STEM-EELS Observation of Particular Ferroelectric State in the PbTiO$_3$/SrTiO$_3$ Superlattice film

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Ferroelectric stability is a limiting factor for miniaturization of electrical devices used for memory and data storage. The PbTiO$_3$ (PTO)/SrTiO$_3$ (STO) superlattices with alternating thin ferroelectric PTO and paraelectric STO layers have recently shown the possibility of improving the polarization stability at the ferroelectric dimensional limit with various types of nanoscale domain structures, such as vortices, flux-closure domains, and 180°-stripe domain structures [1-3]. However, imperfections in the charge screening at the PTO/STO interfaces and discontinuous ferroelectric states often occur when the STO layers are thicker than the PTO layers. This results in a large depolarization field, which is a major obstacle to obtain stable polarization states, and induces a paraelectric state in the PTO layers [4]. In this study, we focus on a superlattice thin film with thin PTO and thick STO layers, wherein the hidden ferroelectricity in the thin PTO layer is revealed from the large depolarization field.

We performed an experiment to compare the ferroelectric states of the PTO single layer and (6PTO/15STO)$_5$ superlattice (0.3 PTO volume fraction), which is known to be near the paraelectric limit. In order to eliminate the ferroelectric dimensional limit, we chose a superlattice structure with six unit-cell-thick PTO layers because it has sufficient thickness to maintain the ferroelectricity. We conducted a scanning transmission electron microscopy (STEM) study, including the high-angle annular dark field (HAADF) image and electron energy-loss spectrum (EELS) analysis with EELS calculation results to observe the ferroelectric states at the atomic scale.

Figure 1 shows the analysis of local ferroelectric state in the (6PTO/15STO)$_5$ superlattice. The results of c/a ratio (Fig 1(b)) and Ti$^{4+}$ displacement ($\delta_{Ti}$, Fig 1(c)) value show that PTO layers in the superlattice have a ferroelectric polarization shift despite the decrease of the tetragonal symmetry. This is inconsistent with other reports, which suggest that the paraelectric property increases with decreasing tetragonality [4]. Our EELS results (Fig 1(d)) also confirms that the PTO layer in the (6PTO/15STO)$_5$ superlattice has a ferroelectric energy state, like the PTO single layer, even though the tetragonality is largely suppressed.

Figure 2 shows the HAADF-STEM image of the (6PTO/15STO)$_5$ superlattice and the polarization vector map along the (100) zone axis. The PTO layers show a local disordered polarization configuration similar to a polar nanoregion (PNR) or a glassy polarization configuration despite the general expectation of the existence of 180° stripes or a vortex domain structure in the PTO/STO superlattice film system. Our atomic scale analysis on (6PTO/15STO)$_5$ superlattice clarifies how the local, disordered polarization configuration occurs in the thin, discontinuous-ferroelectric PTO layer. This ferroelectric polarization configuration may be due to compensation for the large depolarization field, which is caused by the polarization discontinuity of the PTO layers or to an imperfect charge screening between the PTO and STO layers.
References:


**Figure 1.** Analysis of the local polarization state in the (6PTO/15STO)$_5$ superlattice. (a) HAADF-STEM image of the STO/PTO/STO interface. The EELS line scan region is indicated by the green dashed box. (b) c/a ratio and (c) Ti$^{4+}$ displacement ($\delta_{Ti}$) for each unit cell in (a). (d) $\Delta L_3$ of the $t_2g$ and $e_g$ spectra for each unit cell. The red and blue dashed lines in [(b)–(d)] indicate the results for the PTO single layer and STO substrate, respectively.

**Figure 2.** HAADF-STEM image of the PTO/STO superlattice and polarization vector map from the atomic displacements in HAADF-STEM image. The arrows indicate the polarization direction and strength of the expressed color map.