2089 Microsc. Microanal. 21 (Suppl 3), 2015
doi:10.1017/S1431927615011228 Paper No. 1043 

# Atomic resolution studies of the (K, Na)$NbO_3$/$SrTiO_3$ interface using aberration corrected STEM

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Atomically-engineered interfaces between transition metal oxides offer novel electronic and coupled functionalities in thin films that are otherwise unapproachable through bulk synthetic chemistry due to the element composition modulation, lattice strain effect and various dislocations at the interface. Consequently, it is crucial to study the interface at atomic resolution for thin film growth, deposition quality and piezoelectric properties, etc. (K, Na)$NbO_3$ (KNN) as an environment- friendly lead-free piezoelectric material has been extensively studied since the earlier research work achieved by Saito et al [1]. To date, efforts have been concentrated on KNN bulk materials and the KNN-based thin film research is limited. In this paper, a lead-free KNN thin film was epitaxially grown on $SrTiO_3$ (STO) single-crystalline substrates by sol-gel method [2]. The microstructure of the KNN/STO epitaxial interface was investigated by scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS) using JEOL ARM 200F electron microscope with probe spherical aberration corrector. The strain distribution of the KNN/STO epitaxial interface was mapped at the atomic scale from HAADF images by using the geometric phase analysis (GPA) [3].

Fig. 1a shows the HAADF-STEM images of the epitaxial KNN/STO interface region. The clear contrast difference indicates the sharp KNN-STO interface. It is noted that the brightness of one layer of atomic columns (marked by red rectangle) at the interface shows apparent differences in comparison with adjacent atoms. The HAADF-STEM image simulation (WinHREM$^{TM}$) is conducted to quantify the atomic mixture along the electron beam direction in the experimental micrographs. Fig. 1b presents the schematic super-cell model of the KNN/STO interface and the corresponding simulated HAADF image (50 at% Ti was substituted by Nb atoms at the interface layer in the simulated image) is shown in Fig. 1c. The similarity of the intensity line profiles from both the simulated images and the experimental ones (Fig. 1d and 1e) indicates that the single layer at the KNN/STO interface contains 50 at% Ti and 50 at% Nb. In order to verify the intermixing layers along the interface, atomic resolution EELS mapping was applied. Fig. 2 (b-e) shows the EELS spectra image results from the interface region marked in Fig. 1a. It is clear that the Ti and Nb cations coexist at the 'B-site' (A: alkaline or rare-earth ions; B: transition metals in perovskite structure $ABO_3$) which confirms the composition result obtained by the HAADF image simulation.
The piezoelectric properties of KNN thin film will largely depend on the KNN/STO interface, in other words, the strain relaxation is important for its application. Fig 3a shows the HAADF image of the dislocation free interface and Fig. 3b-d are the corresponding GPA strain maps of $E_{xx}$, $E_{yy}$ and $E_{xy}$, respectively. Fig 3b shows the relative *a*-lattice strain at the interface which indicates a gradual increase perpendicular to the thin film growth direction. However, there are little relative strain in perpendicular direction and out-of-plane rotation in both the film and substrate lattices. More

detailed analysis including dislocation at the interface and DFT calculation will also be discussed.

References:

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[4] The authors acknowledge the funding from National Natural Science Foundation of China (51202180), the Fundamental Research Funds for the Central Universities in China and the 111 Project of China (B14040).

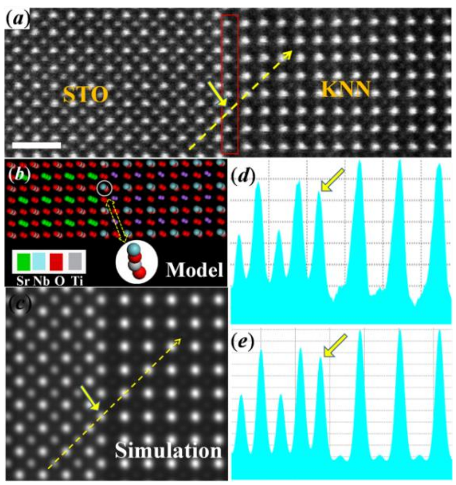


Figure 1. (a) Experimental HAADF image of the KNN/STO interface; (b) schematic atomic model of the interface; (c) simulated HAADF image of the interface, (d, e) intensity profile of the exprimental image and simulated image across the interface (along the dashed line), respectively. Scale bar, 1nm.

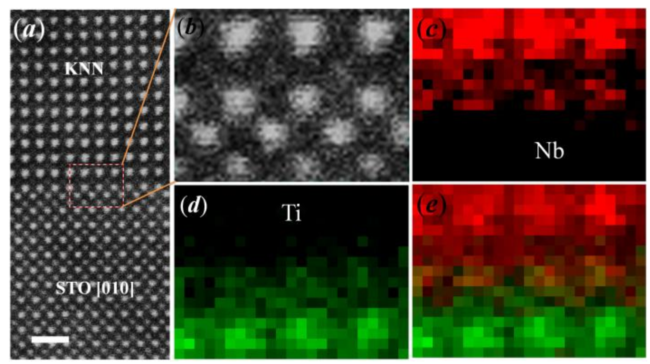


Figure 2. EELS spectra imaging results of the KNN/STO interface. (a) HAADF-STEM image; (b) zoomed mapping area; (c, d) False-coloured Nb and Ti elemental maps, respectively; (e) combined elemental maps with Ti in green, Nb in red. Scale bar, 1nm.

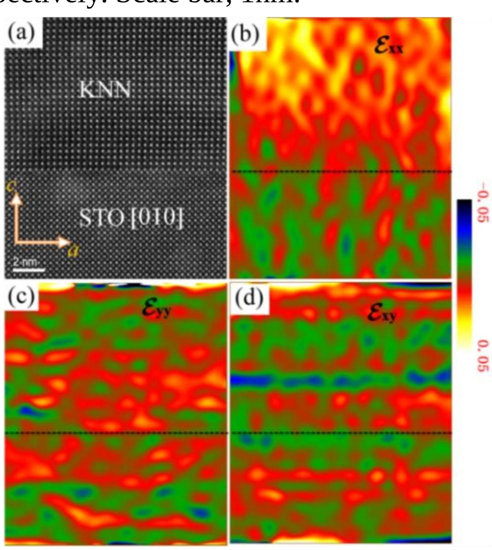


Figure 3. (a) A atomic-resolution HAADF imge of the stress released KNN/STO interface; (b)-(d) the calculated GPA result of $\varepsilon_{xx}$, $\varepsilon_{yy}$, $\varepsilon_{xy}$, respectively(a). Scale bar, 2nm.