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A New Hf-based Dielectric Member, HfLaOx, for Amorphous High-k Gate Insulators in Advanced CMOS

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1. Introduction

HfO_2 has been studied as an alternative gate dielectric film. SiO_2 and Al_2O_3 have been incorporated into HfO_2 to suppress the crystallization. Although HfSiO and HfAlO achieved higher crystallization temperatures, the dielectric constants of them substantially decreased. Further EOT scaling requires new dielectrics with both high dielectric constant and high crystallization temperature. Very recently, it was reported that La_2O_3 introduction to nanophase HfO_2 powders can raise the crystallization temperature (~900°C)[1]. Furthermore, it is expected that incorporating La_2O_3 will not cause the degradation of dielectric constant because La_2O_3 is more ionic oxide than SiO_2 or Al_2O_3. In this work, we report the dielectric properties of thin $HfLaO_x$ films on Si substrate for an amorphous high-k gate dielectric in advanced CMOS, in terms of thermal stability, dielectric film quality and dielectric constant.

2. Experimental

$HfLaO_x$ films were deposited on HF-last p-Si (100) substrates by RF co-sputtering of HfO_2 and La_2O_3 in argon ambient at room temperature. The post-deposition annealing in 0.1%-O_2+N_2 mixture ambient was performed at 600~1000 °C. The composition and thickness of the film were determined by x-ray photoelectron spectroscopy (XPS) and grazing incident x-ray reflectivity (GIXR) measurements, respectively. The crystallinity of films was investigated by x-ray diffraction (XRD) measurement. Au was evaporated for gate electrode formation to measure electrical characteristics of MOS capacitors.

3. Result and Discussion

1) Thermal stability of HfLaOx films

Fig.1 shows XRD spectra of 30nm-thick HfO_2, La_2O_3, and $HfLaO_x$ films annealed at various temperatures. HfO_2 and La_2O_3 films start to crystallize under 600°C, while $HfLaO_x$ films with 33% La and 40% La remain amorphous even after 800°C and 900°C annealing, respectively. The diffraction peak of crystallized $HfLaO_x$ films around 2θ=29 degree corresponds to the (222) planes of the pyrochlore $La_2Hf_2O_7$[2]. XRD results of various Hf-rich HfLaOx samples are plotted in **Fig.2**. A small La_2O_3 introduction stabilizes cubic or tetragonal HfO_2 as same as Y_2O_3 introduction case[3]. With the increase of La concentration in $HfLaO_x$, the film shows higher crystallization temperature.

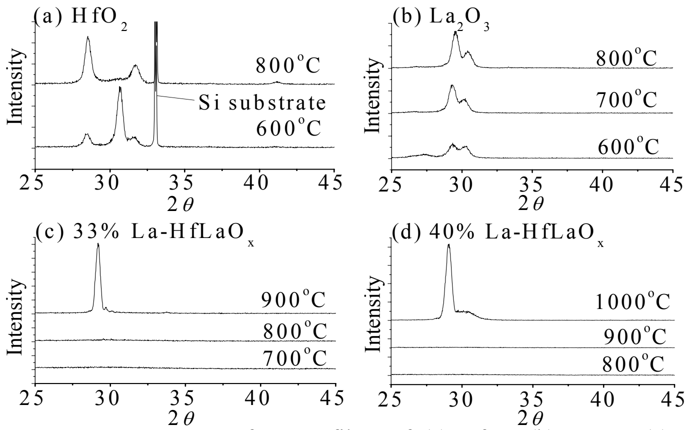

Fig.1 XRD spectra of 30nm films of (a) HfO_2, (b) La_2O_3, (c) 33%La-$HfLaO_x$, (d) 40%La-$HfLaO_x$ annealed at various temperature. HfO_2 and La_2O_3 films crystallize below 600°C. On the other hand, 40%La-$HfLaO_x$ film remains amorphous after 900°C annealing.

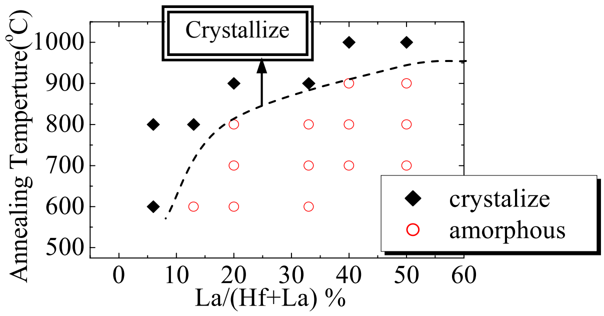

Fig.2 Crystallinity of $HfLaO_x$ films with various compositions after post-deposition annealing. The crystallization temperature rises as La concentration increases.

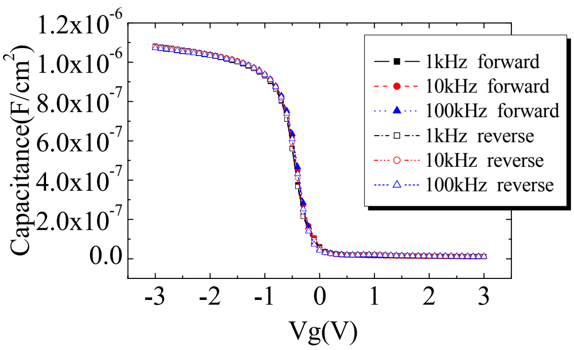

Fig.3 Bi-directional *C-V* characteristics of Au/40%La-$HfLaO_x$/p-Si MOS capacitor annealed at 600°C. The film thickness was 8.4 nm. It shows very small hysteresis and frequency-dispersion

Considering that the ionic radius of Hf^{4+} and La^{3+} are 0.71Å and 1.03Å (at 6 coordination), the relatively large difference of ionic radius may effectively suppress the easy crystallization, which is in contrast with the Y (ion radius = 0.9Å) doping case[3].

2) Film quality

Fig.3 shows the bi-directional C-V characteristics at different frequencies on the Au/40%La-$HfLaO_x$/*p*-Si MIS capacitors. The C-V curves show very small hysteresis and frequency-dispersion, indicating a good quality of bulk film and $HfLaO_x$/Si interface. Dit was around 3×10^{11} eV^{-1} cm^{-2}, roughly estimated by combining the quasi-static capacitance-voltage (QSCV) and the high-frequency capacitance-voltage (HFCV).

Fig.4 indicates a relationship between Vfb and CET, which was determined from the accumulation capacitance at Vg = -3V. Note that Vfb value is almost a constant near the ideal Vfb value at various CET. This result indicates that there are surprisingly small amount of fixed charges and interface traps in $HfLaO_x$ MOS capacitors, which seems to be better than the pure HfO_2 case.

3) Dielectric Constant

Fig.5 shows the CET value vs. physical thickness plot for the samples annealed at various temperatures. From the good linear relationship with very small dispersion, k value is estimated to be 20~22 for all of the samples. The dielectric constants of $HfLaO_x$ at various temperatures are compared with those of pure-HfO_2 in **Fig.6** as a parameter of annealing temperature. The k value of HfO_2 is decreased with the increase of annealing temperature because of crystallization into the monoclinic phase[3], while HfLaOx maintains its high dielectric constant when annealing temperature is increased.

Finally, it is worthy to mention that that La_2O_3 easily forms silicate with Si, while HfO_2 is not the case. Thus, in our sample, the interface might be La incorporated SiO_2, resulting that the interface layer dielectric constant can be higher than SiO_2. This will become another advantage of $HfLaO_x$.

4. Conclusions

We investigated physical and electrical characteristics of $HfLaO_x$ film on Si. $HfLaO_x$ have shown both high crystallization temperature (900 °C~) and high permittivity (~22). From *C-V* characteristics, the good quality of $HfLaO_x$/Si interface and few fixed charge in the film are demonstrated. These results indicate that $HfLaO_x$ is promising candidate for amorphous high-k gate insulator in advanced CMOS.

Acknowledgements

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References

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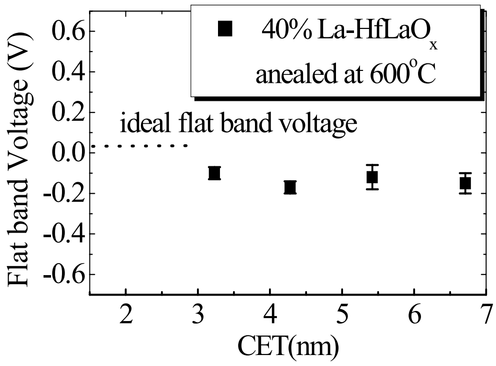

Fig.4 Flat band voltage as a function of the CET of 40% La-HfLaO films annealed at 600°C. The dotted line represents the ideal flat band voltage, assuming that the work function of Au is 5.0eV. The almost constant value of flat band voltage indicates few fixed charge in $HfLaO_x$ film.

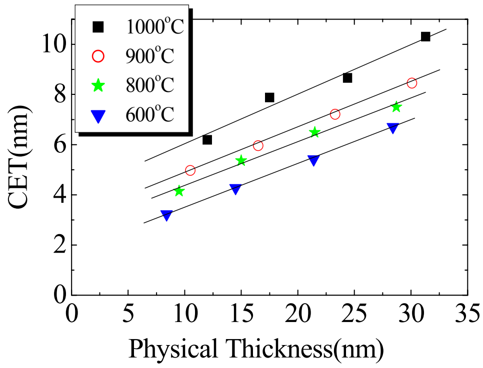

Fig.5 The relationship between CET and film thickness (determined by GIXR) for 40% La-$HfLaO_x$, annealed at 600°C, 800°C, 900°C, and 1000°C. The dielectric constant was estimated from the slope.

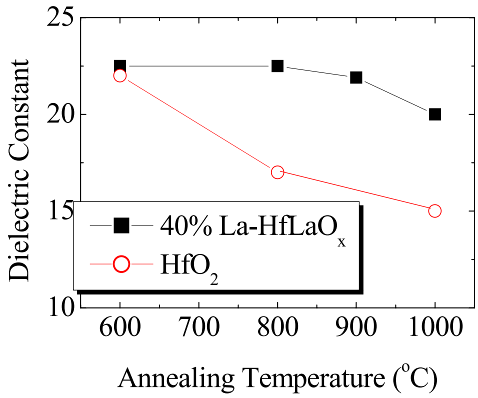

Fig.6 The dielectric constant of 40%La-$HfLaO_x$ and HfO_2 films annealed at 600°C, 800°C, 900°C, and 1000°C. Both films annealed at 600°C show similar k value (=22). But dielectric constant of HfO_2 decreases as annealing temperature increase because of crystallization into monoclinic phase. $HfLaO_x$ does not show significant change of k value.