The 2DEG at the complex oxide heterointerface between LAO and STO was found to have high carrier mobility and high sheet carrier density at room temperature, both several orders of magnitude larger than at the heterointerfaces of III-V-based semiconductors [1]. Much experimental and theoretical work has been done to investigate the fundamental origins of these electronic properties [2, 3]. However, there is still no single mechanism that can explain the formation of the metallic state which is consistent with all observed experimental details. Here, we present a study of the effects of annealing on the LAO/STO 2DEG interface using atomic resolution STEM and EELS.

Five unit cells (u.c.) of LAO films were grown epitaxially on a TiO2-terminated (001) STO single crystal substrates. Two samples were annealed in oxygen atmosphere at 400 ºC and 600 ºC, respectively. One highly-conducting film left in the as-grown condition for comparison. The film annealed at 400 ºC is insulating, whereas the one annealed at 600 ºC show 2DEG behaviour. Atomic-resolution EELS mapping was performed at the interface of the 600 ºC annealed LAO/STO film (Fig. 1). The La M$_{4,5}$ edges map show a gradually decreasing intensity in the STO and drops to zero at a depth of about 5 u.c. below the interface. The Ti L$_{2,3}$ edges map show strong Ti signals in the LAO film, indicating Ti diffusion and its displacement of Al on the B-site. EELS line scans were collected across the LAO/STO interfaces of both three films. Elemental distribution profiles are shown in Fig. 2, along with HAADF images of the regions from which they were acquired. The Ti penetrating slightly farther in the LAO film annealed at 600 ºC than in 400 ºC annealed and as-grown films. La diffused into the STO substrate to a depth of nearly 4 u.c. in the as-grown and 400 ºC annealed films and 5 u.c. in the 2DEG film. The spatial distribution of the Ti$^{3+}$ and Ti$^{4+}$ signals across the LAO/STO interfaces are shown in Fig. 3. The insulating film has a relatively low concentration of Ti$^{3+}$, contained to the 4 u.c. adjacent to the interface with LAO. In comparison, the conducting films show a high concentration of Ti$^{3+}$ through the entirety of the LAO as well as the top 5 u.c. in STO substrate. The high concentration of Ti$^{3+}$ in the film, which can be attributed to the presence of diffused La and oxygen vacancies, creates the conditions necessary for the formation of a 2DEG [4].

In conclusion, we provide a detailed TEM analysis of the origins and the annealing effect of 2DEGs at the LAO/STO interface. We found that the mixed Ti valence is strongly related with the free carrier density, which is result from the competition between the La substitution and refill of oxygen vacancies.

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Fig. 1: Atomic-resolution EELS mapping was performed from the marked area in (a). (b)-(d) are the elemental maps of the O K, La M\textsubscript{4,5} and Ti L\textsubscript{2,3} edges. (e) is the colorized EELS elemental map of the O, La and Ti.

Fig. 2: (a), (b) and (c) are the elemental distribution profiles of as-grown, 400 ºC annealed and 600 ºC films. (c), (d) are the spatial distribution of Ti\textsuperscript{3+} and Ti\textsuperscript{4+} in these two films.

Fig. 3: (a), (b) and (c) are the spatial distribution of Ti\textsuperscript{3+} and Ti\textsuperscript{4+} in the as-grown, 400 ºC annealed and 600 ºC films.