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Electron Energy-Loss Spectroscopy (EELS) Study of NbO_x Film for Resistive Memory Applications

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Niobium dioxide (NbO_2) is one of the Mott insulators that exhibit current-controlled negative differential resistance, also referred as threshold switching, when used in two-terminal devices. This phenomenon is caused by a reversible insulator-to-metal phase transition, which is proposed to induce a conductive channel in the device that bridges the two electrodes [1][2]. As the amount and local distribution of oxygen vacancy play important roles during the switching, characterizing the composition with high spatial resolution at the atomic level is required for understanding the working mechanism and potential failure. Previous EELS study has been conducted on metallic Nb and stable Nb oxides (NbO, NbO_2, Nb_2O_5) in terms of energy-loss near-edge structures (ELNES) of all relevant Nb edges and O-K edge for fingerprints of Nb in different formal oxidation states [3][4]. In this study, we provide a quantitative study on the amorphous NbO_x thin-films by ion beam sputtering for resistive switching applications. The EELS quantification in NbO_x film can provide the variation of local composition and chemical states across the film, which helps to understand the device behavior.

NbO_2 film was deposited by RF magnetron sputtering from an NbO_2 target. The sample substrate was pumped down to below 1E-6 torr and was then heated up in vacuum to 450 °C. 15nm NbO_2 blanket film was deposited in Ar while substrate was maintained at 450 °C. Subsequently, top electrode in the stack of 3nm Ti_4O_7, 6nm TiN, 5nm Pt, and 20nm Cr was deposited over the NbO_2 film through a shadow mask. Cross-sectional samples were prepared using dual beam FEI Helios system. Blanket NbO_2 and Nb_2O_5 films, and Nb_2O_5 crystal powders are also studied as reference samples. The TEM and EELS characterization was done using a FEI Tecnai TF-30 equipped with Gatan GIF Quantum system. The 2D EELS Spectra Image (SI) with O-K (532eV) and Nb-L edges (2371eV) were collected in STEM mode at 300keV with convergence semi-angle 8.7 mrad and collection semi-angle of 19 mrad. The quantification procedure was done by subtracting power law background and integrating cross-section based on Hartree-Slater model from Gatan GMS software.

Figure 1a shows the relative O composition in the NbO_2 and Nb_2O_5 blanket films (~200 nm thick) deposited on a Si/SiO_2 substrate. Nb_2O_5 crystalline powder was used to correct the instrument factor for EELS quantification as shown in Table I. The average of measured value in Nb_2O_5 powder is 60.8% and has been corrected to be 71.4% after multiply an instrument factor of 1.174. The line profiles in the films show the average of 58.7 O% in NbO_2 and 63.4% in Nb_2O_5 after the correction, with higher O composition on the surface due to expose to the air after deposition. The lower O composition in the film than the desired is due to the preferential evaporation of oxygen. Figure 2 shows the NbO_2 resistive switching device with TiN bottom electron. The color elemental mapping was processed from STEM/EELS SI. The line profiles of elements Nb, Cr, O, Pt, and Ti were analyzed and consistent with the nominal thickness. The NbO_2 layer shows similar O deficiency

compared with reference blanked Nb oxide films. The top surface of NbO_2 shows higher O content is due to adjacent Ti_4O_7 layer with higher O content.

In conclusion, we have done quantitative EELS analysis on the O content in the sputtered NbO_2 and Nb_2O_5. These results are important reference to study the dynamic materials evolution during heating and biasing with the advanced *in situ* TEM techniques. Preliminary *in situ* TEM study shows that there is an amorphous-to-crystalline transition at 550ºC in the NbO_2 film.

References:

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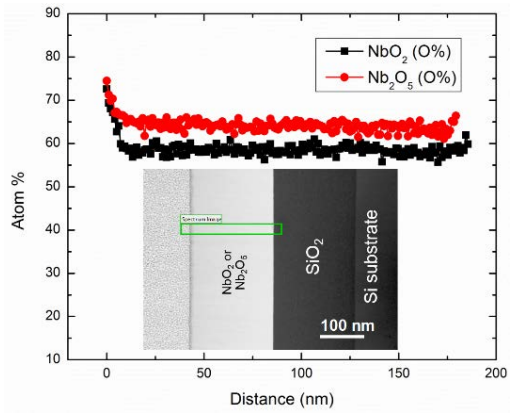

	Nominal O%	Measured O%	O% After correction	*x* in NbO_x
NbO_2	0.667	0.5±0.01	0.587	1.42
Nb_2O_5	0.714	0.54±0.01	0.634	1.73
Nb_2O_5 crystals	0.714	0.608±0.01	0.714	2.5

Table I. EELS quantification results for NbO_2, Nb_2O_5 film, and Nb_2O_5 standard powders from Sigma-Aldrich.

FIG. 1 Relative oxygen composition across NbO_2 and Nb_2O_5 film with one cross-sectional STEM DF image of reference film in the inset.

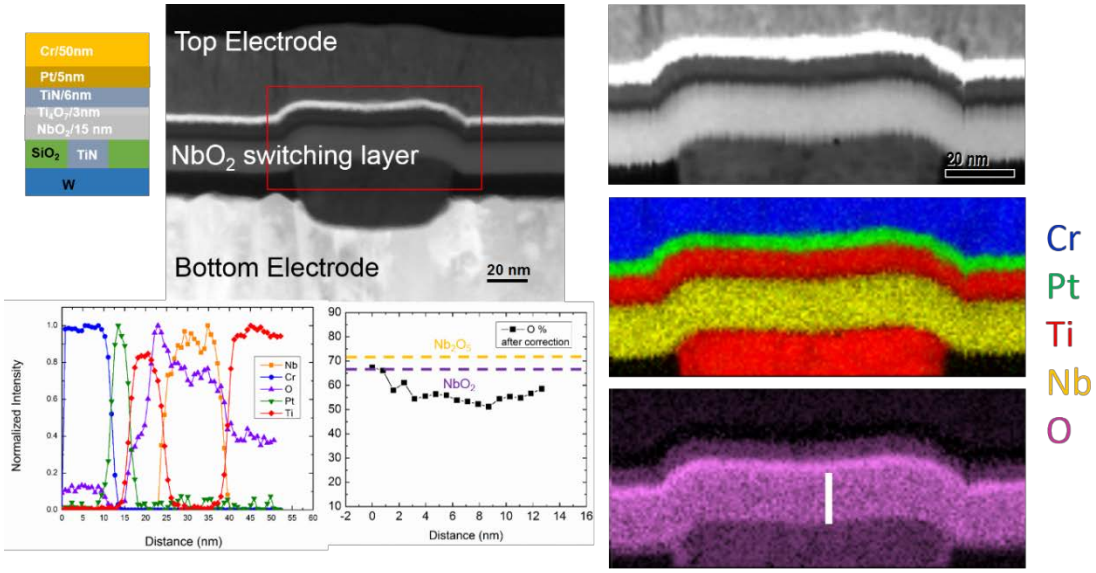

FIG. 2 (a) Cross-sectional STEM Z-contrast image of device TE/NbO_2/BE; (b) elemental color mapping from EELS spectrum image, (c) line profile across the device, (d) relative oxygen composition across NbO_2 layer.