New finding of ferroelectricity of N doped HfO_2 films

Lun Xu[1*], Tomonori Nishimura[1], Shigehisa Shibayama[1,2], Takeaki Yajima[1], Shinji Migita[3], and Akira Toriumi[1]

1. Department of Materials Engineering, The University of Tokyo, Tokyo 113-8656, Japan.
2. JSPS research fellow, PD
3. 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 moderate cation doping, such as Si, Al, Y, Sr, and Zr. [1] For Y doped HfO_2, earlier reports indicate that tetragonal and cubic phases of HfO_2 are stabilized due to trivalent Y doping induced oxygen vacancies (Vo).[2] However, it is not well understood about the origin of HfO_2 ferroelectricity, and if it is related to the Vo or local chemical bonds. Here, N doped HfO_2 (N:HfO_2) were investigated, which indicates HfO_2 ferroelectricity is more sensitive to N doping than Y doping.

In this study, N doped and Y doped 28-nm-thick HfO_2 films were fabricated prepared by rf-sputtering. N_2/Ar gas flow varied from 0.2/19.8 to 10/10 sccm/sccm for N:HfO_2, and Y_2O_3 and HfO_2 were co-sputtered with different power (5/80 to 20/80 W/W) for Y:HfO_2. Then top Au electrodes were thermally evaporated after annealing all HfO_2 stacks at 600 deg C, 30 seconds in 1 atm N_2.

Chemical compositions of doped HfO_2 were estimated by XPS. Also, the binding energy of 397eV for N 1s peaks (not shown) can be attributed to N^{3-} in N:HfO_2 (Hf-N bonds formation). XRD analysis (**Fig.1**) reveals that 0.1% N (atomic ratio) can hugely increase the ratio of high-symmetry phases from 30% to 85%, and further increase to 95% by 0.5% N doping. XRD also indicates N doping can suppress the crystallization process (increase HfO_2 crystallization temperature), while Y doping can increase it (decrease HfO_2 crystallization temperature).

The electrical properties of N:HfO_2 films were analyzed by capacitance-voltage (C-V) and polarization-voltage (P-V) measurement, which are shown in **Fig. 2**. 0.1% N doping maximizes the ferroelectricity of HfO_2, and larger than 0.5% N doping can dramatically suppress the ferroelectricity. By comparing remanent polarization and dielectric constants, we estimated that N induced HfO_2 phase transform direction: monoclinic phase - ferroelectric phase (orthorhombic) - tetragonal or cubic phase - amorphous phase.

In addition, we observed that ferroelectricity of HfO_2 is much more sensitive to N doping than Y doping (**Fig.3**): 0.7% Y doping can maximize ferroelectricity while 0.1% N doping is enough. Here, except Vo, we think Hf-N bonds need to be seriously considered for the ferroelectricity. For few Hf-N bonds (0.1-0.3% N), both ferroelectricity and dielectric constant of HfO_2 are enhanced; for moderate Hf-N bonds (0.5% N), ferroelectricity is suppressed but dielectric constant of HfO_2 is still above 30; for much more Hf-N bonds (5% N), the dielectric constant decreases below 20.

In conclusion, we have demonstrated that HfO_2 ferroelectricity is sensitive to N doping, which might result both from Vo and Hf-N bonds formation.

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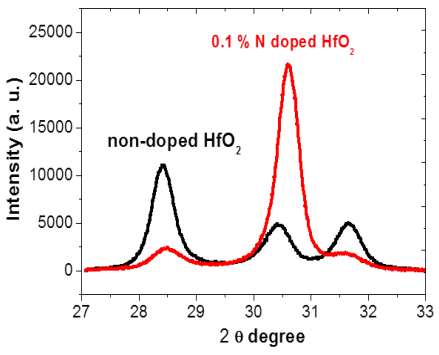

Fig. 1 θ -2 θ XRD scans on non-doped and 0.1% N doped HfO_2

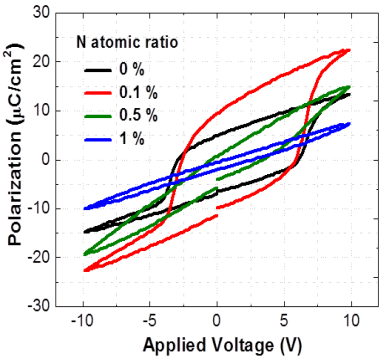

Fig.2 PE characteristics of N:HfO_2 films

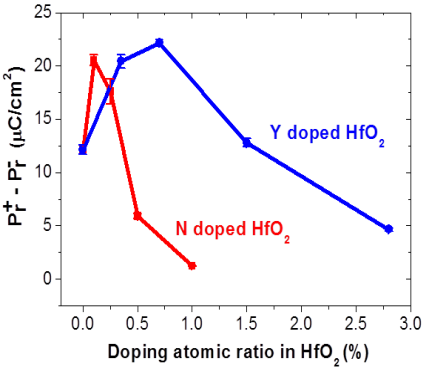

Fig. 3 Remanent polarization for N:HfO_2 and Y: HfO_2 films

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