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Chemical Quantification of Atomic-scale EDS Maps

Ping Lu, Mark Van Benthem, Eric Romero, Sandia National Laboratories, PO Box 5800, Albuquerque, NM 87185
Jie Xiong and Quanxi Jia, Los Alamos national laboratory, Los Alamos, NM 87545
Email: plu@sandia.gov

Abstract

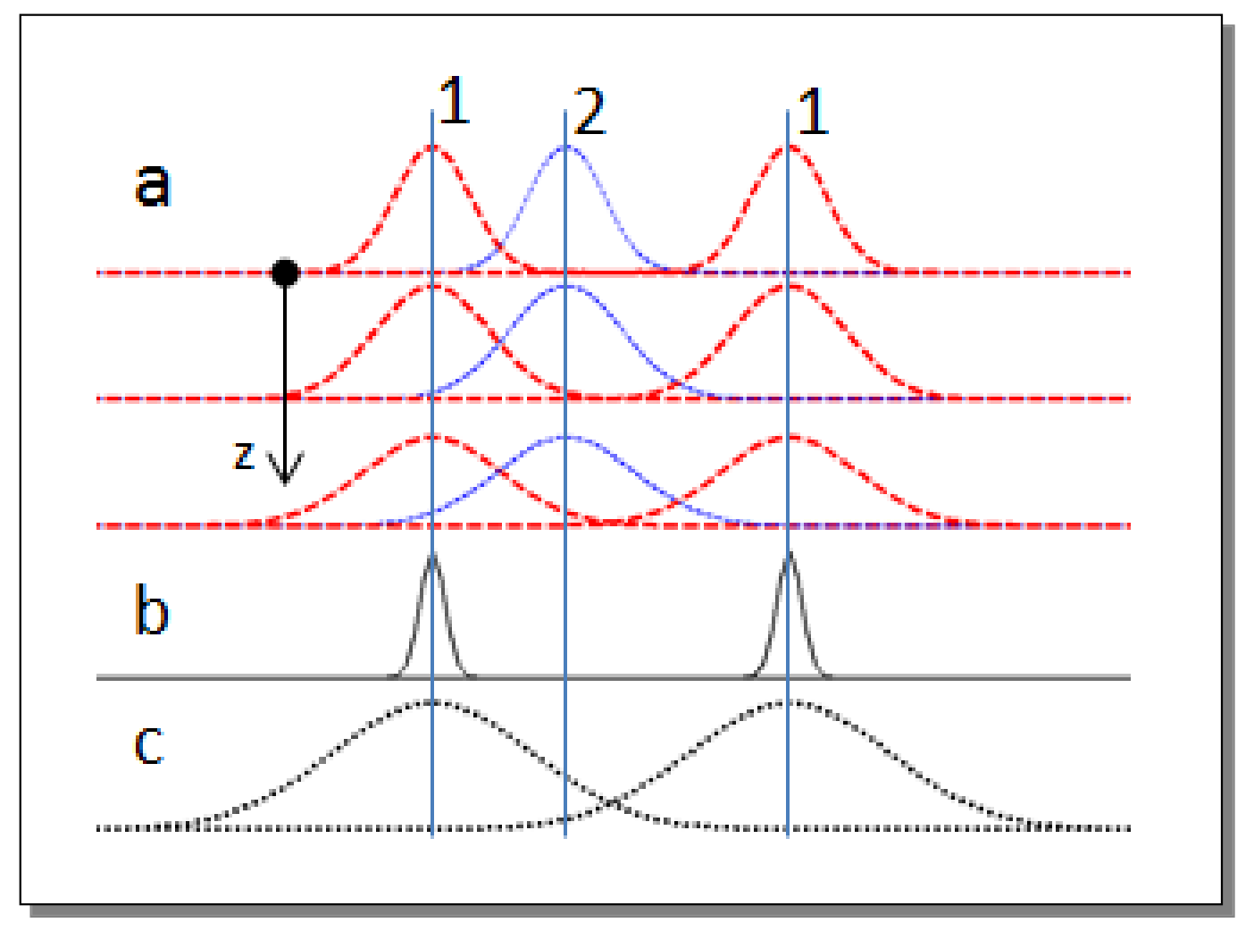
We report our effort to quantify atomic-scale chemical maps obtained by STEM-EDS spectral imaging. Direct quantification of chemical composition at the atomic columns, in general, is very complicated due to multiple effects, including electron beam spreading and channeling as well as de-channeling. Effects of beam spread and de-channeling can lead to relative contributions from neighboring columns, or so-called "cross-talk", even when a fine probe is focused on a specific column of atoms.

In this study, we investigated effects of specimen thickness and the x-ray energy on the atomic-scale EDS maps, and we showed that under a thin specimen condition, EDS x-ray counts resulting from individual atomic columns can be calculated by fitting Gaussian peaks at each of atomic column position, and the counts can be used for quantification of the atomic-scale maps. Furthermore, we applied the method to quantify chemical composition across an interface of ferromagnetic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and antiferromagnetic $BiFeO_3$ (BFO) quantum structure, and an anti-phase boundary of Sm-doped $SrTiO_3$(STO). For the LSMO/BFO interface, we found cation diffusion at both A- and B-sublattice sites; and asymmetric chemical profiles across the interface, consistent with previous studies. For the Sm-doped anti-phase STO boundary, we found that the Sm atoms occupy preferentially the Sr sites than Ti sites, and Sm atoms are depleted at the boundary .

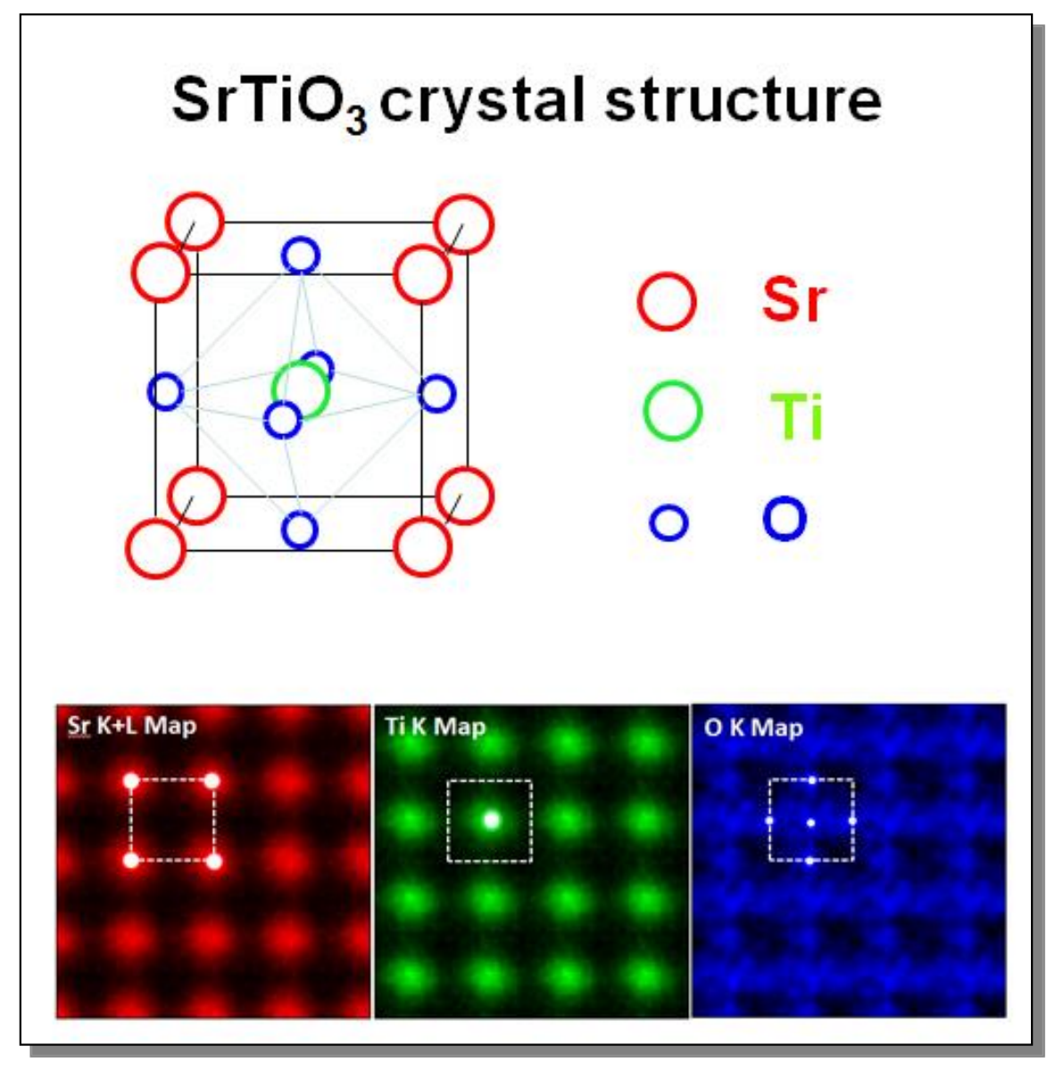
Experimental

A FEI Titan^{TM} G2 80-200 STEM with a Cs probe corrector and ChemiSTEM^{TM} technology (X-FEG^{TM} and SuperX^{TM} EDS with four windowless silicon drift detectors), operated at 200 kV was used in this study. For atomic-scale chemical mapping, EDS spectral image data were axis with an electron probe of size <0.18 nm, convergence angle of 18.1 mrad, and current of ~100 pA. HAADF images were recorded under similar optical conditions using an annular detector with a collection range of 60-160 mrad. Spectral images were acquired as a series of frames, where the same region was scanned multiple times. Frames were spatially drift-corrected to build up spectral image data.

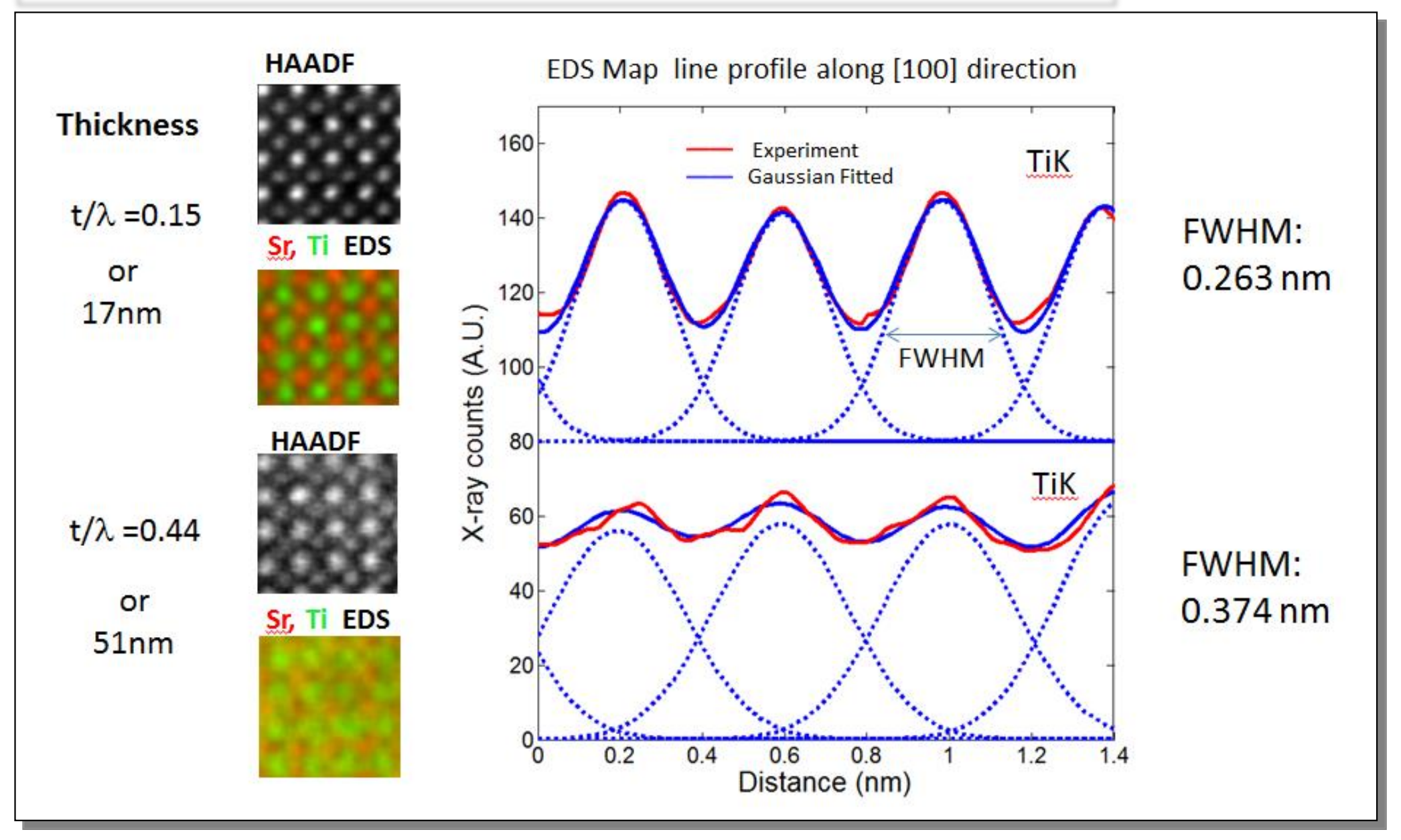
Effect of the specimen thickness and X-ray energy



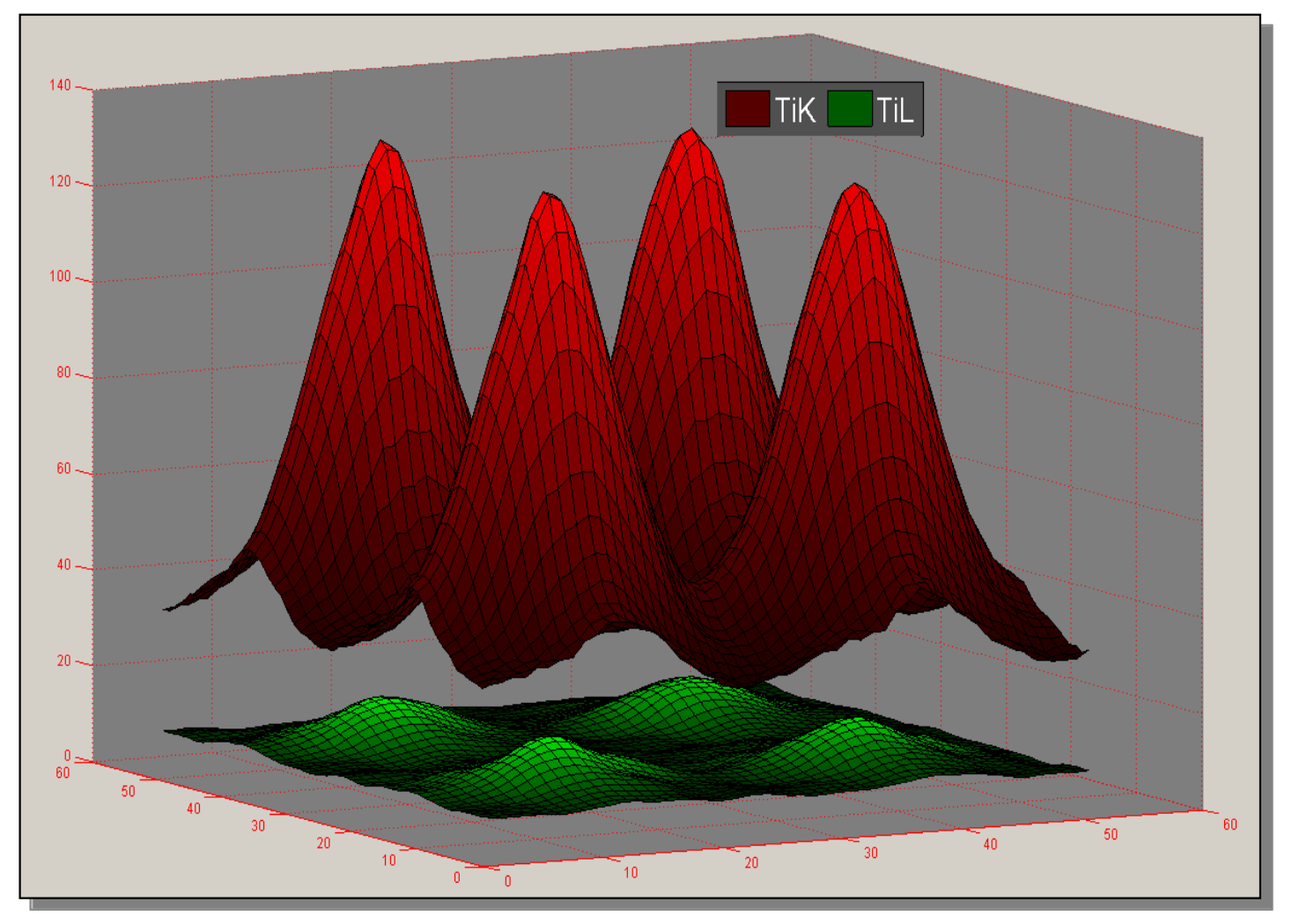
Schematic showing the x-ray generation process in STEM-EDS: (a) Gaussian electron probes at different thickness (z), illustrating beam broadening along z. Position 1 is at the atomic column site and position 2 is away from the site; (b) effective EDS scattering potential localized at the atomic column and (c) overall x-ray profile obtained by the convolution of electron wave at different thickness with EDS scattering potential and integration of the contribution through the sample thickness. The x-ray counts from the atomic column can be fitted with a Gaussian function when the beam broadening due to the specimen thickness is small and the the EDS scattering potential is highly localized.

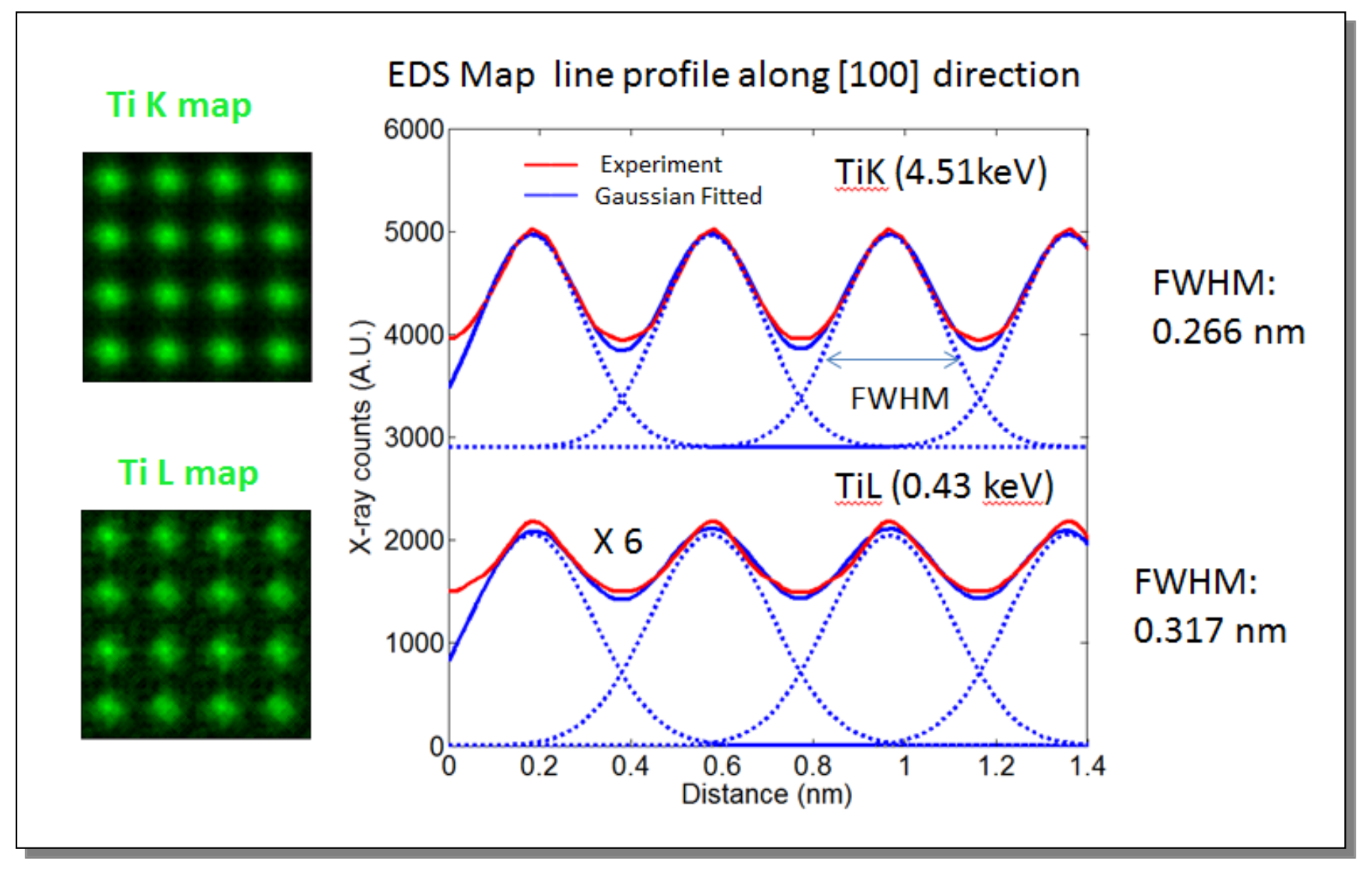


Effect of specimen thickness



Effect of X-ray energy





Example 1- $La_{0.7}Sr_{0.3}MnO_3$\$BiFeO_3$ quantum structure

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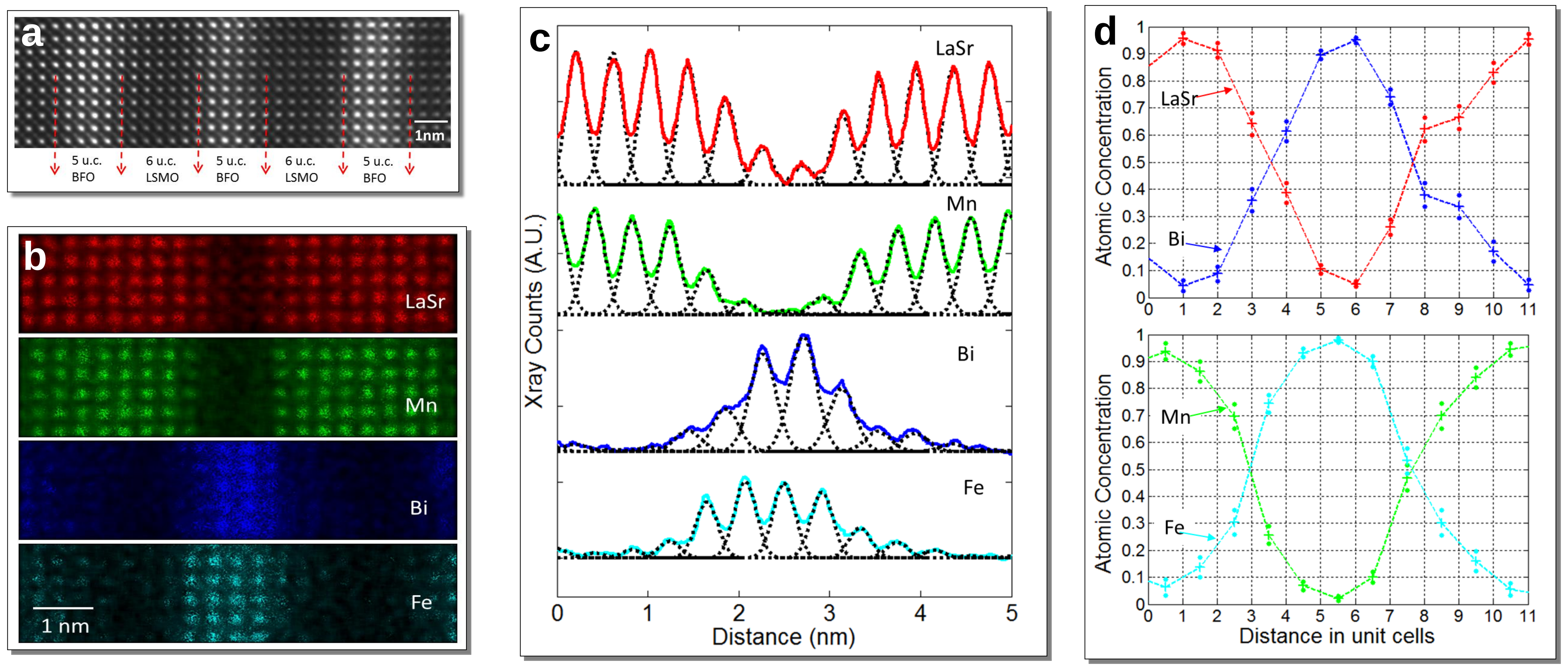
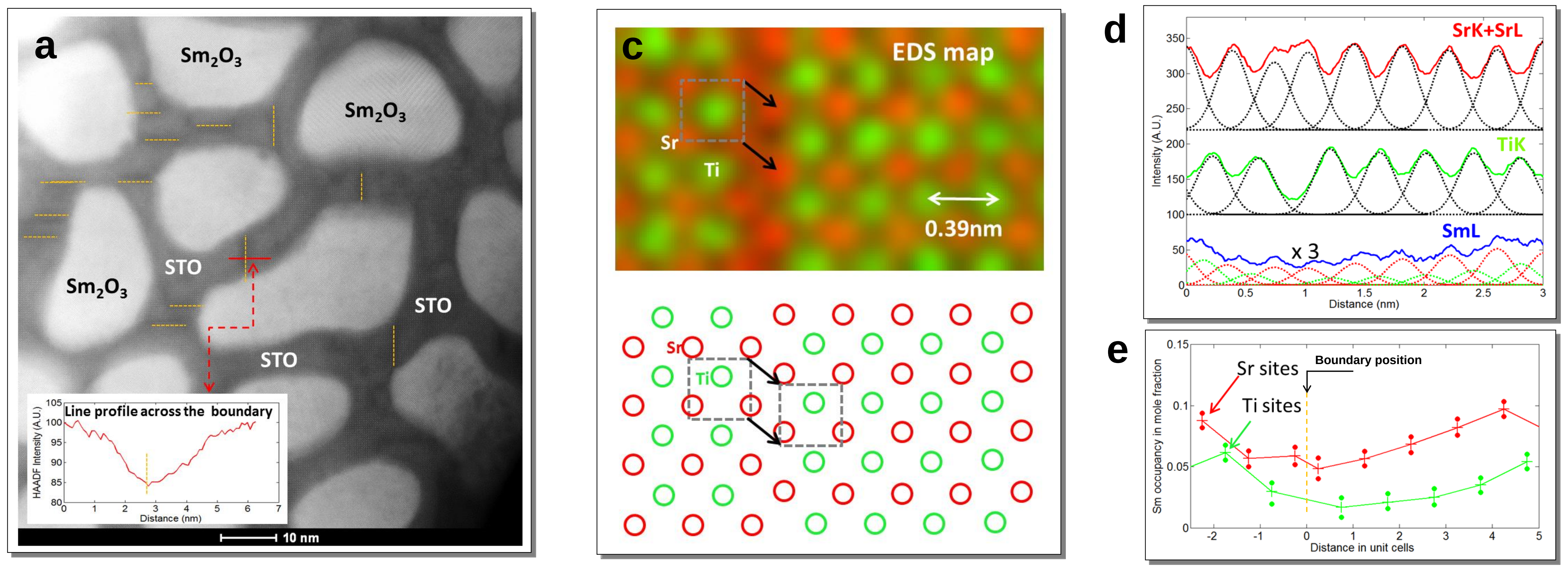


Fig.1. (a) A STEM HAADF image taken in [100] direction showing the LSMO\BFO quantum structure made of roughly five BFO unit cells and six LSMO unit cells; (b) Element maps extracted from EDS spectral images for (La,Sr), Mn, Bi and Fe; (c) EDS line profiles (solid) across the interface along with least-squares fitted Gaussian peaks (dashed). The X-ray counts under each Gaussian peak were integrated as emission from the atoms at the columns and used for the quantification; (d) Quantified atomic-scale concentration profiles across the interface for A-site ((La,Sr) and Bi atoms) and B-site (Mn and Fe atoms). Atomic concentrations were calculated column-by-column using the Cliff-Lorimer method.

Example 2- Sm-doped $SrTiO_3$ anti-phase boundaries

2



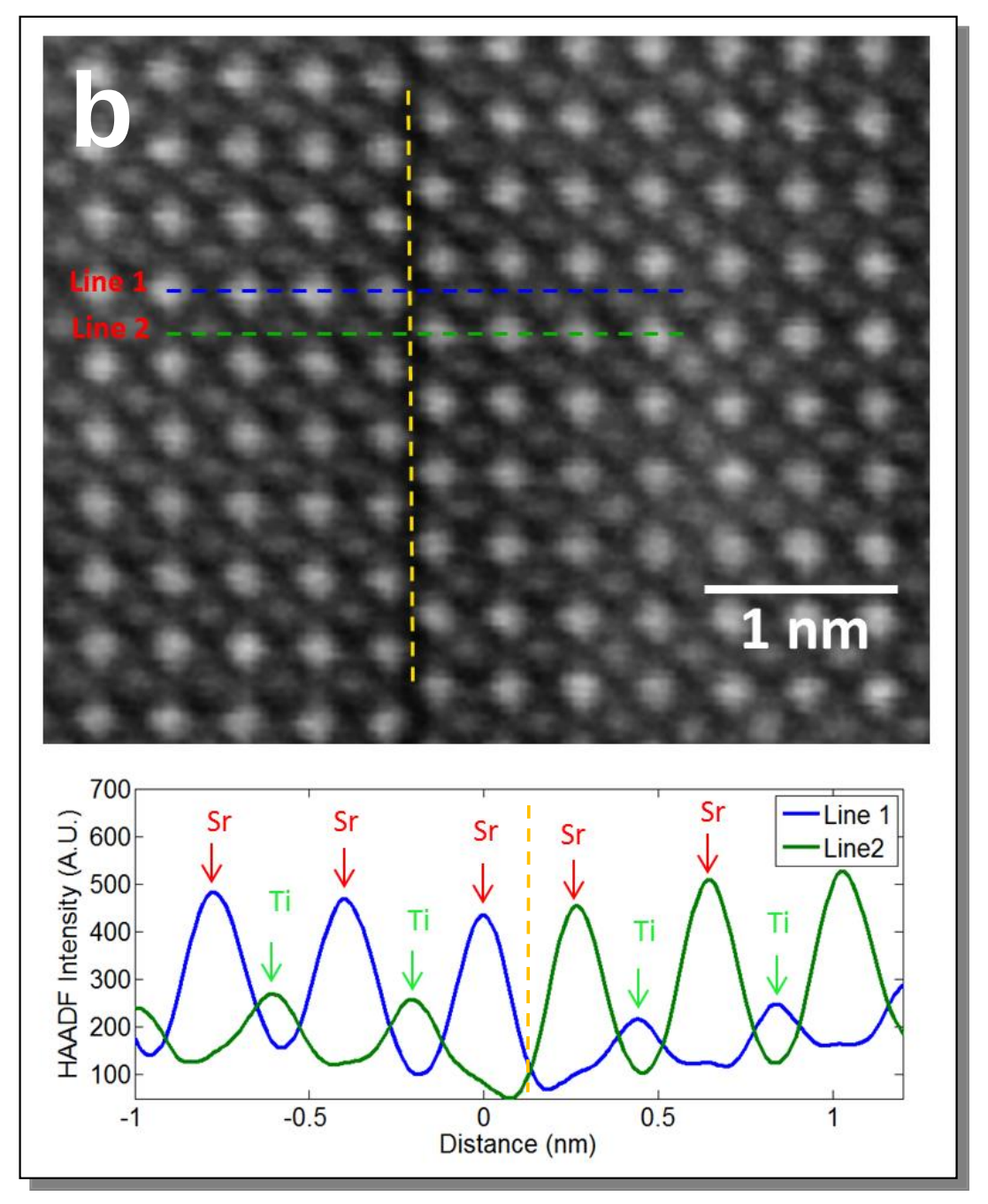


Fig.2. A STEM HAADF image taken in [100] direction showing structure of a Sm_2O_3 and $SrTiO_3$ composite film. Within the STO, anti-phase boundaries with a displacement vector R=1/2[111], are visible and are associated with a darker line contrast shown by the HAADF line-profile across the boundary in inset; (b) High-resolution HAADF image showing the anti-phase boundary along with the line profiles indicating the HAADF intensities at both Sr and Ti sites increases away from the boundary; (c) EDS element (Sr, Ti) map, along with the structure mode, showing the boundary is made of extra layer of Sr atoms; (d) EDS line profiles (solid) across the boundary along with least-squares fitted Gaussian peaks (dashed) for Sr, and Ti and Sm. The Sm EDS profile shows the Sm is depleted at the boundary; and (e) Quantified atomic-scale concentration of Sm across the interface for the Sr-sites and Ti sites. Sm atoms occupy preferentially the Sr sites than the Ti sites, and Sm atoms are depleted at the boundary.

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