HAADF-STEM and EELS study of $SrTiO_{3-x}$:Ny obtained by microwave plasma ammonolysis

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Perovskite oxides have been the subject of intense research on account of their ferroelectric and dielectric properties, which can be used effectively in a wide range of applications, such as nonvolatile ferroelectric and high-density dynamic random access memory devices [1]. Phenomena like 2D-Electron Gas [2] or resistivity switching [3] have been recently discovered in perovskite materials. From the perovskite material knowledge area, the oxynitride-perovskites $AB(O,N)_3$ are a growing class of materials with prospective optical and catalytic properties [4]. One method to introduce N into $SrTiO_3$ (STO) perovskite structure is by mean of microwave induced NH_3 plasma procedure. In this two step treatment, the following modifications of the chemical composition are used to change the electronic structure and properties of STO: i) formation of oxygen vacancies, and ii) an anionic substitution $N^{-3} \rightarrow O^{-2}$. Substitution of O^{2-} with N^{3-} in perovskites is possible due to the similar ion size of both elements. However, due to the charge compensating mechanism complete anionic substitution of O^{-2} by N^{-3} keeping the perovskite type structure cannot be realized without the presence of anionic vacancies (collapsed in dislocations, stacking faults and new structures or superstructures). With the reduction scaling of microelectronic devices, lattice defects in these materials become increasingly important. Recently, it was shown that the formation of stacking fault defects in the perovskite structure during plasma ammonolysis facilitate resistivity switching in Al/$SrTiO_{3-x}$Ny/Al memristors [5].Therefore; it is extremely demanding the careful characterization of defects produced during the ammonia plasma treatment. Several questions arise in this work such as the defect type, how the lattice distortion is around the defect, the local change in composition, and where the N is inserted in the structure.

High-resolution transmission electron microscopy (HRTEM) is the first essential step for research on lattice defects. But, the distinct composition changes around the defects can be better studied by Z-contrast image and mapped with sub-nanometer spatial resolution utilizing EELS in scanning transmission electron microscopy (STEM). On the basis of collected Ti $L_{2,3}$, O and N Kline EELS spectra around defect zones and free defect zones, and combined with high resolution HAADF and HRTEM, composition information will be correlated with the atomic structure of $SrTiO_{3-x}$:Ny. For example, Fig.1 shows the analysis of interface layer between TiN- $SrTiO_{3-x}$:Ny which is formed by plasma ammonolysis with a flux NH_3 < 125 ml/min. The EELS spectrum image in line scan mode shows how the Ti $L_{2,3}$ changed passing the mention interface. Fig. 2 shows the stacking faults produced by a plasma treatment with a flux of NH_3 > 125. The HAADF-STEM image shows the interchange of Sr by Ti in the defect.

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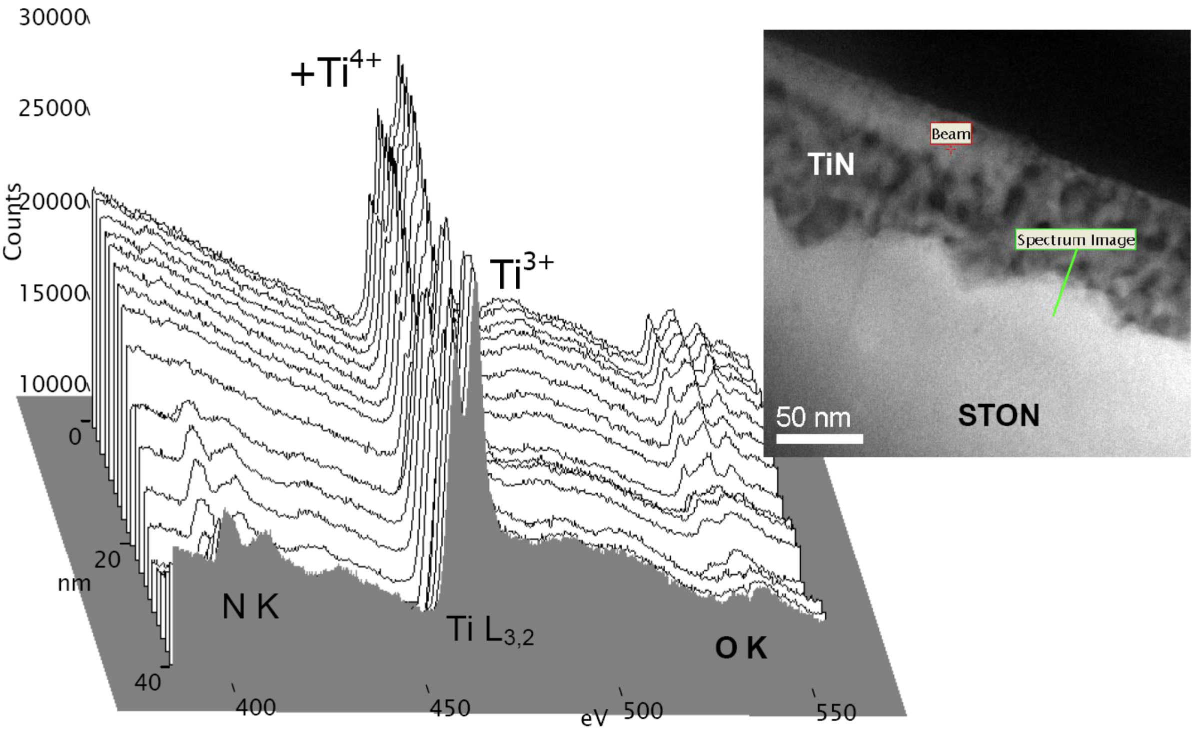

Figure 1: EELS analysis of the interface layer between TiN- SrTiO3-x:Ny which is formed by plasma ammonolysis with a flux $NH_3 < 125$ ml/min. In this case a TiN layer is formed on the top of STON.

a) b)

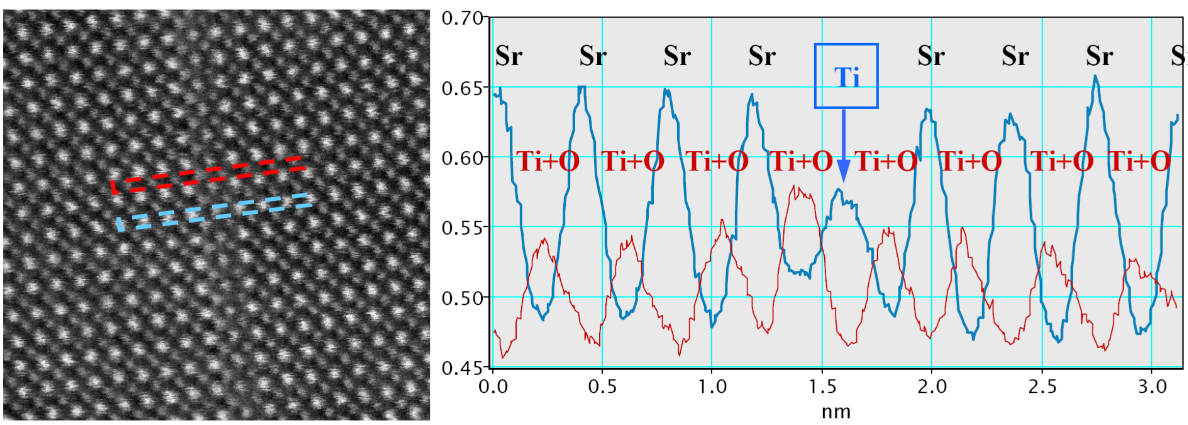

Figure 2: a) HAADF-STEM image of the defect produced by plasma ammonolysis with a flux $NH_3 > 125$ ml/min. In this case only stacking faults are formed on STON (no TiN phase is detected); b) analysis of HAADF-STEM signal.

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