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Top-Surface Aluminized and Nitrided Hafnium Oxide Using Synthesis of Thin AlN and HfO_2 Stacked Layer

Chang Seo Park, Byung Jin Cho, Lei Jun Tang[+], Wiede Wang[*], and Dim–Lee Kwong[++]
Silicon Nano Device Lab, Dept. of Electrical & Computer Engineering, National University of Singapore, Singapore 119260
Tel: 65-6874-6470 Fax: 65-6779-1103 email: elebjcho@nus.edu.sg
[+]Institute of Microelectronics, Singapore, [*]Institute of Materials Research Engineering, Singapore,
[++] Department of ECE, The University of Texas, Austin, USA

Abstract

A new approach to incorporate Al and N into HfO_2 is proposed, using synthesis of ultra thin aluminum nitride (AlN) and HfO_2. The reaction of AlN with HfO_2 during subsequent annealing synthesizes HfAlON near top surface of HfO_2, forming HfAlON/HfO_2 stack structure. The approach suppresses interfacial layer growth and improves thermal stability, resulting in significant improvement in leakage current, and shows no adverse effects caused by N and Al incorporation at the bottom interface.

Introduction

Recently Hf-based high-K dielectrics doped with Al and N have been proposed as promising gate dielectrics because of good thermal stability and immunity to impurity penetration [1-4]. However, Al and N incorporation at the bottom interface of high-K causes degradation of the interface quality such as introduction of negative fixed charge due to Al [6], and increased hysteresis and mobility degradation caused by Al and N at the interface [2,7]. In this study, a new approach to form Hafnium-Aluminum-Oxynitride (HfAlON) is demonstrated, using synthesis of ultra thin AlN and HfO_2, in which only the top surface of HfO_2 film is aluminized and nitrided.

Experiment

The HfO_2 dielectric films were deposited by MOCVD at 400°C. Post deposition anneal (PDA) was done at 700°C for 1 min. Thin AlN films were deposited on top of HfO_2 films using reactive sputtering. The composition ratio of AlN was around 1.0 determined by AES. HfN/TaN stack was used for the gate electrode [5]. The synthesis of AlN and HfO_2 was done by RTA at 950°C for 30s which was required for S/D annealing. Finally, post metallization annealing was done in a forming gas ambient at 420°C. For comparison, HfAlO prepared by single cocktail source MOCVD [6] was also prepared.

Results and Discussion

Figures 1 and 2 show the basic idea of the proposed process and corresponding TEM images. The results clearly demonstrate that HfAlON on top of HfO_2 is successfully formed. AlN is completely consumed by the reaction with HfO_2 during RTA at 950°C. HfAlON layer is in amorphous state even after 950°C RTA. The thin HfO_2 near the bottom interface remains unreacted, indicating that Al and N are incorporated only at the top portion of HfO_2 film. The HfO_2 layer near the bottom is crystallized. Thickness reduction of high-K due to densification during annealing also can be seen in the TEM images. Another important advantage of using AlN layer is the excellent barrier property to oxygen diffusion. No significant additional interface layer growth is observed even after 950°C RTA. In order to verify Al and N incorporation in the synthesized film, XPS and SIMS analysis was done. Fig. 3 shows the XPS spectra of N1*s*, Al 2*p* and Hf 4*f* obtained from various films. After RTA at 700°C, the peaks of Al 2*p* and Hf 4*f* of synthesized HfAlON/HfO_2 stacks shift due to the reaction of AlN and HfO_2. The incorporation of N from AlN into HfO_2 is also confirmed by SIMS (Fig. 4).

EOT variation is evaluated using C-V measurements (Fig. 5). For single HfO_2 layer, the increase in EOT after RTA is found due to interfacial layer (IL) growth. When AlN is inserted on HfO_2, EOT increase is observed before RTA because the AlN is a dielectric layer. However, after RTA, the EOT is reduced back to that of HfO_2 before RTA. It is interesting to observe that for both 1 nm and 2 nm AlN films on HfO_2, the final EOTs are identical. This indicates that AlN film of up to 2 nm thickness is completely consumed by RTA at 950°C. As seen in Fig. 5 (c), the final EOT of synthesized HfAlON/HfO_2 stack is thinner than that of conventional HfO_2 even though additional layer AlN was added. This indicates that when AlN is used, the IL growth during RTA is negligible due to the excellent oxygen barrier property of AlN. The sequence of PDA, AlN and HfN depositions, and RTA also affects the final EOT (Fig. 6), because the final EOT is the result of competing process between IL growth and HfO_2 densification. The thinnest EOT is found when PDA is skipped and RTA is done after deposition of both AlN and HfN layers. In this case, the IL growth is negligible because of double diffusion barriers (both AlN and HfN) and only densification is reflected to the final EOT change.

Figs. 7 & 8 show a significant improvement in gate leakage current (more than 3 orders of magnitude), for synthesized HfAlON/HfO_2 stacks, compared to conventional HfO_2 + PDA process. It is attributed to improved thermal stability and film quality by incorporation of Al and N [1,6]. But when PDA is done prior to AlN deposition, the leakage current improvement is less because the HfO_2 is already partially crystallized during PDA. Degradation in hysteresis by N incorporation, which is usually found in N-incorporated HfO_2 [7] is not found in synthesized HfAlON/HfO_2 stack (Fig. 9). V_{fb} is also not changed by the synthesis process, even though a large amount of Al and N are incorporated, because of incorporation of Al and N only to the top side of HfO_2 film. But as seen in Fig. 9 (b), MOCVD HfAlO shows positive V_{fb} shift due to the negative fixed charge induced by Al, and HfO_2 with surface nitridation shows negative V_{fb} shift due to enhanced positive charges induced by N. Al incorporation from the top surface is also evidenced by Angle Resolved XPS results (Fig 10). Compared to HfO_2 with surface nitridation, improved mobility is obtained for n-MOSFET with synthesized HfAlON/HfO_2 stack, due to less fixed charge at the interface compared to HfO_2 with surface nitridation (Fig. 11).

Conclusions

We demonstrated the HfAlON/HfO_2 stack high-K gate dielectric using the synthesis of AlN/HfO_2. The process can easily be implemented using conventional HfO_2 process, yet a significant improvement is achieved in thermal stability, leakage current, and mobility.

References

[1] C.H. Choi et al, *IEDM* 2002. [2] C.S. Kang et al, *IEDM* 2002. [3] S. Inumiya et al, *VLSI Tech. Sym.Dig.*, 2003. [4] T. Nabatame et al. *VLSI Tech. Sym. Dig.*, 2003. [5] H. Yu et al, *IEDM* 2003. [6] M.S. Joo et al, *IEEE TED*, vol.50, no.10, p.2088, 2003. [7] M. Koike et al, *IEDM* 2003. [8] H.J. Cho et al, *IEDM* 2001.

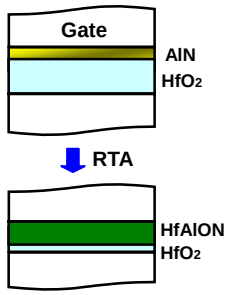

Fig. 1. Schematic diagram of process flow for top located HfAlON formation on HfO_2 using synthesis of AlN/HfO_2.

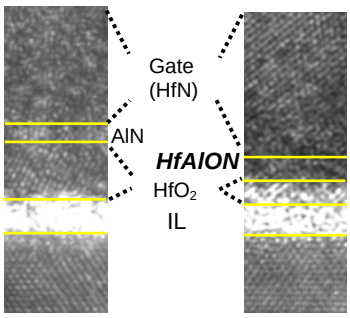

Fig. 2. XTEM images of $HfN/AlN/HfO_2$ stack (a) as–deposited (b) after RTA at 950°C. HfAlON remains amorphous and thin HfO_2 is crystallized. No significant extra interface layer growth is observed after 950°C RTA.

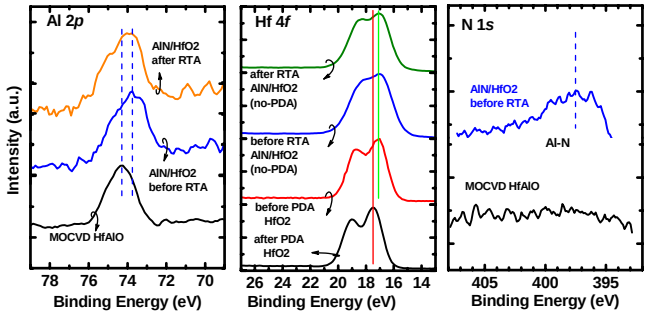

Fig. 3. XPS spectra on various films. Noted that Al 2*p* peaks are observed near 74.3 eV (Al-O) and 73.8 eV (Al-N). Shift of Hf 4*f* peak is attributed to N incorporation. N 1*s* peaks are observed near 397.1 eV (Al-N). RTA was done at 700 °C without capping layer.

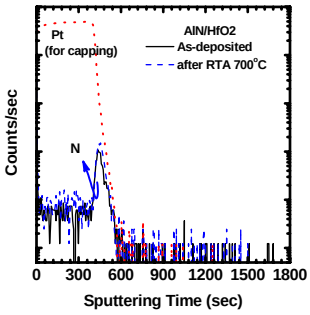

Fig. 4. Nitrogen profile obtained from SIMS analysis. No significant difference in N profile is observed between as-deposited and after RTA, indicating that almost all N atoms in AlN is incorporated into HfO_2.

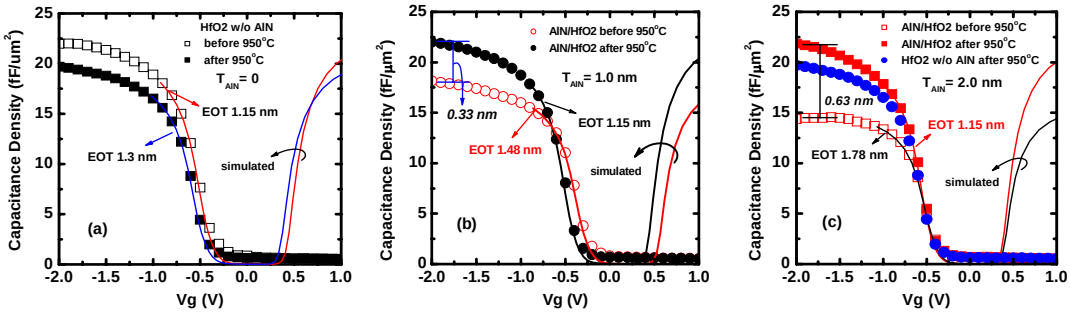

Fig. 5. (a) High frequency C-V curves of HfO_2 MOS capacitor. PDA was done at 700 °C for 1 min right after HfO_2 deposition. No AlN was deposited on top of HfO_2. Increase in EOT due to IL growth is observed. (b) High frequency C-V curves of AlN(1.0 nm)/HfO_2 MOS capacitors, (c) C-V curves of AlN(2.0 nm)/HfO_2. PDA was skipped after HfO_2 deposition. Final EOTs of synthesized $HfAlON/HfO_2$ stacks are identical regardless of initial AlN thickness, indicating complete consumption of AlN during RTA. In (c), it is observed that final EOT of synthesized $HfAlON/HfO_2$ stack is thinner than that of conventional HfO_2 even though the additional layer AlN is added.

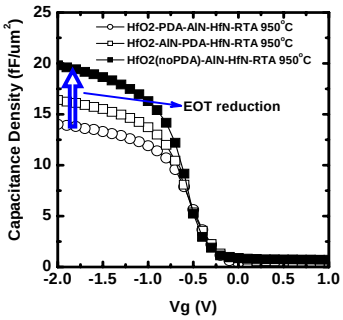

Fig. 6. EOT reduction is found when AlN is used. The amount of EOT reduction depends of the process sequence. Thicker HfO_2 (4.8 nm) is used in this case.

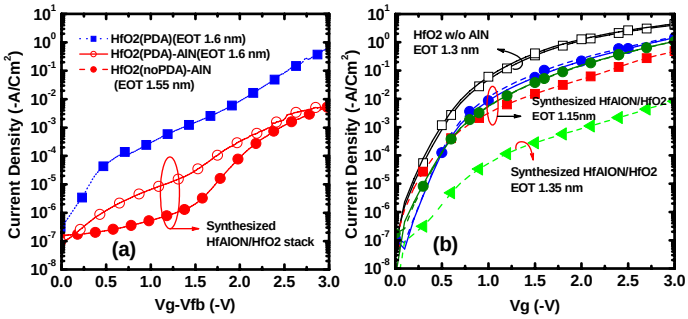

Fig. 7. Leakage current characteristics of synthesized $HfAlON/HfO_2$ stack formed using (a) AlN(1.0nm)/thick-HfO_2 and (b) AlN(1.0~2.0nm)/thin-HfO_2. For the synthesized $HfAlON/HfO_2$ stack samples, PDA was skipped. For all the samples, RTA at 950°C for 30s was conducted.

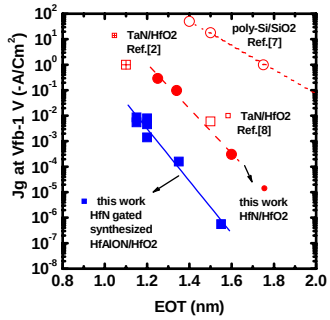

Fig. 8. EOT versus leakage current. the $HfAlON/HfO_2$ stack show significantly improved leakage current, compared to conventional HfO_2 + PDA process

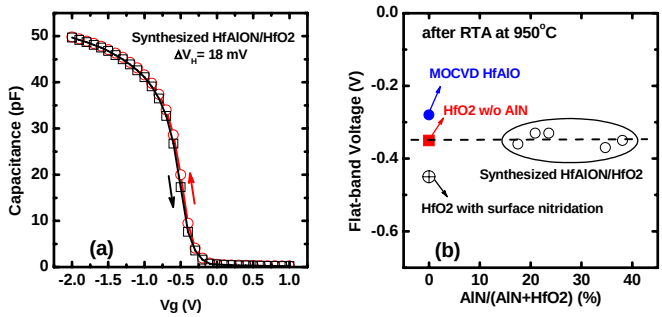

Fig. 9. (a) The hysteresis of the synthesized $HfAlON/HfO_2$ stack MOS capacitor after 950°C RTA. (b) The flat-band voltage with various AlN/(AlN+HfO_2). HfAlO shows positive Vfb shift due to Al at the interface while the surface nitrided HfO_2 shows negative Vfb shift due to increased fixed charge. The $HfAlON/HfO_2$ shows no change in Vfb.

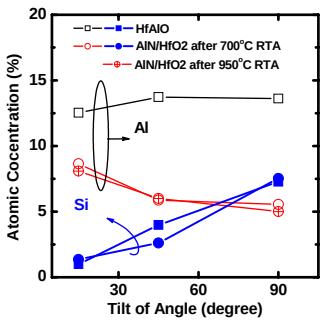

Fig. 10. Al and Si atomic concentration of $HfAlON/HfO_2$ stack obtained by Angle Resolved XPS. Most of Al atoms exist near top surface of HfO_2 after RTA.

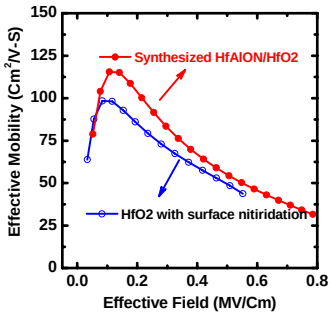

Fig. 11. Comparison of effective electron mobility of $HfAlON/HfO_2$ stack and HfO_2 with surface nitridation. EOT = 1.15 nm.