

NH₃ treatments of Hf-based layers for application as NVM active dielectrics

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Introduction

High- κ materials are currently under investigation for application to non volatile memories (NVMs) thanks to the important benefits they offer in terms of coupling, in particular when they are used as interpoly (IPD) layers¹⁻⁴. However, the important charge trap density which characterizes these new materials constitutes a serious roadblock, the device reliability being affected by the trap-assisted gate leakage currents⁵. Hence, today a major challenge is the process control of the high- κ trapping properties. In this paper, we advance the state of the art on these topics by investigating the influence of nitrogen (N) incorporation, by ammonia (NH₃) treatments, on HfO₂ and HfAlO high- κ materials in the 6-14nm thickness range (suitable for NVM applications). Through physical and electrical analyses, we demonstrate that an appropriate nitridation can significantly reduce the parasitic charge trapping phenomena. We argue that the lower trapping behavior is related to a smaller ratio of the crystalline phase of the high- κ layers, which is indeed strictly linked to the nitridation process.

Sample description

HfO₂ and HfAlO were integrated as trapping layers in capacitor devices. The high- κ films were deposited on a 2nm-thick thermal tunnel oxide and capped with 10nm-thick HTO. Two different high- κ materials, deposited by ALCVD, were studied: Hafnium Oxide (HfO₂) and Hafnium Aluminate (HfAlO). In HfAlO films, the Hf concentration is 57%. Different thicknesses were fabricated: 6nm, 10nm and 14nm. The high- κ viewed different thermal treatments (summarized in Table 1 for samples A to F), two post-deposition anneals: (i) nitridation treatment, NH₃ PDA at 750°C during 30min ; (ii) non nitridation treatment, but the similar thermal budget: N₂ PDA at 750°C during 1 min. Finally, two high temperature anneals were carried out on some samples, simulating the dopant activation of a full CMOS process flow: (iii) a spike at 1050°C and (iv) an annealing at 950°C during 15s.

Materials study

Auger characterization was used to monitor the incorporation of nitrogen in HfO₂ and HfAlO layers (6nm) after NH₃ nitridation. To this aim blanket wafers where the high- κ layers were directly deposited on silicon substrates were fabricated. We observe that for HfO₂ the nitrogen incorporation is localized at the interface between the Si substrate and the high- κ layer; the bulk absorption being negligible. However, for the HfAlO layer, we observe an important nitrogen absorption (~15%) both in the bulk and at the interface of the material (Fig. 1).

High Resolution TEM observations of the capacitor samples were performed to analyze the layer crystallinity (Fig. 2). The HfAlO layer presented different crystalline states depending on the thermal budget applied to the sample. With a 750°C N₂ PDA, HfAlO remained amorphous, while after a final spike anneal, the structure became polycrystalline, with large crystals of ~15nm in diameter. For nitridated layers submitted to final spike anneals, the crystalline ratio was reduced: only small grains (~6nm) are observed in an amorphous matrix.

In other words, the NH₃ anneal limited the crystallization of the HfAlO layer, which, indeed, can be attributed to an increase of the crystallization temperature^{7,8}.

Trapping properties

We study here the modification of charge trapping phenomena of capacitors with nitrated HfO₂ and HfAlO storage layers. To evaluate the trapping capabilities, we monitored the evolution of the flatband voltage as a function of time when the devices were submitted to gate stresses. As shown in Fig. 3, a continuous V_{FB} shift was observed in the HfAlO sample, suggesting the progressive electron trapping in the stack as the stress time increases. These observations were also carried out in the HfO₂ sample.

We can see that the final high temperature treatments increase the electron trapping, which can be attributed to the higher crystalline state of the HfAlO layer as shown on the TEM images. Moreover, in HfAlO dielectrics, the NH₃ anneal allowed to reduce the threshold voltage shift due to trapping of ~1V, which can be once again explained by the smaller ratio of the crystalline phase of nitrated HfAlO layers. In order to identify the vertical location of trapped electrons in the gate stack, we characterized capacitors with different high- κ thicknesses. We applied to the measured programming characteristics two types of normalizations, corresponding to two possible charge locations: (1) charges were considered at the interface between the tunnel oxide and the high-k layer; (2) charges were considered in the high-k bulk.

We can observe in Fig. 4 that the interface normalization is consistent for each HfAlO thickness, while this is not the case for the volume normalization. This allows us to argue that, at the first order, most of the trapped charges are located at the HfAlO/bottom oxide interface and that the HfAlO bulk contribution is negligible. Indeed, this result can be understood by remembering that traps located far from the cathode have a higher charging time constant⁵. Moreover, we found that the HfO₂ sample lead to the same behavior (not shown).

Conclusions

In this paper we investigated the effect of nitridation on the trapping properties of HfO₂ and HfAlO layers in the 6-14nm thickness range. We showed that the trapping capability increases with the crystalline ratio of the high- κ layers. Results indicate that in our devices the electron trapping mainly occurs at the bottom oxide/high-k interface. Nitridation modifies the trap properties at this interface and decreases the trap concentration. Finally, we argued that NH₃ anneals can be used to reduce the parasitic trapping phenomena in thick high-k layers in view of application as NVM active dielectrics.

References

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Table 1. Summary of the different thermal treatments.

Thermal treatment	Sample					
	A	B	C	D	E	F
(i) NH ₃ 750°C 30min	X		X		X	
(ii) N ₂ 750°C 2min		X		X		X
(iii) N ₂ 1050°C spike			X	X		
(iv) N ₂ 950°C 15s					X	X

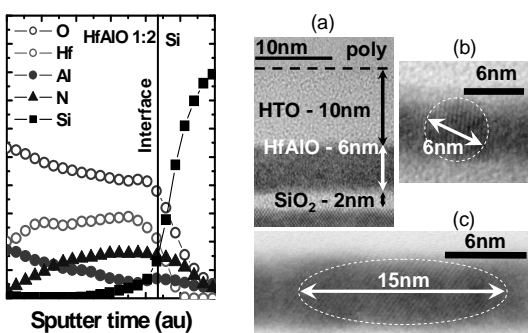


Figure 1. Auger depth profiles of nitrogen in HfAlO/Si stack.

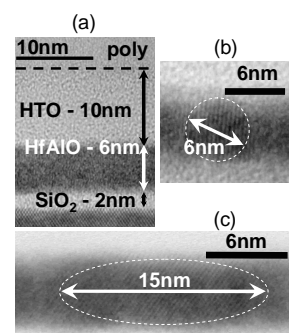


Figure 2. TEM cross sections of HfAlO stacks submitted to different anneals: (a) sample B, (b) sample C, (c) sample D.

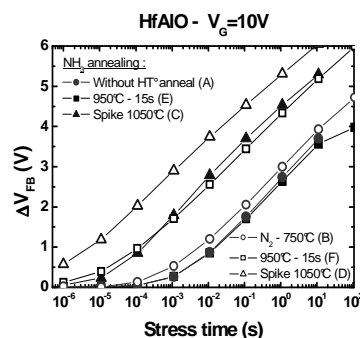


Figure 3. Programming characteristics of HfAlO samples with various anneals. The HfAlO thickness is 6nm.

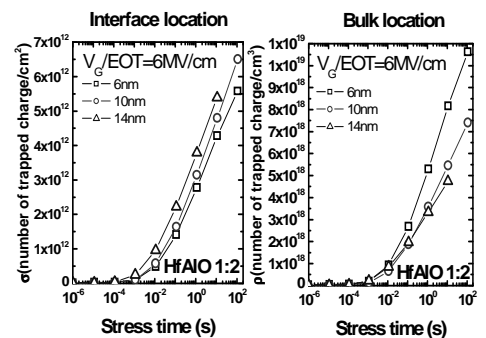


Figure 4. Extracted trapped charge in the high- κ layers (sample E) with various thicknesses at constant programming V_G/EOT . We assume that the charges are localized either at the interface between the tunnel oxide and the high- κ layer (left) or distributed in the bulk material (right).