Opportunity of ferroelectric phase formation in nitrogen-doped HfO$_2$

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Abstract: We report that nitrogen (N) doping into HfO$_2$ induces the para-/ferroelectric transition more sensitively rather than metallic cation doping, for the first time. Directional N bonds are responsible for distorting HfO$_2$ structure and thus contribute to a dramatic effect on HfO$_2$ para-/ferroelectric phase transition. This is in striking contrast to the cation doped HfO$_2$ ferroelectricity, although other ferroelectric properties such as Ec or Pr are not so different from the cation doped cases.

1. Background and objective

Recently, ferroelectric HfO$_2$ has attracted a lot of interests owing to its possible application for nonvolatile memories and low-power field effect transistors.[1, 2] Most results so far reported on HfO$_2$ ferroelectricity have been demonstrated by various cation doping into HfO$_2$ (Si, Y, Al, Zr, La, Sr, and Gd).[3] Although the role of dopants is still not well understood, ferroelectric phase is believed to originate from the structural stabilization of non-centrosymmetric phase of HfO$_2$ thanks to the cation doping. It looks like dopant induced martensitic phase transition of ZrO$_2$ studied a lot in the fine ceramics community, in which two possible reasons have been conjectured. One is the charge balance and the other is the ionic radius. In the ferroelectric HfO$_2$ case, the charge balance to keep the net charge neutrality, particularly, the oxygen vacancy (Vo) formation, may also be responsible for the ferroelectric phase transformation. Vo formation can make the ionic transport much easier and the structural phase transformation might be substantially facilitated. On the other hand, N may serve as a network former in oxides as well as may change the charge balance in oxides. Therefore, in this study, we report effects of nitrogen doping into HfO$_2$ from the viewpoint of ferroelectric phase transition.

2. Formation of Hf-N and N-O bonds in N-doped HfO$_2$

N-doped HfO$_2$ (N:HfO$_2$) films were grown by rf-sputtering in the mixture of N$_2$ with Ar, in which the gas flow ratio (N$_2$/(N$_2$+Ar)) was varied from 1% to 50% with 20 sccm total gas flow rate. In the present experiments, N-doped HfO$_2$ film thickness was controlled around 28 nm, and top Au electrodes were thermally evaporated after the post deposition annealing (PDA) at 600ºC in 1-atm N$_2$ for 30s.

**Figure 1** show N 1s XPS spectra of non-doped and 7% (total atomic ratio) N doped HfO$_2$ films. The O 1s peak was fixed at 530.4 eV as the reference. On the one hand, N:HfO$_2$ exhibits a strong peak at 396 eV owing to the formation of Hf-N bonds.[4] It indicates that N atoms replace O atoms, and thus it possibly causes HfO$_2$ phase transition from the view of charge balance and directional N bonds distortion effect. On the other hand some N-O bonds, roughly 15% in total N bonds, also exist because of the N 1s peak at 403 eV. These anion-anion bonds can break Hf-anion unit cell and form a network structure.

**Fig. 1** N 1s XPS spectra of 7% N-doped HfO$_2$ and non-doped HfO$_2$.

3. N-doping induced para-/ferroelectric transition

P-V and C-V characteristics of N-doped HfO$_2$ films are shown in **Figure 2(a)** and (b). It is interesting to see that only 0.3% N doping (total atomic ratio, N concentration was estimated by SIMS after PDA) can clearly enhance the ferroelectricity, which is comparable to cation-doped HfO$_2$ ferroelectricity. **Figure 3** shows both switchable polarization $P_{SW}=P_{r}^+ - P_{r}^-$ and relative dielectric constant as a function of N doping concentration. A small amount of N doping (0.3%) is enough to maximize the ferroelectricity of HfO$_2$, while the ferroelectricity is drastically suppressed when the doping concentration is increased to more than 1%.

**Fig. 2** (a) Polarization-voltage (100 Hz) and (b) capacitance-voltage (10 kHz) characteristics of 28-nm-thick 0.3% N-doped HfO$_2$ films.

GIXRD patterns of N:HfO$_2$ films are shown in **Figure 4**, which indicates that N doping suppresses HfO$_2$ monoclinic phase and enhance high-symmetrical phases (orthorhombic, tetragonal or cubic). They are consistent with electric properties of N-doped HfO$_2$ in **Figure 3**. For non-doped HfO$_2$ film, the major phase is monoclinic one, and thus the dielectric constant of HfO$_2$ is around 22, while for 0.3% N-doped HfO$_2$, the ferroelectricity is enhanced and dielectric constant is over 30 owing to the formation of the ferroelectric phase. However, the ferroelectricity will be drastically suppressed when N doping
concentration is over 1%. This is because the phase transition from ferroelectric phase to tetragonal or cubic phase. Moreover, by further increasing N doping over 2%, the dielectric constant of HfO\(_2\) will decrease although high-symmetric phases are dominated in GIXRD pattern. For example, the dielectric constant of 7% N-doped HfO\(_2\) decreases to 18 (Fig. 3).

\[ \alpha_{\text{ferro}} \propto C_{\text{ferro}} \gamma_{\text{ferro}} \]

in which \( \alpha_{\text{ferro}} \), \( C_{\text{ferro}} \) and \( \gamma_{\text{ferro}} \) are the activity, concentration, and activity coefficient of Vo. In both cases, \( \alpha_{\text{ferro}} \) increases with \( C_{\text{ferro}} \) initially. However, that in N-doped HfO\(_2\) sharply decreases around 0.7 % owing to N bonds effects, while it is not the case in Y-doped HfO\(_2\). It is noted that we are not directly discussing about the ferroelectric phase transition, but by considering that the activity behavior may characterize the structural phase transition, the dopant sensitivity in para-/ferroelectric transition is schematically shown in Fig. 6.

4. Comparison of N doping and Y doping

To compare N-doped HfO\(_2\) with cation-doped case, Y-doped HfO\(_2\) was grown by co-sputtering. Figure 5 shows \( P_{\text{sw}} \) both for N-doped and Y-doped HfO\(_2\) as a function of doping concentration. It is noted that 0.3% N is enough to maximize the ferroelectricity and 2.2% N can totally suppress it, while 0.7% and 6.5% Y are for Y-doped case. Intuitively speaking, both two N atoms (replace O) and two Y atoms (replace Hf) can make one oxygen vacancy just in the valency consideration, but it should be taken into consideration that N can bond with O as well as with Hf atoms. Here, since Vo is the key ingredient for structural phase transition and both systems can be regarded a small diluted doping, we assume that the key parameter in N-doped case is still oxygen vacancy motion, and that the ferroelectric phase should be between monoclinic and high symmetric phases. Therefore, we discuss the results in Fig. 5 thermodynamically from the viewpoint of the activity of Vo as follows.

\[ \alpha_{\text{Vo}} \propto \gamma_{\text{Vo}} C_{\text{Vo}}. \]

Fig. 3 Remnant polarization and relative dielectric constant of 28-nm-thick HfO\(_2\) films with different N doping concentration. \( P_r^+ \) and \( P_r^- \) were remanent polarization at zero bias condition. The dielectric constant is estimated from the capacitanc at the center position of CV curves.

Fig. 4 GIXRD patterns of annealed HfO\(_2\) films with different N doping concentration. The relative intensity can be compared among different N-doped HfO\(_2\) films. The red, blue and black stars represent for ferroelectric orthorhombic, cubic and monoclinic phases, respectively.

Fig. 5 Comparison between N- and Y-doping effects on para-/ferroelectric transition of 28-nm-thick HfO\(_2\) films. \( P_r^+ \) and \( P_r^- \) were remanent polarization at zero bias.

Fig. 6 Schematic description of Y-doping and N-doping induced para-/ferroelectric transition. Vo can cause phase transition from monoclinic to high-symmetric phases, and thus cause the para-/ferroelectric transition. Whereas, in N-doped HfO\(_2\) case, Vo activity is suppressed due to the low activity coefficient, and thus a dramatic change from ferroelectric to paraelectric is observed.

5. Conclusions

In this study, structural phases and electrical properties of N-doped HfO\(_2\) have been investigated. To our knowledge, this is the first observation that N-doping is effective for driving the ferroelectricity of HfO\(_2\). The para-/ferroelectric phase transition in HfO\(_2\) seems to be more sensitive to N-doping than to Y-doping, which is understandable from the viewpoint of compromise between positive and negative effects on the ferroelectric phase transition by N-doping. Technically, this fact may provide a freedom for designing the appropriate ferroelectric film, though further study is obviously need.

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6. References