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Cubic-HfN Formation in Hf-based High-k Gate Dielectrics with N-Incorporation and Its Impact on Electrical Properties of Films

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1. Introduction

N-incorporation into Hf-based high-k gate dielectrics is reported to improve thermal stability of the films: the increase in crystallization temperature [1-5] and the suppression of boron penetration [2,4,6]. In addition, we have found that Hf-N bonds in HfSiON enhance the dielectric constant (K) of films, realizing aggressive scaling of the equivalent oxide thickness (EOT) to as thin as 0.6 nm with poly-Si [7]. On the other hand, N-incorporation in Hf-based gate dielectrics exhibits some detrimental effects in regard to the material properties of these films: 1) band gap narrowing due to Hf-N bonds creation [7,8] and 2) cubic-HfN (c-HfN, metallic phase) precipitation which has been observed only in the case of HfAlON with high Hf/(Hf+Si) (Hf-ratio) of over 50% [3]. In regard to the c-HfN segregation in N-incorporated Hf-based materials, a more comprehensive understanding of the phenomenon is necessary, since c-HfN significantly changes the electronic structure of films and causes great increase in gate leakage current [3].

In this study, we examined the effect of the annealing temperature on the c-HfN segregation phenomenon in the HfAlON system. We found that the low-temperature annealing leads to the inhibition of the c-HfN segregation and results in remarkably reduced film leakage current. In addition, we carefully checked the c-HfN segregation in the HfON and HfSiON systems. As a result, c-HfN formation was observed in the HfON film. However, the HfSiON film never causes the segregation even with Hf-ratio of 80 %.

2. Experimental

HfAlON, HfSiON, and HfON films with nitrogen concentration ([N]) of over 20at.% were deposited on HF-cleaned Si (100) wafers by means of the sputtering deposition technique. In order to clarify the effect of the annealing temperature on the structural and electrical change of HfAlON, films with various Hf-ratio were annealed at 850°C for 30 minutes or at 1000°C for 30 seconds, with poly-Si cap layers. HfON and HfSiON films were annealed at conditions of 1065°C spike or 1000°C 30 minutes. Electrical properties of films after annealing were investigated by means of MIS capacitors with n^+poly-Si gate electrodes. Structural properties of films were examined with X-ray photoemission spectroscopy (XPS) and X-ray diffractometry (XRD).

3. Results and Discussion

Figure 1 shows the effect of the annealing temperature on the leakage current of n^+poly-Si/HfAlON/p-Si capacitors with the Hf-ratio ranging from 35% to 64%. As shown in this figure, leakage current decreases by 2~4 orders of magnitude by lowering the annealing temperature from 1000°C (30 seconds) to 850°C (30 minutes). We also found that the c-HfN segregation is completely suppressed at the 850°C annealing (in-plane XRD, Fig. 2). We think that the annihilation of c-HfN micro-crystals results in widening of band gap for HfAlON films, leading to the reduced leakage current (Fig. 1). It is also possible that the homogeneous film microstructure due to the suppression of c-HfN segregation is responsible for the reduced leakage current [9,10].

The change in microscopic structure of HfAlON films according to the change in annealing temperature was examined by XPS (Fig. 3). In the films with 1000°C annealing, a peak of c-HfN is clearly observed (indicated by an arrow). In contrast, the c-HfN signal is below the detection limit of XPS analysis in the HfAlON film with the 850°C annealing. These XPS results are in good agreement with the in-plane XRD result (Fig. 2). In addition, we confirm in Fig. 3 that the Hf4f peaks for the 850°C specimen slightly shift to lower binding energy than those in the HfAlO film: this means that Hf-N bonds are sustainable through the 850°C annealing without long-range order of the c-HfN.

Figure 4 shows typical C-V curves of n^+poly-Si/HfAlON (10 nm)/p-Si capacitors fabricated with the 850°C 30 minutes activation. The lowering of the annealing temperature (and resulting reduction of film leakage current) enables us to correctly determine the capacitance value. As shown in Fig. 4, accumulation capacitance values increase with increasing the Hf-ratio, indicating higher K for a higher Hf-ratio. Figure 5 shows the Hf-ratio dependence of K values for HfAlON, determined by the EOTs dependence on physical thicknesses of HfAlON. K values for HfAlO without nitrogen (in amorphous state [9,12,13]) are also shown. It is demonstrated that K values of HfAlON are higher than those of HfAlO, presumably due to the Hf-N bonds in the film (Fig. 3). As a result, we conclude that lowering the annealing temperature to 850°C makes the application of the amorphous HfAlON insulator to future LSIs realistic accompanied by enhanced dielectric constant up to 22.

In order to compare the thermal stability of HfAlON with alternative N-incorporated Hf-based gate dielectrics, we investigated the change in material properties of HfON and HfSiON through over 1000°C annealing. In Fig. 6, the structural and electrical differences between HfON ([N]=40at.%) and HfSiON (Hf-ratio=80%, [N]=20at.%) after the 1065°C spike annealing are shown. We found that c-HfN forms in HfON after the annealing, whereas HfSiON keeps an amorphous state (Fig. 6(a)). C-HfN formation in the HfON results in short circuit of the n^+Si/HfON/p-Si capacitor, whereas, on the contrary, the HfSiON capacitor shows considerably low gate leakage current (Fig. 6(b)). Moreover, we confirmed that the c-HfN phase never emerges in HfSiON even under the excessive annealing condition of 1000°C for 30 minutes (Fig. 7). Table 1 summarizes the HfN and HfON precipitation in N-incorporated Hf-based dielectrics. We can regulate the HfN segregation by taking the low annealing temperature in HfAlON. However, HfSiON is especially suitable for the conventional CMOS process flow, since it reveals no HfN segregation even at the elevated temperature of over 1000°C.

4. Conclusion

By a careful choice of the annealing temperature (850°C), cubic-HfN (metallic) segregation is found to be avoidable even in the HfAlON film, resulting in reasonably low film leakage as well as high dielectric constants. We also found the cubic-HfN precipitation in HfON at 1065°C spike annealing, giving rise to short circuit of the film. In contrast, cubic-HfN never forms in HfSiON even through 1000°C 30 minutes annealing. Based on these experimental results, we conclude that, as far as high-temperature activation process at over 1000°C is concerned, HfSiON is most suitable for the conventional CMOS process flow.

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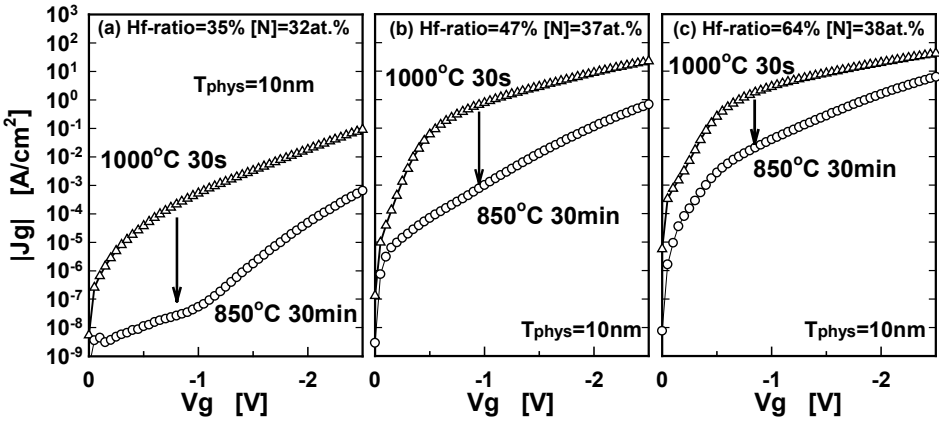

Fig.1. Change of J-V characteristics of n^+Si/HfAlON/p-Si capacitors for HfAlON films with Hf-ratio of (a)35%, (b)47% and (c)64% according to the change in the activation condition. By lowering the annealing temperature from 1000°C to 850°C, great reduction in gate leakage current by 2~4 orders of magnitude is obtained.

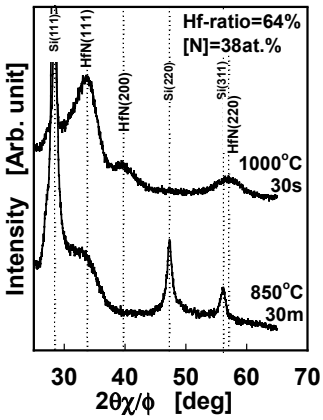

Fig.2. In-plane XRD results for HfAlON film with Hf-ratio=64%, [N]=38at.%. Cubic-HfN formation was suppressed at 850°C.

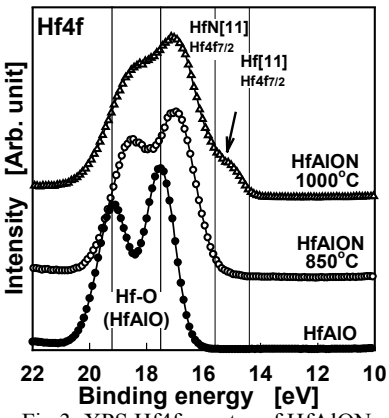

Fig.3. XPS Hf4f spectra of HfAlON films (Hf-ratio=64%, [N]=38at.%). Results for HfAlO film (Hf-ratio=47%) are also shown.

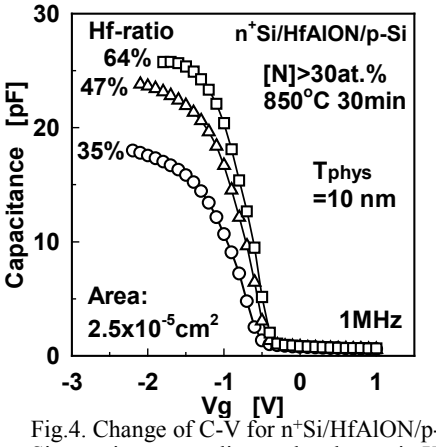

Fig.4. Change of C-V for n^+Si/HfAlON/p-Si capacitors according to the change in Hf-ratios of HfAlON films. The activation condition was 850°C, 30 minutes.

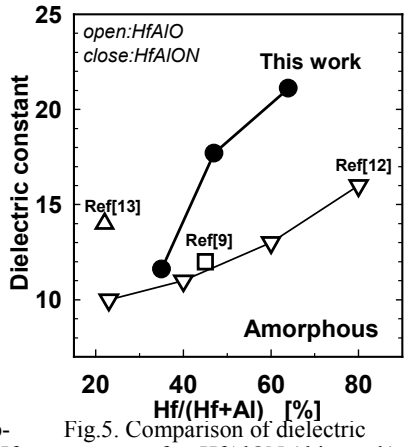

Fig.5. Comparison of dielectric constants for HfAlON (this work) and HfAlO (literatures). All films in this figure are in amorphous state.

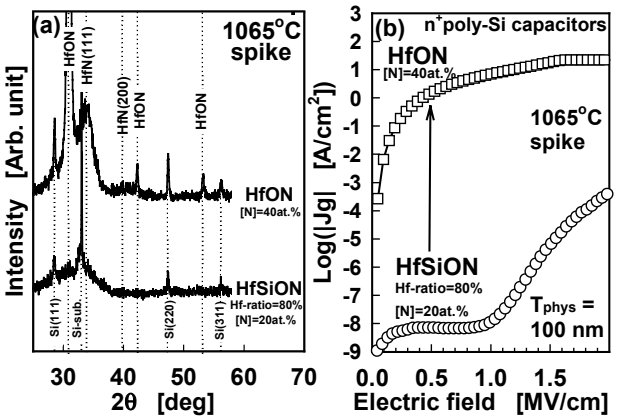

Fig.6. (a) XRD spectra for HfON ([N]=40at.%) and HfSiON (Hf-ratio=80%, [N]=20at.%) after 1065°C spike annealing. (b) J-E curves for the n^+Si/HfON or HfSiON/p-Si structures.

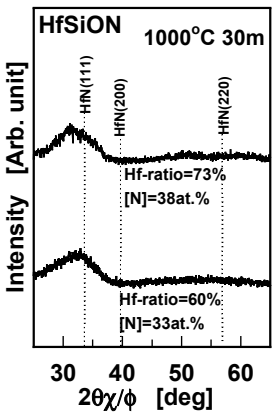

Fig.7. In-plane XRD spectra of the HfSiON films annealed at 1000°C for 30m.

Table 1. Comparison of HfON and HfN micro-crystallization in HfON, HfAlON and HfSiON under various thermal budget. HfSiON reveals no segregation of HfON and HfN even through 1000°C,30m.

Material	HfON se-gregation	HfN se-gregation	Thermal budget
HfON	YES	YES	1065°C spike
HfAlON	NO	NO	850°C 30min
	NO	YES	1000°C 30sec
HfSiON	NO	NO	1065°C spike
	NO	NO	1000°C 30min