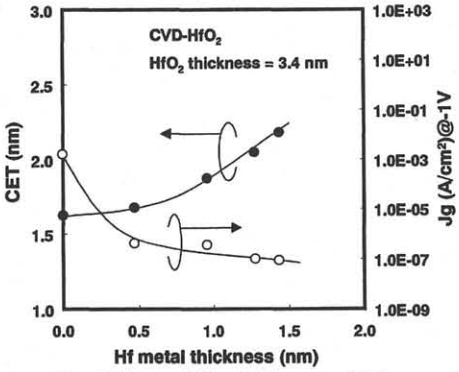

Fig. 2 Effects of Hf metal layer on CET and Jg in CVD-HfO_2

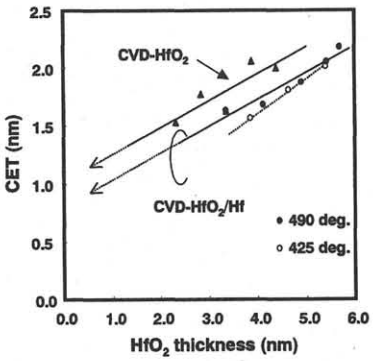

Fig. 3 CET dependence on HfO_2 thickness in CVD-HfO_2

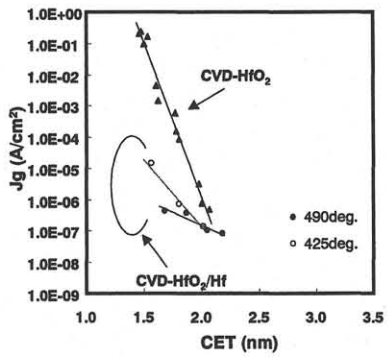

Fig. 4 CET vs Jg in CVD-HfO_2

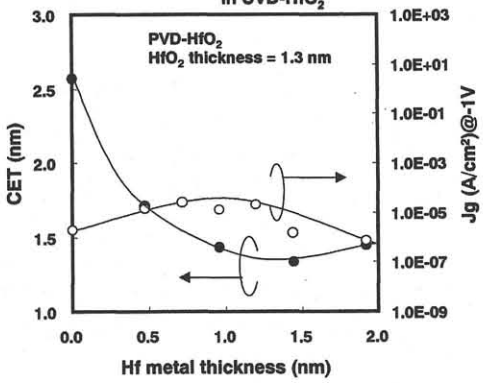

Fig. 5 Effects of Hf metal layer on CET and Jg in PVD-HfO_2

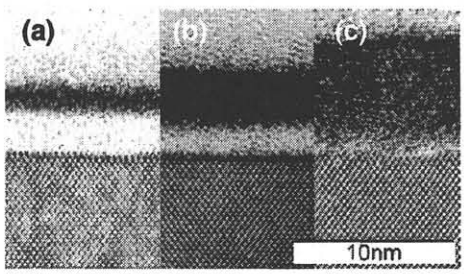

Fig. 6 TEM images of PVD-HfO_2/Hf

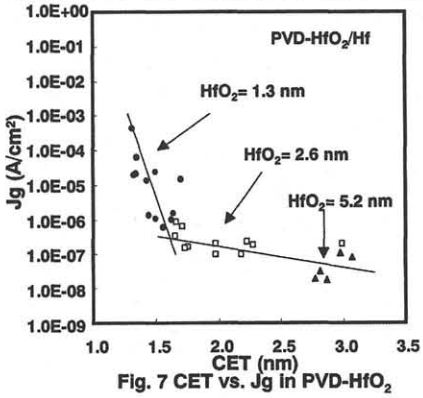

Fig. 7 CET vs. Jg in PVD-HfO_2