Revealing atomic structure and composition in ultrahigh energy storage density ferroelectric thin-films using (scanning) transmission electron microscopy

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Ferroelectric thin film material is positioned to be a strong candidate for nano/microelectronics component with ultra-high energy storage density with low electric field [1]. One of the key strategies to achieve such high energy storage density is by creating a secondary phase nanostructure around the morphotropic phase boundary. Here we show detailed characterisation of (Bi, Na)TiO$_3$ (BNBT) and BiFeO$_3$ (BFO) thin films grown on SrTiO$_3$ single crystal substrate. The nanostructures in the thin films as well as their electronic structures and composition variations were characterised using a range of (S)TEM techniques including high angular dark field (HAADF-STEM), and 4D STEM, as well as Negative Cs phase contrast TEM imaging (NCIS). In addition electron energy loss spectroscopy (EELS) was used to probe the composition and the electronic structure across the nanostructured domains. These techniques were performed on the newly installed double aberration corrected JEOL GrandARM300F2 (S)TEM instrument at UNSW.

We found that there is Bi segregation forming strips of half unit cell wide β-Bi$_2$O$_3$ layers. Such composition is confirmed by the atomic resolution EELS maps, showing no presence of Ti within the β-Bi$_2$O$_3$ bright strips. The effect of the β-Bi$_2$O$_3$ layers is to laterally displace the lattice above the defect by half a unit cell, resulting a morphotropic anti-phase domain boundary. In addition, the Bi$_2$O$_3$ segregation layer gives about 22% longer c-axis for the 3 unit cell around the defect. Such large expansion of c-axis is attributed to the presence of the super-tetragonal phase (super-T) [2-3]. The electronic structures of Ti and O sites adjacent to the β-Bi$_2$O$_3$, measured using EELS Ti L edge and O K edge, is consistent with the lattice distortions, measured from NCIS HRTEM and 4D STEM. Such complex nanostructures with multiple structure phases co-existent forming nanodomains is found to be the key for the ultra-high performance of such ferroelectric thin films.

**Figure 1.** a) HAADF-STEM image showing the structure of the Bi segregation into half unit cell of β-Bi$_2$O$_3$. b) Atomic resolution EELS map of Ti L edge and Bi M edge elemental maps from the same region shown in a), and c) the integrated differential phase contrast image derived from the 4D-STEM dataset showing the oxygen sites.


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