

Effects of nitrogen bonding on para-/ferroelectric transition of HfO₂

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We report that the HfO₂ ferroelectricity can be driven by nitrogen (N) doping thanks to the phase transition from the monoclinic (M) to the highly symmetric phase (orthorhombic/tetragonal/cubic, O/T/C). The role of N-doping is discussed from two aspects, the oxygen vacancy (Vo) formation as required by charges neutrality, and the Hf-N and N-O bonds formation. Here, we demonstrated that N bonds can strongly affect HfO₂ structural and electrical properties, and contribute to both positive and negative effects on the HfO₂ ferroelectricity.

In this study, 28-nm-thick HfO₂ films were fabricated by rf-sputtering. N₂/(N₂+Ar) gas flow ratio varied from 1% to 50% with 20 sccm total gas flow for N-doped HfO₂; Sc-doped and Y-doped HfO₂ were co-sputtered with 20 sccm Ar gas flow. Top Au electrodes (5.7×10⁻⁵ cm²) were thermally evaporated after post-deposition annealing at 600 °C, 30 seconds in 1 atm N₂.

Chemical compositions of doped HfO₂ were estimated by SIMS and XPS. N 1s XPS spectra of N-doped HfO₂ exhibits two peaks at 396 eV and 403 eV, indicating the formation of Hf-N and N-O bonds, respectively.^[1] For the Hf-N bond, N atoms can replace O atoms, and thus it will generate oxygen vacancies in HfO₂ from the charge balance viewpoint.^[2] While for the N-O bond, HfO₂ structure seems easier to be distorted thanks to broken Hf-anion unit cells. Therefore, N-doped HfO₂ structural and electrical properties should be strongly affected by these N covalent bonds.

In Fig. 1, the highly symmetric phase ratio (R_H) is shown as a function of doping concentration (total atomic ratio, %) according to the equation $R_H = I_{O/C/T(111)} / [I_{M(-111)} + I_{O/C/T(111)} + I_{M(111)}]$, where I is the XRD peak area intensity. Considering Hf-N bonds, two N atoms generate one Vo by the replacement of O atom.^[2] Also, two trivalent cations can make one Vo by the replacement of Hf atom. However, N-doping presents a more drastic transition than Sc- and Y-doping initially, which indicates the N bonds distortion effect might play an important role on the HfO₂ phase transition. In addition, the suppression of the phase transition was also observed when increasing N doping concentration. It might be related to the suppressed oxygen vacancy motion as the existence of a lot of covalent N bonds. For trivalent cation doped HfO₂ (Sc³⁺ and Y³⁺), they present quite similar behaviors owing to the same phase transition origin, that is the oxygen vacancy formation.

The switching polarization ($P_{sw} = P_r^+ - P_r^-$, P_r: remanent polarization) of doped HfO₂ was summarized in Fig. 2. For the Vo dominated phase transition, the similar para-/ferroelectric transition behaviors were observed in Sc- or Y-doped HfO₂. However, N doping exhibits a drastic para-/ferroelectric transition, which should be related to N bonds effects. The distortion effect of N bonds can enhance the HfO₂ phase transition process initially, while a lot of directional N bonds will strongly suppress the atomic motion as the strong covalent properties.

In conclusion, HfO₂ structural and electrical properties can be affected by Hf-N and N-O bonds, and thus N-doping is more sensitively than trivalent cation doping for the HfO₂ para-/ferroelectric transition.

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[2] K. Xiong *et al.*, J. Appl. Phys. **99**, 044105 (2006).

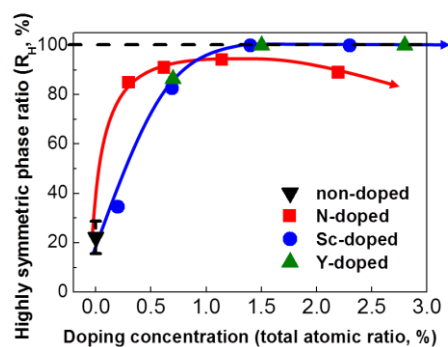


Fig. 1 HfO₂ highly symmetric phase ratio (O/T/C) with different N, Sc or Y doping concentration

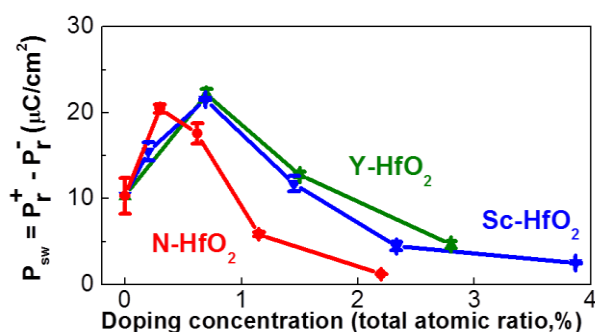


Fig. 2 The switching polarization (P_{sw}) of 28-nm-thick HfO₂ films with different N, Sc, and Y doping concentration