Microsc. Microanal. 28 (Suppl 1), 2022
doi:10.1017/S1431927622007954

STEM-EELS Analysis of Niobium Oxide Multilayer Films for High Temperature Memristor Devices

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Neuromorphic computing relies on electronic components that mimic the biochemical “spike” action of neurons in the human nervous system. Memristor devices are being developed as a key component to these systems, where the device may be switched between multiple conduction states dependent on external factors [1]. NbO_2 is a promising phase-change material that has recently been demonstrated in memristor prototypes [2-4], having a reversible transition between an insulating rutile crystal structure (R-NbO_2; $E_g = 1$ eV) and a conducting tetragonal structure (T-NbO_2) [5]. One benefit of NbO_2-based memristors is that they operate at high temperatures, around the insulator-to-metal phase transition temperature of ~800 °C. Transitionable NbO_2 films with precise stoichiometric layering have been achieved with ALD deposition [4] but depends on careful control of growth and annealing conditions. NbO_x can crystallize into multiple phases [6], and microscopy techniques like scanning-transmission electron microscopy (STEM) can help to identify and characterize which phases form during growth and annealing processes. Here we investigate the stoichiometry and electronic structure of ALD-deposited NbO_x thin films annealed at different temperatures in order to understand the phase transitions that occur to reach the final NbO_2 device material.

Three thin films were investigated: (1) as-deposited amorphous NbO_x, (2) NbO_2 fully annealed at 1000 °C for 20 min., and (3) NbO_x partially annealed at 800 °C for 20 min. The partially annealed film contains islands of crystalline material throughout (Figure 1A). A previous electron diffraction study of such films identified multiple crystalline Nb_2O_5 and NbO_2 phases within partially annealed samples, indicating a complex sequence of phase transitions from amorphous $Nb_2O_5 \rightarrow$ T-$Nb_2O_5 \rightarrow$ B-$Nb_2O_5 \rightarrow$ R-$NbO_2 \rightarrow$ T-NbO_2 [7]. Electron transparent lamella for STEM were prepared by focused ion beam (FIB) liftout with a Thermo Fisher Helios G3 (Figure 1B). For our films, we applied energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) with an aberration-corrected Nion UltraSTEM 200-X at NRL to identify and map the distribution of phases across the three films. The microscope was operated at 200 keV, and Gatan Enfinium and Bruker X-Flash 100 spectrometers were used to acquire EELS and EDS maps, respectively. EELS data were acquired at a 0.05 eV/channel dispersion. Using Gatan GMS 3.4 software, the spectrum images were noise filtered with principal component analysis and distribution maps of characteristic phase spectra were generated by multiple linear least squares (MLLS) fitting.

High-angle annular dark field (HAADF) imaging and EDS mapping show the bulk composition of the NbO_x thin film and SiO_2/Si substrate (Figure 1C,D). O K-edge EELS spectrum images reveal laminar structural changes in the NbO_x thin films, representative of different configurations and connections between NbO_6 octahedra. Taking the partially annealed sample as an example, three major layers can be distinguished within one of the island features (Figure 2). The top 16 nm of the film show an EELS spectrum similar to that of the high-temperature monoclinic H-Nb_2O_5 phase, while the lower 32 nm of the film show a spectrum similar to that of tetragonal NbO_2 [8]. It should be noted that both this high temperature H-Nb_2O_5 phase and the medium temperature B-Nb_2O_5 phase identified previously in these films by [7] will have nearly identical O K-edge spectra, since both crystal structures are composed solely of corner-sharing NbO_6 octahedra. The center of the film shows an EELS spectrum that does not match any library spectrum, but is likely either amorphous Nb_2O_5 or one of the intermediate, crystalline NbO_x phases for which a library spectrum does not yet exist. These data show progressive reduction of Nb atoms during annealing beginning at the bottom of the film, although it is not yet clear to what extent initial heterogeneities in Nb:O in the amorphous as-deposited ALD film affect this reduction.

Future work will also involve depth profiling with sputter x-ray photoelectron spectroscopy (XPS) and identification of dopants and impurities with atom-probe tomography (APT). The combination of these three analytical techniques can provide a more complete picture of the complex phase assemblages that may influence the manufacture and performance of NbO_x-based memristor devices.

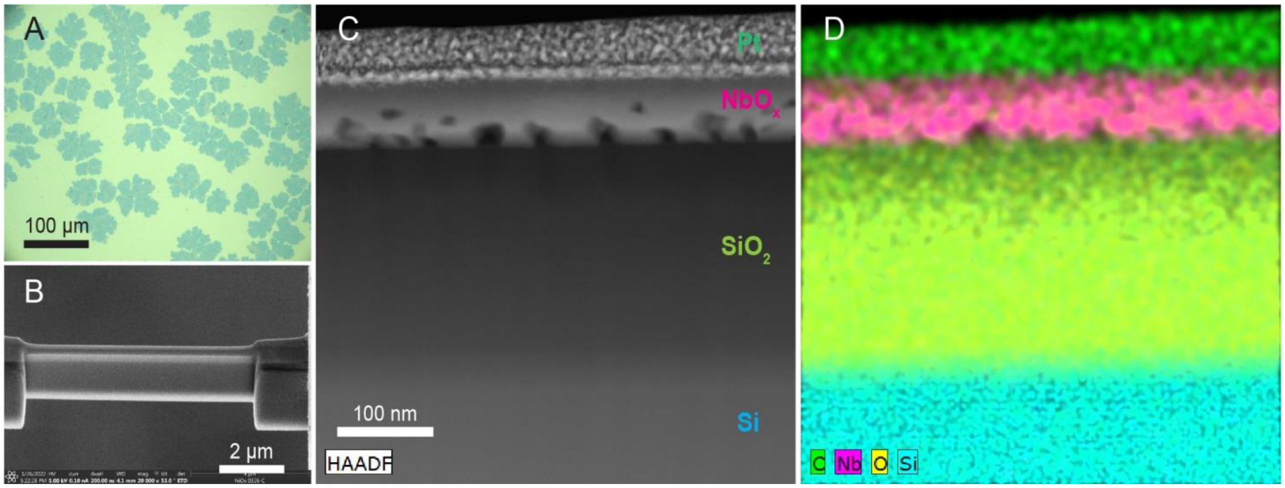

Figure 1. (A) Optical image of partially-annealed NbO_x ALD thin film. (B) FIB liftout. (C) High-angle annular dark-field (HAADF) image of a 70 nm, partially-annealed NbO_x film and underlying substrates. (D) STEM-EDS mapping to identify each major phase.

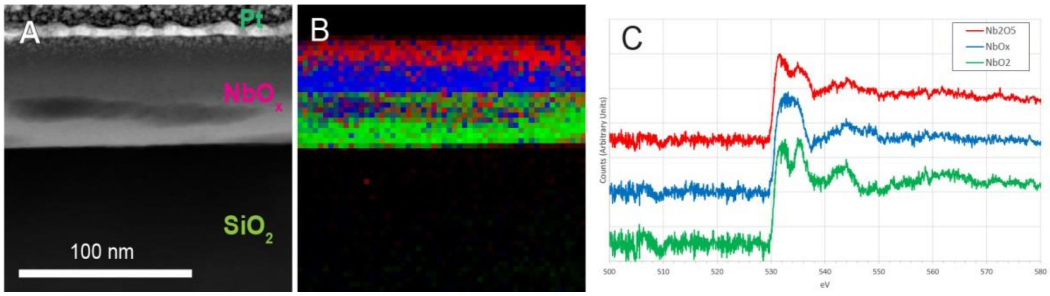

Figure 2. (A) HAADF image of partially-annealed NbO_x thin film. (B) Result of MLLS fitting from O K-edge EELS spectrum image. (C) Three MLLS end-members present in the NbO_x film used for fitting.

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