Applications of aberration-corrected STEM and atomically-resolved EELS on the study of high-T_c superconductors in epitaxial films and layered heterostructures

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Layered oxide compounds are extensively studied for their application potentials as superconductors and ionic conductors. These layered structures can be considered as stacking sequences of perovskite layers, either with or without intervening rock-salt layers separating them, where planar defects such as stacking faults are often present. These structurally anisotropic defects, particularly near substrate interfaces in epitaxial thin film, can have dramatic effects on physical properties such as low-dimensional transport, diffusion and growth [1]. In this study we focus on the interfacial microstructure and defects in $YBa_2Cu_3O_{7-x}$ (YBCO) thin films grown on $(LaAlO_3)_{0.3}$ $(Sr_2AlTaO_6)_{0.7}$ (LSAT) substrates. These films are ultimately intended for use in transport studies of multilayers comprising YBCO and $La_{1-x}Ca_xMnO_3$ (LCMO).

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was used in our study. The STEM imaging was carried out with an FEI Titan[3] 80-300 TEM, equipped with a CEOS-designed hexapole-based aberration corrector for the probe-forming lens and imaging lens. The instrument is fitted with a high-brightness electron source and a Super-Twin lens, in order to achieve sub-Ångstrom resolution for phase contrast imaging, STEM, and electron energy loss spectroscopy (EELS) mapping, along with a monochromator in order to achieve energy resolutions as low as 0.1 eV [2]. Measurements were carried out at either 80 or 200 keV in order to reduce knock-on damage.

From HAADF intensities, we can unambiguously identify the sequence of layers and the intergrowths of Cu-O layers and extra Cu-Y-Cu layers (as indicated by arrows in Figure 1). From these images, we can identify the local fraction of the $YBa_2Cu_4O_8$ (YBCO-124) phase and its structural role in the nature of the interface between ultrathin YBCO and LCMO layers. These intergrowths generate non-planar growth as demonstrated by the “waviness” of the YBCO layers. It was also found that interfaces have a different layer arrangement within the first few unit cells of the film, and that the films can present a high fraction of YBCO-124 under certain growth conditions. Other layer arrangements and their effect on physical properties will also be discussed. Our results demonstrate that smooth interfaces, at the atomic level and over several microns, can be obtained and thus very high epitaxial quality of the samples can be achieved. In spite of the known beam sensitivity of this material, we successfully carried out preliminary atomically-resolved EELS mapping of $YBa_2Cu_3O_{7-x}$ as shown in Figure 2(a) where we can clearly distinguish each Y layer and even Ba atomic column positions. Due to the high energy of the Cu $L_{2,3}$ edge, maps for Cu show relatively well-resolved Cu columns. An apparent higher intensity in the oxygen map can be seen in the BaO-CuO_2-Y-CuO_2-BaO block than in the CuO layer. This effect should be understood in terms of possible oxygen deficiency but also, more importantly, based on the dynamical elastic contributions in the inelastic scattered intensities at the O K edge loss. At the interface with the LSAT substrate, our EELS maps show that it is possible to identify the terminating layer of the substrate, in this case an AlO layer whereas the first layer of the film is BaO as shown in Figure 2(b). Further analysis of the LCMO-YBCO interface, including difficulties due to edge overlaps in this system (Figure 2b) as well as the analysis of intergrowths, will be discussed [3].

References

[1] *Habermeier H.U. et al.*, Physica C, **364-365** (2001), p. 298-304.
[2] *Botton, G.A.et al*, Ultramicroscopy, **110** (2010), p. 926-934.
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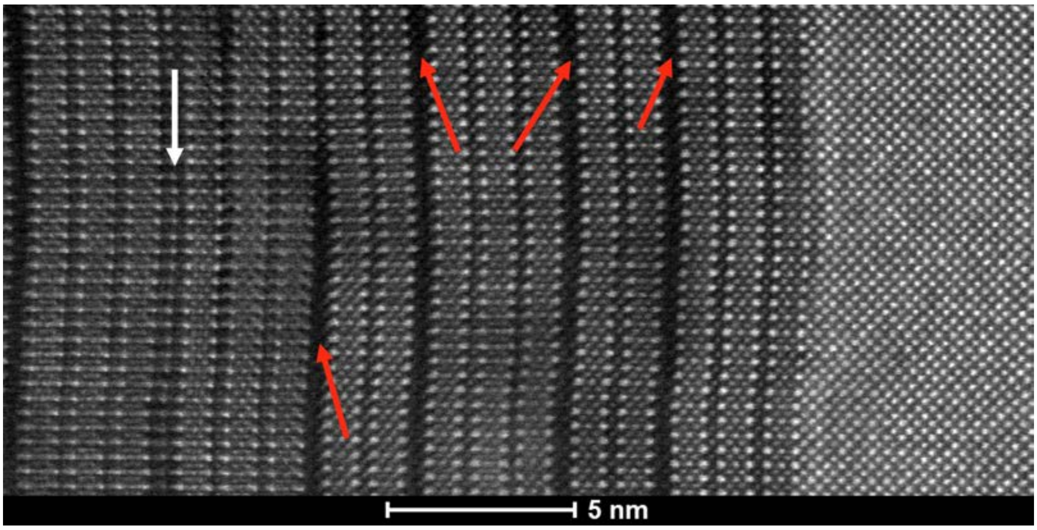

Figure 1. *HAADF-STEM image of the interface between LSAT substrate (right side of the micrograph) and YBCO film. The arrows indicate two different types of defects: an extra CuO layer leading to* $YBa_2Cu_4O_8$ *(red arrows) and an inclusion of a CuO-Y-CuO block (white arrow).*

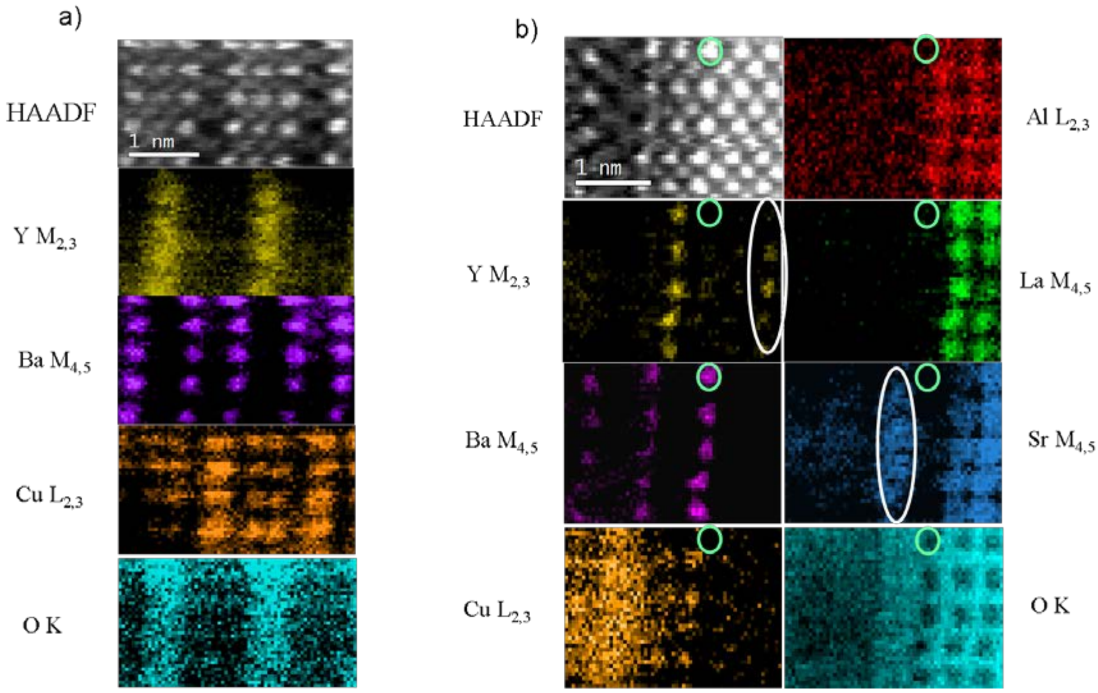

Figure 2. *Atomically-resolved EELS maps of YBCO/LSAT interface. The maps were acquired at 200keV with 20ms/pixel dwell time, and the data was subsequently processed with MSA-weighted principal component analysis. a) Preliminary elemental maps of* $YBa_2Cu_3O_{7-x}$*. b) Interface structure between YBCO and LSAT revealed by EELS atomic mapping. Due to the overlap between the Y* $M_{2,3}$ *edge and the Sr* $M_{4,5}$ *edge, areas with potential artifacts in atomic positions (highlighted by ellipses) are shown. The Ba-O layer is the first atomic plane in the YBCO in contact with the substrate. The maps show that La and Sr are (as expected) on the same site in the LSAT substrate. Blue circles mark the same atom as a guide for the eye.*