Growth and Ferroelectric Characterization of Lanthanoid-Doped Epitaxial HfO_2 Thin Films

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1. Introduction

Since the first report of ferroelectricity in HfO_2-based thin films[1], this material system has attracted considerable attention for its use in next-generation nonvolatile memory applications. Doping with suitable elements is recognized to be particularly effective for the stabilizing ferroelectric orthorhombic phase. Although doping stabilizes the ferroelectric phase via combined changes in average ionic radius and oxygen vacancy formation, the indivisual effect of the average ionic radius on ferroelectric properties has remain unsolved.[2]-[4]

In this study, we investigate the effect of the average ionic radius of the cation on ferroelectricity. (111)-oriented epitaxial HfO_2-based films were grown, and trivalent lanthanoid elements with various ionic radius were doped with various contents.

2. Experimental Procedure

Lanthanoid–doped HfO_2 thin films (Ln^{3+}; La, Nd, Sm, Tm, Lu) with various contents were grown at room temperature on (111) ITO//(111) YSZ substrates by pulsed-laser deposition. Post-deposition heat treatment was performed by lamp annealing at 1000 °C for 10 min under an atmospheric N_2 gas flow. Crystal structure and film composition were evaluated by X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. Circular Pt top electrodes were formed by electron-beam evaporation. Ferroelectric properties were evaluated by polarization–electric-field (*P*–*E*) measurements.

3. Results and Discussion

Figure 1 shows *P*–*E* hysteresis loops of $xLnO_{1.5}$–$(1–x)HfO_2$ (Ln = La, Nd, Sm, Tm, Lu) films as a function of dopant content. All dopants showed ferroelectricity for appropriate *x* values within the present study. Notably, dopants with larger ionic radius (*e.g.*, La) showed a broader composition window exhibiting ferroelectricity than those with smaller radius (*e.g.,* Lu). Figure 2 summarizes the dependence of the saturated polarization (P_{sat}) and coercive field (E_c) on the average cationic ionic radius estimated from the film compositions. P_{sat} monotonically increased with increasing average ionic radius. Based on the measured P_{sat} values, the spontaneous polarization (P_s) was estimated and shown in Figure 3(a). P_s increased from ~20 to ~40 μC cm^{-2} as the average ionic radius increased within 0.077–0.080 nm. We further estimated P_{sat} assuming random grain orientations from P_s value, and compared with the reported data for lanthanoid-doped HfO_2 (see Figure 3(b))[3], [5]-[10]. The estimated values almost agreed with reported ones and exhibit the same increasing trend with ionic radius, supporting the validity of our estimation.

4. Conclusions

Effect of the average ionic radius of trivalent lanthanoid dopants on the ferroelectric properties in epitaxial HfO_2 thin films was systematically investigated using well-defined (111)-oriented epitaxial films. Clear ferroelectricity was observed for films doped with all dopants. Saturation polarization (P_{sat}) and coercive field (E_c) almost proportionally increased with increasing average ionic radius as well as the estimated spontaneous polarization (P_s) value.

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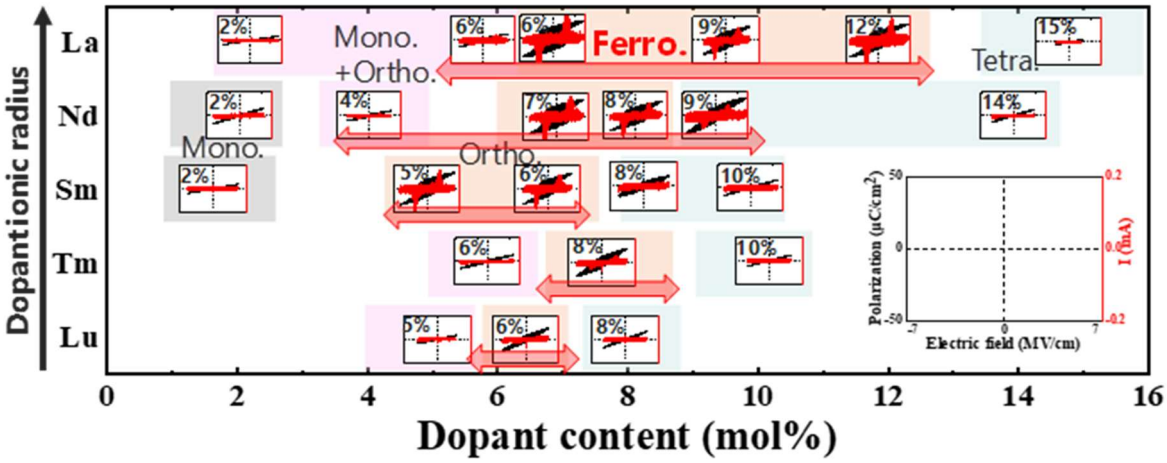

Fig. 1 *P-E* and *I-E* curves for xLnO$_{1.5}$–(1−x)HfO$_2$ thin films with various dopants a function of dopant content. Scale of the electric field, polarization and current are shown in the inset figure located at the right bottom edge.

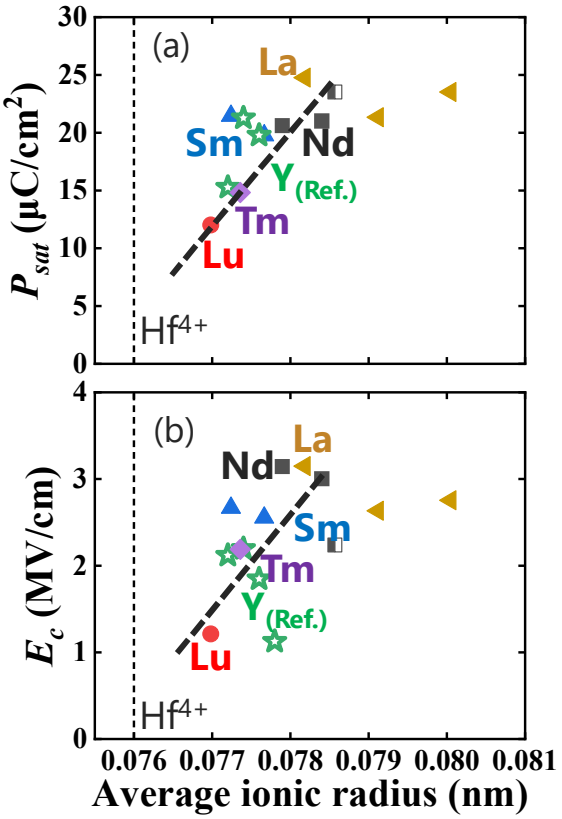

Fig. 2 (a) $P_{sat.}$ and (b) E_c as functions of the average ionic radius of xLnO$_{1.5}$–(1−x)HfO$_2$ thin films.

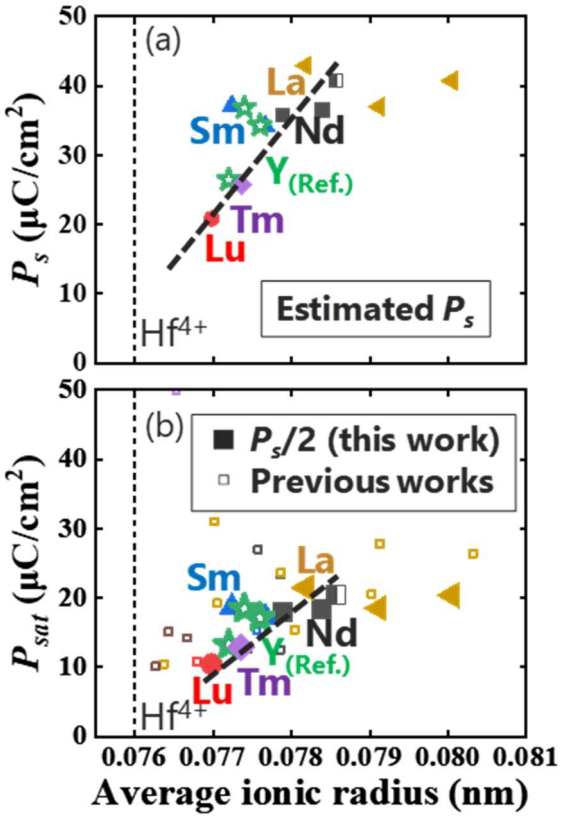

Fig. 3 (a) Estimated spontaneous polarization (P_s) and (b) expected saturation polarization ($P_{sat.}$) value assuming polycrystalline films (P_s/2) based on the estimated P_s value as a function of average ionic radius. Reported data for the lanthanoid-doped HfO$_2$ thin films are also shown in (b) as small open symbols.