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Effect of the Film Composition of HfAlON Gate Dielectric on the Structural Transformation and the Electrical Properties through High-temperature Annealing

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1. Introduction

Hf-aluminate (HfAlO) is one of the most promising candidate high-k gate dielectrics for near-future, low-power CMOS [1-3]. It was reported that it remained amorphous even after 1000°C if Hf/(Hf+Al) (Hf-ratio) was 25%. However, it crystallized at 900°C in the case of 50% Hf-ratio [3]. The k-value of HfAlO (25% Hf-ratio) is reported to be less than 14 [3]. Thus, in order to realize an amorphous HfAlO with k-value of >14 even after high-temperature annealing, some measure must be taken to suppress the crystallization of the film with Hf-ratio >25%.

In our previous work, we reported that 20at.% nitrogen (N) incorporation into Hf-silicate (HfSiO) did suppress the segregation of HfO_2 crystals even after 1000°C annealing [4]. Based on this result, we expect that N is also effective for inhibiting HfAlO crystallization. Recently, Jung et al. studied N incorporation into HfAlO by NH_3-anneal of HfO_2-Al_2O_3 laminates [5]. In their study, however, N piled up at the HfAlO/Si interface and N in HfAlO was less than 10at.%, and the effect of N on the thermal stability of the film was not investigated. Thus, in this study, we thoroughly investigated the effect of N-incorporation (N=0~40at.%) into HfAlO on the structural and electrical properties of the film.

2. Experimental

In order to incorporate N into HfAlO effectively, we performed the film deposition by means of co-sputtering of Hf/Al targets in an $Ar/O_2/N_2$ atmosphere on HF-treated Si substrates. The composition of the films was changed by controlling Hf/Al target power ratio and was precisely determined by RBS. Some films were annealed at 1000°C for 30s in N_2 with and without poly-Si cap layers. Bonding states of these films were analyzed by XPS and crystallinity of the films was investigated by TEM and XRD. Electrical properties of the films were investigated by n+poly-Si/HfAlON/p-Si capacitors.

3. Results and Discussion

Fig.1 shows XPS Hf4f and Al2p spectra of as-deposited HfAlO and HfAlON films. In the case of the HfAlON film (Hf-ratio=35%, N=41at.%), both *Hf-N* and *Al-N* peaks are clearly shown besides *Hf-O* and *Al-O* signals. Unfortunately, most N atoms bonded to Hf or Al outdiffused during 1000°C annealing in N_2, as shown in XPS N1s spectra (Fig.2). It is also revealed that higher Hf-ratio in HfAlON results in lower N concentration after the annealing (Fig.3). We think that the N-outdiffusion is caused by O impurity in the atmosphere that replaces N-site of both *Hf-N* and *Al-N* during the annealing. This speculation is partly supported by the fact that much N remained in the HfAlON even after 1000°C annealing if the films were capped with poly-Si (Table 1). Note that HfSiON films show better N-keeping ability than HfAlON (Fig.3), meaning *Al-N* has poorer resistance to oxidation than does *Si-N*.

In the case of HfAlO without N, films are crystallized after 1000°C annealing regardless of Hf-ratio (XRD, Fig.4). HfAlON with 9at.% N reveals almost the same XRD pattern as HfAlO after the annealing (Fig.5), meaning 9at.% N is insufficient to suppress the crystallization. Based on the in-plane XRD pattern shown in Fig.5, crystals in HfAlON (N=9at.%) are confirmed to be *orthorhombic(o)* -HfO_2 [6]. On the contrary, it was shown that *o*-HfO_2 peaks are diminished by 32at.% N-incorporation (Fig.5). These results indicate that 30at.% N-incorporation into HfAlO substantially inhibits HfO_2 segregation through 1000°C annealing, similar to HfSiON [4].

Fig.6 shows a typical C-V curve of an n+poly-Si/HfAlON/I.L. /p-Si capacitor. Capacitance equivalent thickness (CET) of 22.7Å was demonstrated by the stacked structure of HfAlON (Hf-ratio=35%, N=32at.%, 5nm thick) and the interfacial layer (1nm thick). By analyzing the dependence of CETs on the film thickness (inset in Fig.6), we determined the k-value of the HfAlON (Hf-ratio=35%, N=32at.%) to be ~17; this is the highest k-value so far reported for amorphous high-k dielectrics after high-temperature annealing. In Fig. 7, we compare the k-value of the HfAlON film with those of HfSiON with various compositions [4][7]. It is clearly shown that higher k-value can be obtained in the case of HfAlON than in the case of HfSiON at the same Hf-ratio. This is reasonable because Al_2O_3 reveals higher k-value (~10) than SiO_2 (3.9). This is an apparent advantage of HfAlON over HfSiON, since higher Hf-ratio in HfAl(Si)ON leads to smaller bandgap energies [8,9], giving rise to increase in leakage current of the films.

Unfortunately, it is found that the leakage current density through the HfAlON film (N>30at.%) increases drastically as Hf-ratio increases (Fig.8). In order to clarify the cause of this degradation in leakage current, the change of the film structure through 1000°C annealing with the change of the film composition was carefully investigated. As shown in the plan-view TEM image (Fig.9), it is confirmed that HfAlON with Hf-ratio=35% and N=32at.% keeps homogeneous film structure after the annealing. On the contrary, HfAlON with higher Hf-ratio (Hf-ratio=64%, N=38at.%) results in phase separation and growth of tiny crystal grains after the annealing (Fig.10). Fig.11 shows in-plane XRD patterns of annealed HfAlON films with high N content (>30at.%) and Hf-ratio ranging from 35 to 64%. As Hf-ratio increases, three peaks that are not identical to *orthorhombic*-HfO_2 become more apparent (Fig.11). Analyzing 2θ-values and ratio of each peak-height in Fig.11, it was concluded that the crystal precipitates in HfAlON (N>30at.%) after the annealing are *cubic(c)-HfN* [6]. It is worth noting that *c-HfN* crystalline peaks are never detected in the case of HfSiON with Hf-ratio=60% and N=35at.% after 1000°C annealing (Fig.11). Since *c-HfN* is an electrical conductive material [10], we conclude that *c-HfN* crystals buried in the film are responsible for the severe increase in gate leakage current as shown in Fig.8.

Fig.12 represents XPS Hf4f and Al2p spectra of HfAlON after the annealing (N>30at.%). It was confirmed that, Hf-N bonds survive through 1000°C with poly-Si cap (Fig.12(a)). On the other hand, Al-N bonds are completely diminished irrespective of Hf-ratio (Fig.12(b)). We think that HfN phase would be energetically more stable than AlN in HfAlON system under 1000°C, leading to phase separation of HfN from HfAlON and resulting in the crystallization of *c-HfN* (Fig.10,11). This case is different from that of HfSiON in which no HfN crystallization occurs even after 1000°C (Fig.11).

4. Conclusion

We have intensively investigated the structural and the electrical change of HfAlON gate dielectric through 1000°C annealing, changing the film composition. We have found that 30at.% N-incorporation substantially suppressed the *orthorhombic*-HfO_2 segregation after the annealing. As a result, amorphous HfAlON film with k-value of 17 after 1000°C was demonstrated at the composition of Hf-ratio=35% and N=32at.%. At the higher Hf-ratio, however, we found crystal grains of *cubic-HfN* emerged from HfAlON after the annealing. This phenomenon was never observed in the case of HfSiON. It was also confirmed that the *cubic-HfN* included in the HfAlON drastically increased the leakage current. Based on these results, we conclude that HfAlON has a major disadvantage compared with HfSiON so far as conventional poly-Si gate process is concerned, especially in the composition range of higher Hf-ratio (>50%).

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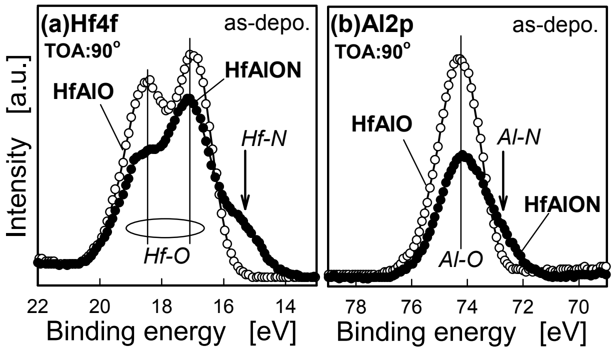

Fig.1. (a)Hf4f and (b)Al2p XPS spectra of HfAlO and HfAlON thin films prepared by co-sputtering of Hf/Si.

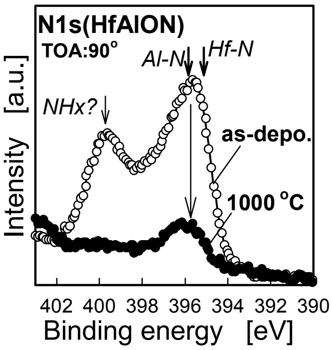

Fig.2. N1s XPS spectra of HfAlON before and after 1000°C annealing.

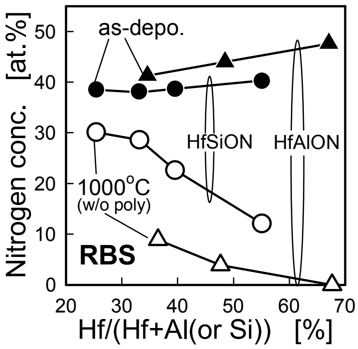

Fig.3. N-outdiffusion from HfAlON and HfSiON measured by RBS.

Table 1. Hf-ratio (Hf/(Hf+Al)) and N conc. of HfAlON before and after the annealing measured by RBS.

sample	as-depo.		1000°C 30s N2 (w/o poly-Si)		1000°C 30s N2 (w/ poly-Si)	
	Hf-ratio %	N at.%	Hf-ratio(%)	N at.%	Hf-ratio(%)	N at.%
#1	35	41	37	9	35	32
#2	49	44	48	4	47	37
#3	67	48	68	0	64	38

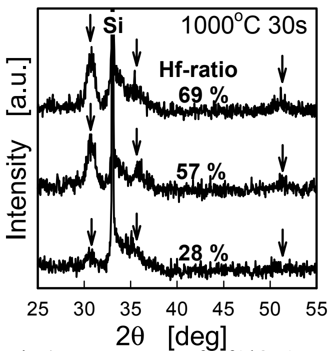

Fig.4. XRD spectra of HfAlO. Arrows indicate HfO2 crystalline peaks.

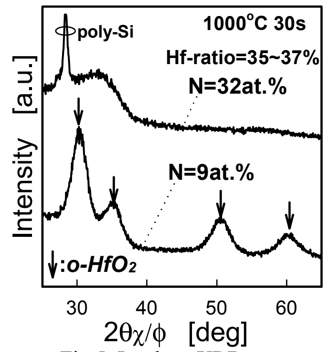

Fig.5. In-plane XRD patterns of HfAlON (N=9, 32at.%).

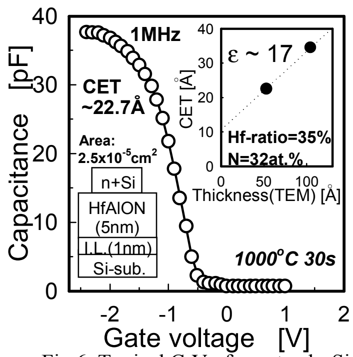

Fig.6. Typical C-V of an n+poly-Si gate HfAlON MIS capacitor.

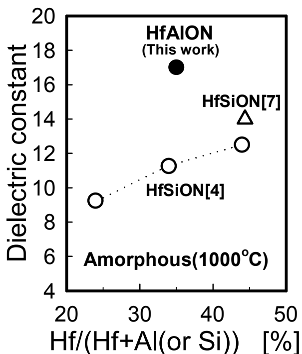

Fig.7. Dielectric constants of HfAlON and HfSiON.

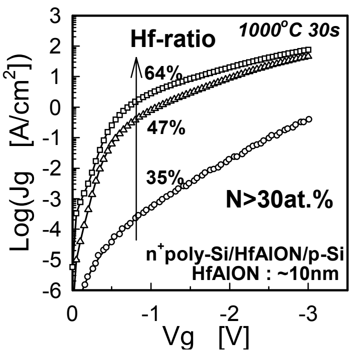

Fig.8. J-V curves of n+poly-Si gate HfAlON(~10nm) MIS capacitors.

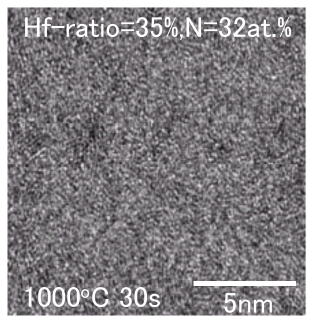

Fig.9. HfAlON (Hf-ratio=35% N=32at.%) remains amorphous after 1000°C 30s annealing.

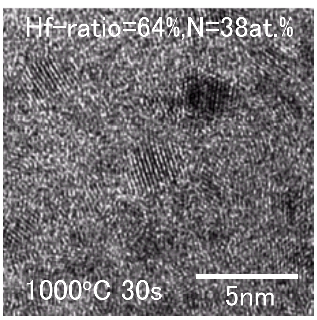

Fig.10. HfAlON (Hf-ratio=64% N=32at.%) cause phase separation after 1000°C 30s annealing.

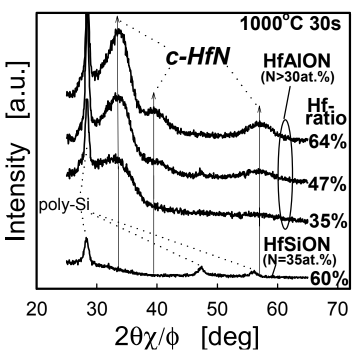

Fig.11. In-plane XRD of HfAlON (N>30at.%) and HfSiON.

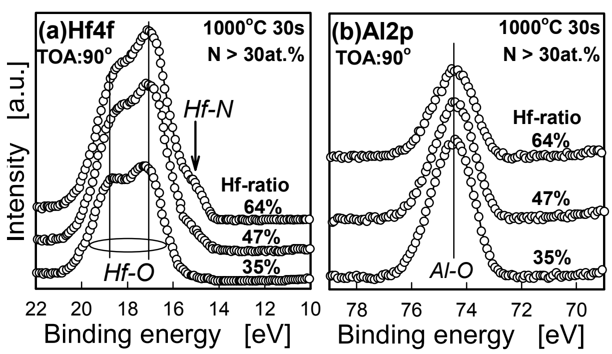

Fig.12. (a)Hf4f and (b)Al2p XPS spectra of HfAlON thin films annealed at 1000°C for 30s (capped with poly-Si).