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Dielectric Constant Behavior of Hf-O-N System

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1. Introduction

Hf-based high-k dielectrics are promising candidates for the gate insulator. However, higher dielectric constant is preferred for further future gate insulator. Although some oxides of rare earth elements, such as La_2O_3 or PrO_x [1] show high dielectric constants, their thermal instability and high hygroscopicity might prevent their usage in real LSIs. On the other hand, it is reported that the dielectric constant increased by the change of crystal structure of HfO_2 from monoclinic to cubic-like structure such as tetragonal or cubic by the doping of yttrium [2] or lanthanum [3]. In this report, we will show that much more ordinary material such as nitrogen can achieve the similar function for the enhancement of the dielectric constant by the realization of cubic like structures [4, 5]. Close investigation on the nitrogen concentration [N] =N/(Hf+O+N) dependence of dielectric constant as well as band gaps has revealed there exists the optimum nitrogen concentration in this method.

2. Experimental

HfON thin films of 100nm in thickness are reactively sputtered by hafnium target on HF treated Si-substrate. Nitrogen concentrations are determined by RBS (Rutherford Backscattering Spectrometry). Dielectric constants were measured by making Au-electrodes on the HfON films. Areas were measured by optical microscopy for each Au-electrodes. Thickness of the HfON thin film and refractive index were estimated by ellipsometry. Crystal structures were determined by X-ray diffraction measurement. XPS (X-ray Photoelectron Spectroscopy) peak shifts were measured. REELS (Reflection Electron Energy Loss Spectroscopy) was used to estimate the band gap energy.

3. Results and Discussion

The variation of dielectric constant of HfON thin films for nitrogen concentration [N] from 0 at. % to 25 at. % is shown in Figure 1. Dielectric constant increased non-linearly with increasing nitrogen concentration. After an uphill trend from 0 at. % to 7.6 at. %, dielectric constant reached a plateau until 22 at. %, and then it increased again. This non-linear behavior has been firstly revealed by the detailed variation of nitrogen concentration.

Refractive index is plotted in Figure 2. It increased monotonically and almost linearly with increasing nitrogen concentration up to 18.3 at. %, then it seemed to ascend steeply. No anomaly was observed at around 7.6 at. %.

X-ray result is shown in Figure 3. Monoclinic and cubic-like crystals appeared under 7.6 at. %, whereas only cubic-like crystals existed over 7.6 at. %. Because the X-ray diffraction profiles of polymorphs of HfON are very similar, we could not exactly distinguish the cubic-like profile from γ_1-$HfO_{1.80}N_{0.10}$, γ_2-$Hf_7O_{11}N_2$, γ_3-$Hf_7O_8N_4$, or γ_4-Hf_2ON_2 [4], by the S/N ratio or peak resolution. Nitrogen concentrations of these are 3, 10, 21, and 40 at. % respectively. Monoclinic HfO_2 and γ_x-HfON including β"-ZrON type structure might coexist [6] under the concentration of 7.6 at. %. The nitrogen concentration of the inflection point of dielectric constant coincided with the disappearance point of the monoclinic crystals.

Energy shifts of Hf4f and N1s peaks are shown in Figure 4. Peak energy was corrected to avoid charge-up effect by O-KLL peak energy. Hf4f peak energy increased abruptly between 18.3 at. % and 24.5 at. %. N1s peak also started to shift between the same concentrations and approached the Hf_3N_4 value [7], yet metallic HfN [7] component was nonexistent or very small. This result indicates that the short range order of Hf_3N_4 like crystal obeying Pauling's 2nd rule is created in the HfON films of nitrogen concentration higher than 24.5 at. %. It is suggestive that nitrogen atoms can be located at farther sites from hafnium atom under 20 at. % because multiple anion sites exist in the Bevan type of γ_2 and γ_3 except for γ_4 structure [4].

Although the dielectric constant had a shoulder at 7.6 at. % of nitrogen concentration, neither refractive index nor XPS peak shift showed anomaly, but monoclinic crystal disappeared. Thus we conclude that the crystal structural transition of HfO_2 is responsible for the increase in dielectric constant up to 7.6 at. % of nitrogen concentrations. On the contrary, refractive index and XPS chemical shift increased abruptly at around 20 at. % accompanied by increase in the dielectric constant. This indicates that the enhancement of electronic polarization due to Hf-N bonds leads to higher dielectric constant of HfON at this composition.

Figure 5 shows band gap and band offset energies of HfON/Si measured by REELS and XPS. Band gap energy of HfON was larger than 4.6eV under 18.3 at. %. Unfortunately it decreased to 3.04 eV at over 24.5 at. % of nitrogen concentration, presumably due to the contribution of Hf-N bonds (Figure 4). In order to discuss the optimum composition of HfON for the maximum performance as a gate insulator, we compared the Figure of Merit (F.O.M) of this material defined as a product of relative dielectric constant ε and the square root of barrier height φ_b (=ΔE_C) [8, 9]. The largest value, 38, is obtained in the range from 7.6 to 16.7 at. % of nitrogen concentration (Figure 6). Considering that

the leakage current decreases exponentially with the F.O.M. [8, 9], this difference should give great impact on the leakage current through the dielectrics.

3. Conclusions

Dielectric constant of HfON thin films increased non-linearly with the increase of nitrogen concentration. The inflection point of dielectric constant at the nitrogen concentration of 7.6 at. % coincided with the disappearance of monoclinic crystal, whereas no anomaly was found in refractive index or Hf4f peak energy. These results indicate that the change of crystal structure is the primary cause of the non-linear enhancement of dielectric constant. The nitrogen concentration in the range from 7.6 to 16.7 at. % showed the best Figure of Merit for a gate insulator.

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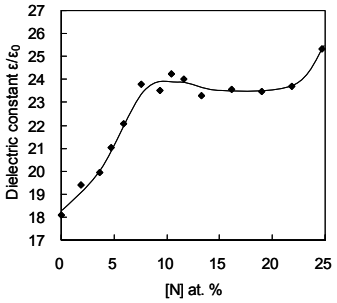

Fig. 1 Dielectric constants.

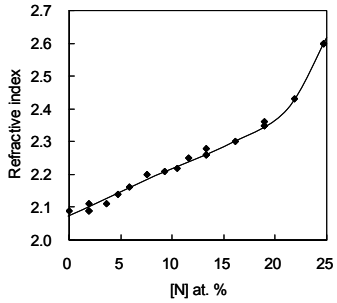

Fig. 2 Refractive index.

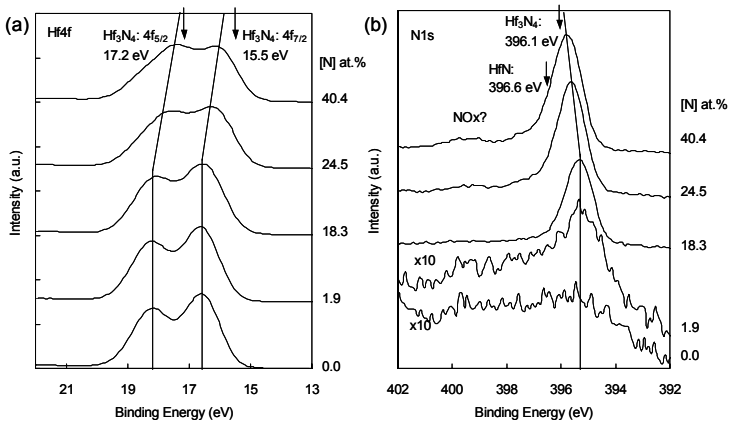

Fig. 4 Binding energy by XPS. (a) Hf4f peak shift. (b) N1s peak shift.

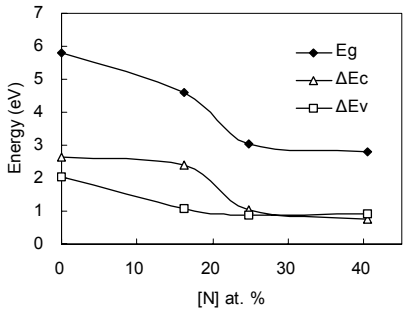

Fig. 5 Band gap and band offset energy estimated from REELS and XPS.

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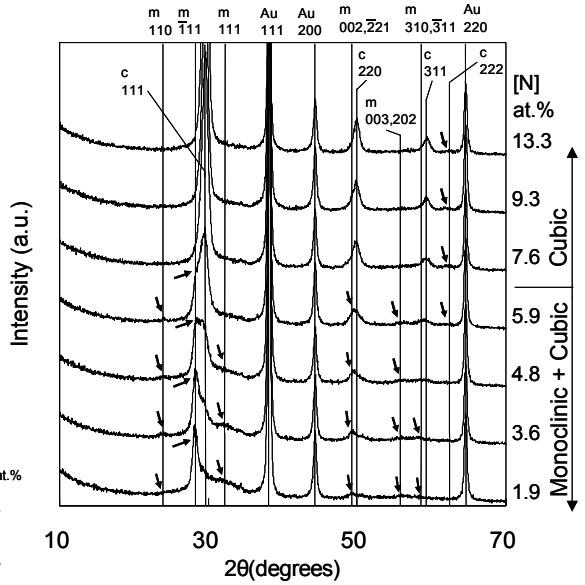

Fig. 3 Crystal structures by X-ray diffraction.

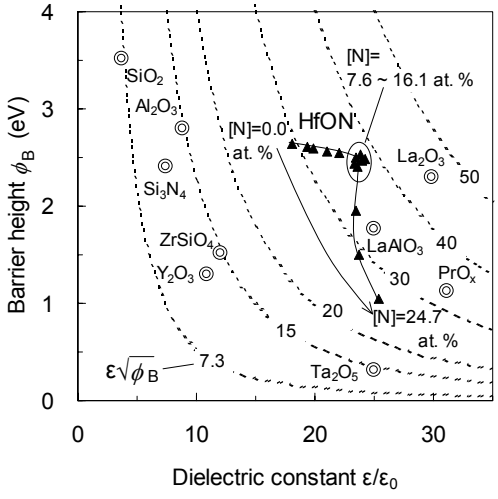

Fig. 6 Figure of Merit.