

## TEM and EELS Analysis of Anodized Nb<sub>2</sub>O<sub>5</sub>: Stoichiometry and Field-Induced Crystallization

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The push towards miniaturization in the electronics industry is driving the development of capacitors with the ability to store large amounts of energy in a smaller volumes. In order to diminish the volume of a capacitor, it is necessary to dramatically increase the charge per gram (CV/g) which is typically accomplished by creating surface area. Porous solid electrolytic capacitors manufactured from sintered powders of tantalum (Ta), niobium (Nb) and niobium oxide (NbO), are next generation products for low voltage, high capacitance applications. As Ta and Nb are both valve metals, when anodized they (as well as NbO, which has highly metallic properties) form an amorphous dielectric pentoxide (Ta<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub>) on the order to ten to hundreds of nanometers thick (Figure 1A). One of the major issues with miniaturization though is that at these length scales and geometries, materials properties can vary drastically from their bulk counterparts. In order to understand the materials in these new products, transmission electron microscopy (TEM) must be utilized. This study focuses on the study of capacitors produced from Nb and NbO anodes.

As mentioned above, increasing surface area per volume is an optimal manner in which to miniaturize capacitors, but an increase in surface area must be accompanied by very sharp interfaces. Solid electrolytic capacitors produced from Nb and NbO anodes have nearly atomically flat interfaces, as seen in the high-angle annular darkfield (HAADF) image in Figure 1B. Using HRTEM and HAADF we have studied interfaces in capacitors formed from Nb and NbO at formation voltages of 10, 20 and 65 V<sub>f</sub>, and have not observed any flaws (such as delimitation or cracking) which could lead to failure of the part. Another physical defect that can increase the leakage characteristics is the crystallization of the amorphous pentoxide. We have been using TEM to study field-induced crystallization and have been able to identify anodization regimes under which it occurs. Interestingly, the crystallization (Figure 1C) occurs within the interior of the dielectric layer and appears to be homogeneously nucleated. Comparing both the structure and EELS analysis of the crystalline defects, they have been identified as the monoclinic pentoxide with stoichiometry resembling that of the amorphous dielectric.

The stoichiometry of the dielectric is also a critical issue which can lead to large leakage currents. In order to perform EELS quantification, it was imperative that the shape of each stable niobium oxide spectrum and accuracy of theoretical partial scattering cross-sections be determined (Figure 2). Measuring Nb concentrations at integration windows of 25 eV increments, it was shown that above 130 eV wide measurements the cross-sections (O-K, Hydrogenic and Nb-M, Hartree-Slater) accurately predicted the stoichiometry for each stable oxide. Using STEM to gain high spatial resolution (Figure 3A), EELS measurements were measured across the dielectric layer of a Nb anode capacitor. By measuring the Nb concentration, we demonstrate that there is no concentration gradient across the dielectric layer. These data show the capabilities of TEM to fully characterize solid electrolytic capacitors for research into next generation technologies.

Figures:

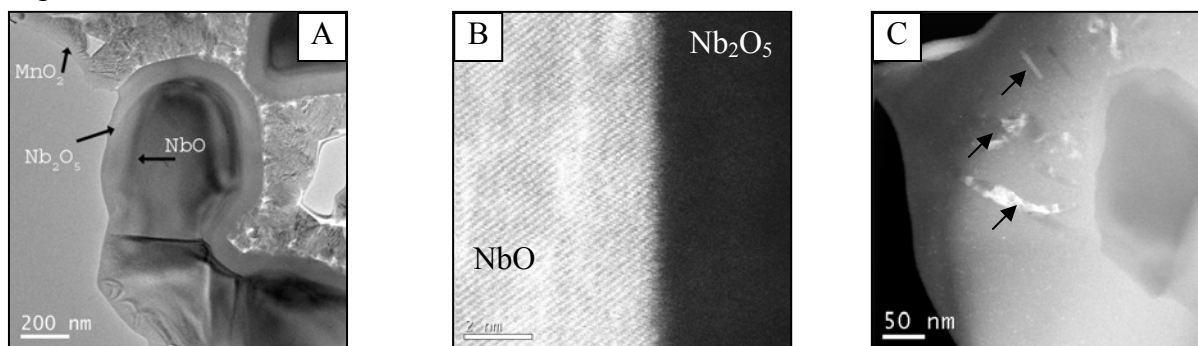


Figure 1: Transmission electron micrographs of niobium oxide (NbO) solid electrolytic capacitors. A. Bright-field image of finished NbO capacitor. Bar = 200 nm. B. High-angle annular darkfield (HAADF) image of the sharp NbO (anode)/Nb<sub>2</sub>O<sub>5</sub> (dielectric) interface. Bar = 2 nm. C. DF image of crystalline defects that have nucleated in the pentoxide dielectric layer (Arrows). Bar = 50 nm.

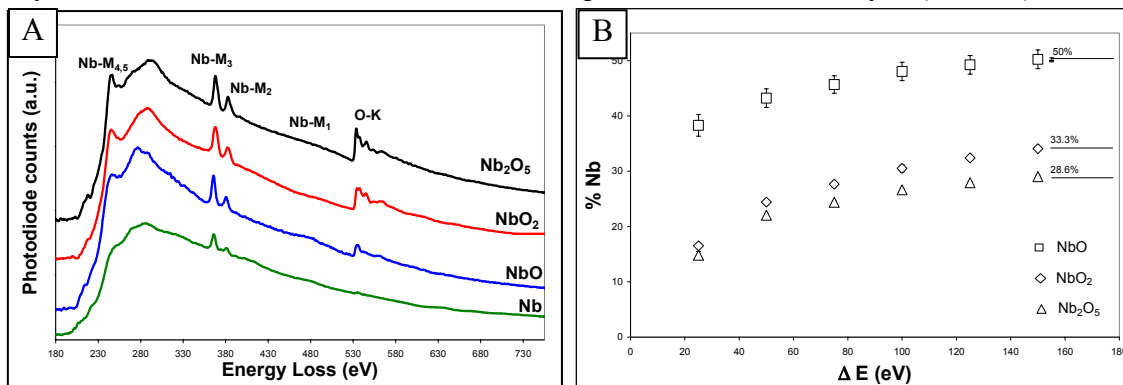


Figure 2: Electron energy loss spectroscopy (EELS) data taken from powder standards of niobium (Nb) and stable niobium oxide compounds. A. Core-loss data illustrating the differences between Nb metal and its stable oxides. B. EELS quantification of each oxide spectra showing that the theoretical partial scattering cross-sections (O-K, Hydrogenic, Nb-M Hartree-Slater) accurately predict stoichiometry at integration windows greater than 130 eV.

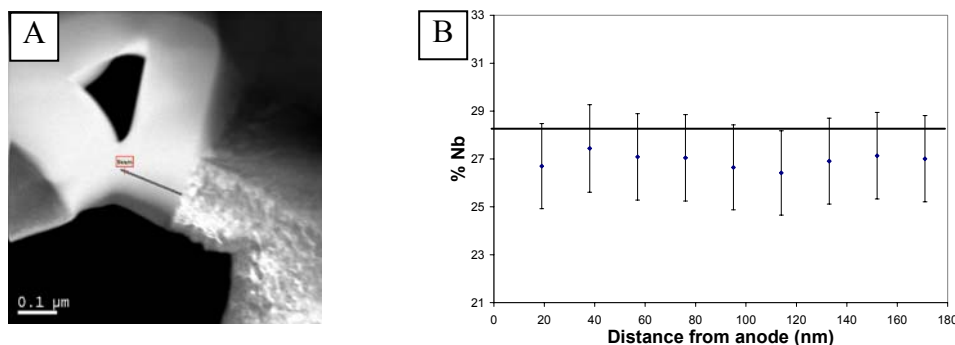


Figure 3: Analytical analysis of the dielectric layer in a Nb (anode) solid electrolytic capacitor. A. STEM DF image of the capacitor, where the line indicates where EELS data was taken across the dielectric layer. Bar = 100 nm. B. Plot of % Nb as measured as distance from the anode, illustrating that the dielectric layer is Nb<sub>2</sub>O<sub>5</sub> across the dielectric. Horizontal line represents the Nb concentration of stoichiometric Nb<sub>2</sub>O<sub>5</sub>.