

MOCVD HfAl_xO_y Gate Dielectrics Deposited Using Single Cocktail Liquid Source

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1. Introduction

HfAl_xO_y alloy film has drawn great attention as a strong candidate for high-K gate dielectric because of its improved thermal stability and acceptable band offset and high dielectric constant value [1-3]. Until now, HfAl_xO_y has been formed by using two separate precursors in CVD and ALD, two sputtering targets in JVD, or PVD [1-5]. In this paper, we demonstrate for the first time the successful deposition of high quality HfAl_xO_y film with excellent capability of controlling Hf-Al ratio using a single cocktail liquid source in a MOCVD system. This is the most suitable technique for mass production in terms of process simplicity and reproducibility.

2. Experiments

MOCVD HfAl_xO_y (hereafter HfAlO) films were deposited using a multi-chamber cluster tool, so that all the processes including surface nitridation (SN), HfAlO deposition, and post deposition annealing (PDA) were carried out without breaking the vacuum. SN and PDA were performed at 700°C for 1 minute in an NH₃ and an N₂ ambient, respectively. HfAlO films were then deposited at 350°C ~ 600°C using a single cocktail source, HfAl(MMP)₂(OiPr)₅, without O₂ flow. This precursor was introduced into the process chamber by Liquid Delivery System (LDS) with argon as a carrier gas. TaN was deposited for gate electrode using reactive sputtering. For comparison, pure HfO₂ samples were also prepared by MOCVD at 400°C using bubbler source, Hf(OC(CH₃)₃)₄ with O₂ flow. For investigation of thermal stability of the high-K films, RTA at 950°C for 30 sec was added either before or after TaN deposition. All devices received a forming gas anneal at 420°C after metallization.

3. Results and discussions

For HfAlO films, there exists an optimum ratio between Hf and Al for achieving the best electrical properties. Therefore, we first study the compositional control and how it is influenced by process parameters. First, the effects of flow rates of argon carrier gas, oxygen reaction gas, and liquid precursor were investigated. As seen in Fig. 1, the composition ratio was not much affected and the controllable range by flow rate variations is between 70 ~ 80 % of HfO₂ in HfAlO. Next, the deposition temperature was varied ranging from 350°C to 600°C. As shown in Figs. 2 and 3, the deposition temperature plays a major role in the composition ratio control and a wide range of composition ratio between 45 to 90 % of HfO₂ in HfAlO was achieved by varying the deposition temperature. Higher temperature deposition introduces more hafnium into the film but there is

a turn-around point of the composition ratio at 450°C where the HfO₂ percentage is maximum of around 90% (Al₂O₃ 10%). It is interesting to note that the composition ratio has a very strong correlation with the deposition rate, as can be seen in Fig. 2.

Figure 4 shows XRD spectra of HfO₂ and HfAlO. The HfAlO was deposited at 450°C and the Al₂O₃ fraction was only around 10%. However, 10% Al in HfO₂ improves the thermal stability greatly. As-deposited HfO₂ was already crystallized while HfAlO remains amorphous up to 800°C of annealing. XRD spectra also indicate that strong (-111) peak of HfO₂ was not observed in HfAlO. The same trend is also found in XTEM images shown in Fig. 5.

Figure 6 shows increment of interfacial layer of HfAlO and HfO₂ before and after high temperature RTA at 950°C. While HfO₂ with SN shows the interfacial layer increase of around 4.5 Å, HfAlO with SN has almost no change in interfacial layer thickness. This is attributed to reduced oxygen diffusion by introduction of Al into HfO₂. In Fig. 7, dielectric constant value shows a very strong dependence on HfAlO deposition temperature. As expected, higher amount of Al incorporation significantly decreases K value. HfAlO film deposited at 450°C, which contains 10% of Al₂O₃, shows acceptable K value of 19. Since the HfAlO deposited at 450°C shows relatively high K value and still shows dramatic improvement in thermal stability, it can be regarded as the best condition in our work. The results in Figs. 8 - 9 were obtained from HfAlO films deposited at 450°C.

Figure 8(a) shows the leakage currents, before and after RTA at 950°C, with HfAlO and HfO₂ having similar physical thickness of 40 Å. As can be seen, HfAlO shows lower leakage current and higher breakdown voltage compared to HfO₂ due to improved thermal stability and larger band offset. The reason for relatively smaller difference in leakage current after RTA is due to the large increment of IL (and thereby the increment of final EOT of HfO₂) after RTA. Figure 8(b) shows the trend more clearly. Thermal stability with top metal electrode was also investigated and the result is shown in Fig. 9. In this case, the RTA at 950°C was done after the formation of TaN electrode. The pure HfO₂ shows tremendous increase in leakage current after RTA while HfAlO shows much smaller increase, which indicates better compatibility with TaN metal electrode.

4. Conclusion

We demonstrate that high quality HfAlO film can be successfully deposited, with adjustable HfO₂-Al₂O₃ ratio, using a single cocktail liquid source in a MOCVD system.

The deposited HfAlO film showed superior characteristics compared to pure HfO₂, suggesting that MOCVD HfAlO deposition using single cocktail source is a promising candidate for advanced gate dielectric formation technique.

References

[1] W. Zhu, *et al.*, IEDM Tech. Dig., p. 463, 2001.
 [2] H. Y. Yu, *et al.*, Applied Physics Letters, **81**, p. 376, 2002.
 [3] G.D. Wilk *et al.*, Symp. VLSI Tech., p. 88, 2002.
 [4] J. H. Lee *et al.*, Symp. VLSI Tech., p. 84, 2002.
 [5] L. Manchanda *et al.*, Microelectronic Eng., **59**, p. 351, 2001.

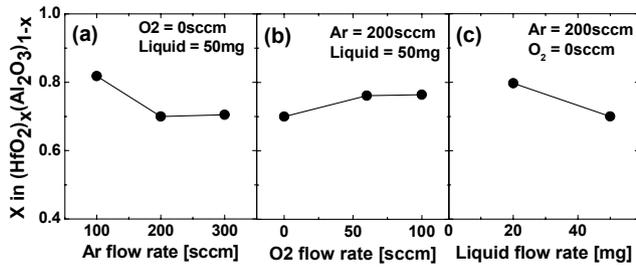


Fig. 1. Dependence of composition ratio on process parameters such as (a) Ar carrier flow rate, (b) O₂ flow rate, and (c) Liquid precursor flow rate. Deposition temperature is 400°C. The composition ratio is not much affected by the flow rates.

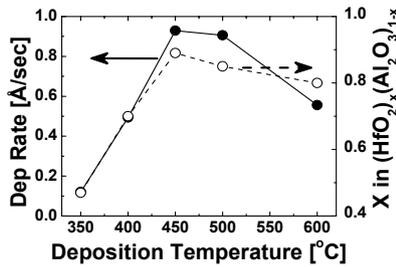


Fig. 2. Temperature dependence on deposition rate and composition ratio of HfAlO. The composition ratio changes over a wide range and shows a very strong correlation with the deposition rate.

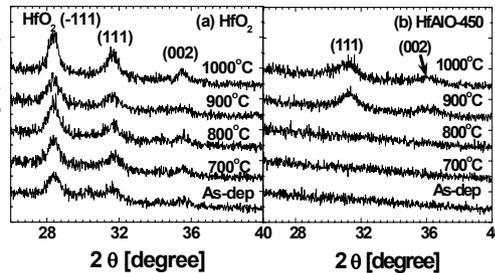


Fig. 4. XRD spectra of (a) HfO₂ (b) HfAlO after annealing at different temperatures. HfAlO remains amorphous up to 800°C.

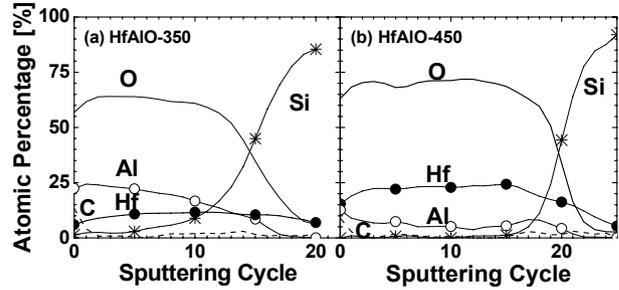


Fig. 3. XPS depth profiles of HfAlO films deposited at (a) 350°C and (b) 450°C. The 350°C sample exhibits Al-rich property while the 450°C sample exhibits Hf-rich.

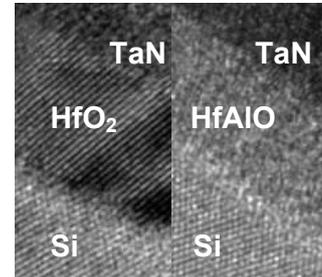


Fig. 5. XTEM images of HfO₂ and HfAlO after 700°C *in-situ* PDA treatment. HfAlO layer remained amorphous while HfO₂ was crystallized. Both films were deposited at 400°C without surface nitridation.

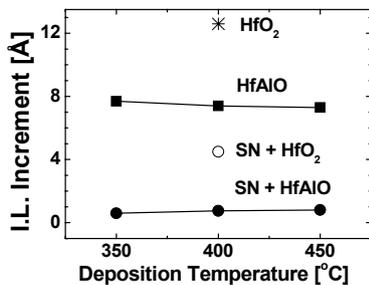


Fig. 6. Increment of interfacial layer (I.L.) of HfAlO and HfO₂ before and after high temperature RTA at 950°C for 30 sec.

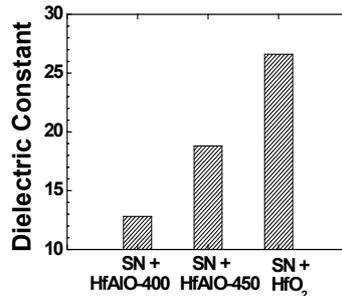


Fig. 7. K-values of HfO₂ and HfAlO films. HfAlO deposited at 450°C shows acceptable K value of 19.

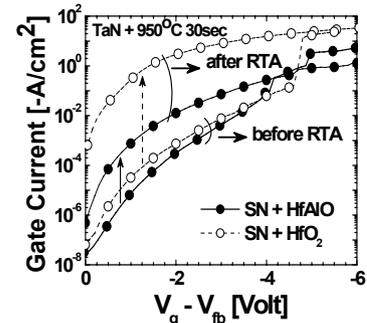


Fig. 8. (a) Leakage currents of 40Å HfAlO and HfO₂ before and after 950°C RTA. RTA was done after the formation of TaN electrode.

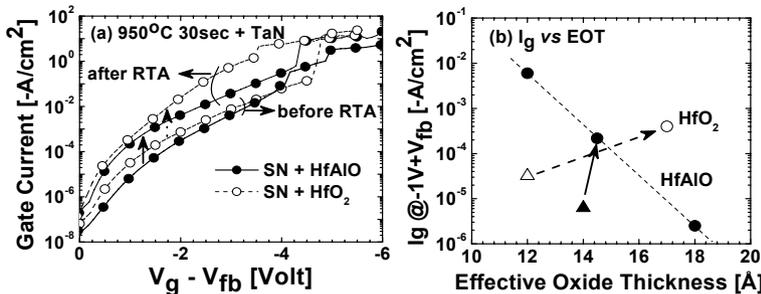


Fig. 8. (b) *I_g* vs EOT characteristics of HfAlO and HfO₂ before (▲,△) and after (●,○) 950°C RTA treatment.