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[2], 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.[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 μm^2 area, which was followed by −5 V V_{DC} in 1×1 μm^2 area. After this, we scanned 2×2 μm^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.

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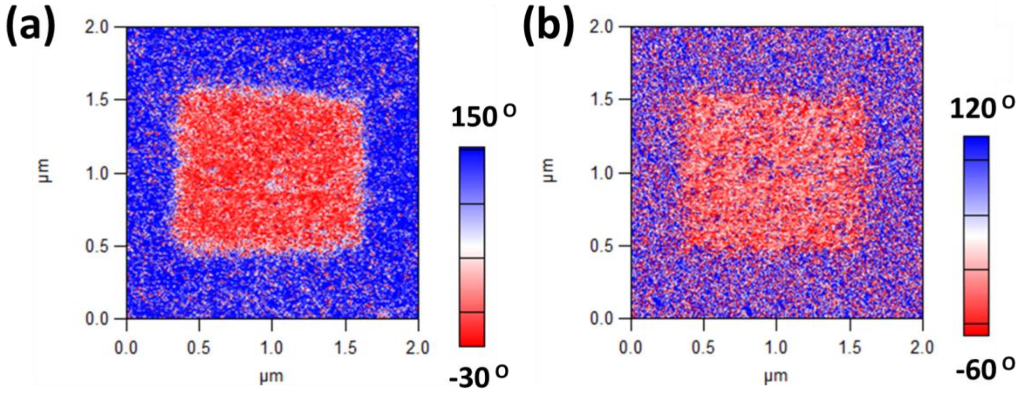

Fig. 1 PFM phase images of 2×2μm^2 area for (a) 0.3% N-doped HfO_2 and (b) 0.7% Y-doped HfO_2 scanned at V_{DC} = 2 V and V_{AC} = 0.7 V after writing scan with V_{DC}=9 V in 2×2 μm^2 and V_{DC}= −5 V in the central 1×1 μm^2 area, respectively.