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Atomic-Scale Characterization of Ferro-Electric Domains in Lithium Niobate- revealing the Electronic Properties of Domain Walls

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Ferroelectric Doman Walls (DWs) are playing an increasing role in nanoelectronics [1-4]. One of the most prominent features of the ferroelectric domain DWs is their electrical conductivity, which was observed in a number of ferroelectric materials, such as $BiFeO_3$, $Pb(Zr,Ti)O_3$, $ErMnO_3$. Here, we combine scanning transmission electron microscopy (STEM) and –spectroscopy (down to the atomic level) with local probe techniques to investigate the conducting properties of the charged DWs in focused ion-beam (FIB) sliced single-crystalline $LiNbO_3$ lamellae of sub-µm thickness. STEM shows large inclination of the electrically-generated 180º DWs away from the polar z-axis (with inclination angles reaching 16°) suggesting that these DWs are strongly charged. Atomic column STEM imaging revealed the dipolar kinked configuration of the Nb atoms along the inclined DWs. Piezoresponse force microscopy (PFM) in combination with conductive atomic force microscopy (CAFM) performed both on z- and x-cut surfaces revealed that head-to-head DWs exhibit much higher conductivity than tail-to-tail DWs, suggesting an electronic type of conductance. One of the most important findings is the possibility of DW conductivity modulation by an external voltage. It has been demonstrated that the resistance of the $LiNbO_3$ thin film capacitors can be changed continuously by orders of magnitude by controlling the DW perimeter allowing development of multi-level resistive switching devices [5].

To further investigate and prove the conducting behaviour of the DWs on a highly (nm) spatially resolved scale, electron energy loss spectroscopy (EELS) was employed. Low loss EELS can reveal localized changes in the density of states at the conducting DWs by changes in the signal of the energy loss region around bandgap energies (see fig.2b and c). Signal enhancement of the energy loss intensity in the 2 - 3.5 eV regime at the DWs, shown in the line scan across two domain walls meeting at a ~22ºangle (fig.2d), indicates changes in the conductive behaviour. The increase of the density of states in the bandgap region agrees with an enhancement in the conductivity. Additionally, the effect of a strong polarization change across the wall was revealed by an abrupt contrast change due to deflection of the electron beam (see fig.1).

In summary, this presentation details the observation of sub-atomic shifts, thereby enabling the establishment of maps of dipole constellations and arrangements. Furthermore, measurements of the local density of states within domains and at DWs revealed changes in the density of energy states in the bandgap regime across the DWs, by which their conductive or insulating character can be established [6].

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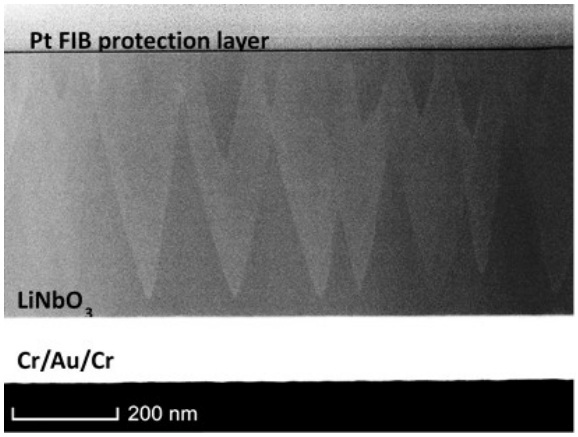

Figure 1. STEM HAADF image of FIB lamella showing domains in $LiNbO_3$ with inclined walls meeting at ~22^0.

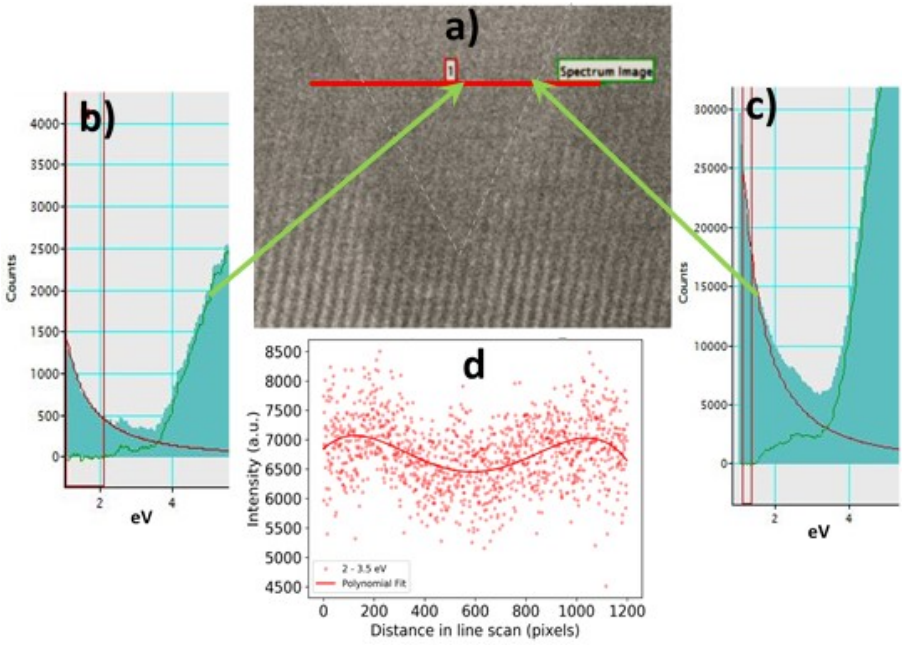

Figure 2. a) HAADF STEM image of domains with the red bar indicating the line along which the EELS spectrum image (SI) was taken; b) and c) spectra extracted from the EELS SI at locations indicated by the green arrows. The red line is a fit to the zero loss peak, the intensity of which was subtracted from the turquoise shaded spectra, resulting in the background subtracted green spectra, which show the loss intensity in the bandgap region; d) loss intensities in the energy region of 2-3.5 eV along the scan line. The red, solid line is a polynomial fit to the experimental values (red dots).

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