Study of polarization uniformity in N-doped ferroelectric HfO$_2$
by piezo-response force microscopy

Lun Xu$^{1,}$, Shigehisa Shibayama$^{1,}$, Tomonori Nishimura$^{1,}$, Takeaki Yajima$^{1,}$, Shinji Migita$^{3,}$, and Akira Toriumi$^{1}$

1. Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan.
2. National Institute of Advanced Industrial Science & Technology, Tsukuba, Ibaraki 305-8569, Japan

* E-mail: xulun@adam.t.u-tokyo.ac.jp

The ferroelectricity of HfO$_2$ can be enhanced by cation doping, such as Si, Al, Y, Sr, and Zr.$^{[1]}$ It is believed that the oxygen vacancy (Vo) formation is responsible for the HfO$_2$ phase transition from monoclinic phase to tetragonal and cubic phases,$^{[2]}$ and thus polar orthorhombic phases (Pca2$_1$, Pmn2$_1$) can form.$^{[3]}$ Recently, N doping is reported to be effective to enhance the HfO$_2$ ferroelectricity, and N directional bonds exhibit strong effects on structural and electrical properties of HfO$_2$.\cite{4}$^{[4]}$ Compared with trivalent cation doping, N doping is more sensitively for the HfO$_2$ para-/ferroelectric transition. This difference should be related to N bonds formation. The distortion effect of N bonds can enhance the HfO$_2$ phase transition process initially, while a lot of directional N bonds will strongly suppress the atomic motion as the strong covalent properties. Considering that N bonds would influence the local polarization properties, we use the piezo-response force microscopy (PFM) to study the local polarization properties of N-doped HfO$_2$.

In this study, 28-nm-thick HfO$_2$ films were fabricated by rf-sputtering. N$_2$/(N$_2$+Ar) gas flow ratio varied from 1% to 50% with 20 sccm total gas flow for N-doped HfO$_2$; Sc-doped and Y-doped HfO$_2$ were co-sputtered with 20 sccm Ar gas flow. Post-deposition annealing was carried out at 600 °C, 30 seconds in 1 atm N$_2$. In PFM writing process, 9 V DC bias ($V_{DC}$) was applied in 2×2 $\mu$m$^2$ area, which was followed by −5 V $V_{DC}$ in 1×1 $\mu$m$^2$ area. After this, we scanned 2×2 $\mu$m$^2$ with $V_{DC}$ = 2 V and $V_{AC}$ = 0.7 V. The PFM phase images of 0.3% N-doped and 0.7% Y-doped HfO$_2$ were shown in Fig 1 (a) and (b). Although both PFM phase images exhibit the ferroelectricity of N-doped and Y-doped HfO$_2$ films, N doped HfO$_2$ presents tougher and more uniform polar states. This observation indicates N bonds formation might improve the local polarization stability.

In conclusion, we demonstrate the different local polarization in N-doped and Y-doped HfO$_2$ by using PFM. The results indicate that N bonds might stabilize HfO$_2$ polar states.

This work was supported by JST-CREST.


Fig 1 PFM phase images of 2×2 $\mu$m$^2$ area for (a) 0.3% N-doped HfO$_2$ and (b) 0.7% Y-doped HfO$_2$ scanned at $V_{DC}$ = 2 V and $V_{AC}$ = 0.7 V after writing scan with $V_{DC}$ = 9 V in 2×2 $\mu$m$^2$ and $V_{DC}$ = −5 V in the central 1×1 $\mu$m$^2$ area, respectively.