

Interfacial reactions between Ni and BaTiO₃: An Analytical Transmission Electron Microscopy Study

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The structure and chemistry of metal-ceramic interfaces are of immense technological importance in multilayer ceramic capacitors (MLCCs), as they can profoundly affect physical and electrical properties of the devices. Only recently it is becoming fully appreciated that interface structure can be a strong function of local oxygen activity [1]. Since it is important to have a high interfacial Schottky barrier to prevent electron injection into the dielectric layer, the chemistry of the electrode interface is of critical importance to the electrical behaviors of the capacitor. In this work we study the chemical stability of Ni-BaTiO₃ interfaces processed in heavily reducing atmospheres, which are typical of commercial processes.

The Ni-BaTiO₃ MLCCs were fabricated by co-firing Ni internal electrodes with BaTiO₃ dielectric layers at ~ 1300 °C in a PO₂ of ~ 10⁻¹⁰ atm to avoid Ni oxidation. TEM observations of thinned specimens were performed using a JEOL 2010F transmission electron microscope equipped with a field-emission gun operated at 200 kV. Electron energy-loss spectroscopy (EELS) was performed with a Gatan Enfina parallel electron energy-loss spectrometer attached to the JEOL 2010F microscope. EEL spectra were recorded in TEM-diffraction mode with a collection angle of 14 mrad, and analyzed with Gatan Digital Micrograph software.

The formation of interfacial layers between Ni and BaTiO₃ were identified by high-resolution TEM (HRTEM) observations coupled with EELS analysis. Figure 1 (a) shows a typical HRTEM image of the Ni-BaTiO₃ interface. The interfacial layer is noted by arrow pairs. Shown in figure 1 (b) are electron energy-loss spectra obtained from BaTiO₃ (spectrum 1), interfacial layer (spectrum 2), and Ni electrode (spectrum 3), respectively. As expected, Ti L_{2,3}, O K and Ba M_{4,5} edges are present in the spectrum obtained from BaTiO₃. In the spectrum obtained from the interfacial region (spectrum 2), the edges of Ti L_{2,3}, Ba M_{4,5} and Ni L_{2,3} are found. The metallic nature of Ni electrode is determined by the shape of L_{2,3} edges [2]. The fine structures of Ni L_{2,3} edges in spectrum 2 and spectrum 3 are identical, indicating that Ni within the interfacial layers is also metallic. The chemical composition of the interfacial layer is qualitatively determined as 8.9 at. % of Ti, 88.7 at. % of Ni, and 2.4 at. % of Ba.

Figure 2(a) shows a bright field image of BaTiO₃ grains adjacent to a Ni electrode. The series of EEL spectra is obtained from positions numbered as 1-10 in grains #1-3. The fine structures of the Ti L_{2,3} and O K edges vary as a function of distance from the Ni electrode and the changes are highlighted by the selected spectra shown in figure 2 (b). The calculated stoichiometry as a function of distance from the Ni electrode is shown in figure 2 (c). The lowest oxygen content is found in the grain region near the Ni electrode and the oxygen content increases gradually away from the Ni electrode. Eventually the oxygen concentration in the BaTiO₃ lattice becomes uniform when the distance from the electrode is larger than 0.5 μm. The formation of the interfacial layer is associated with the extreme low oxygen concentration in BaTiO₃ grain regions next to the Ni electrodes.

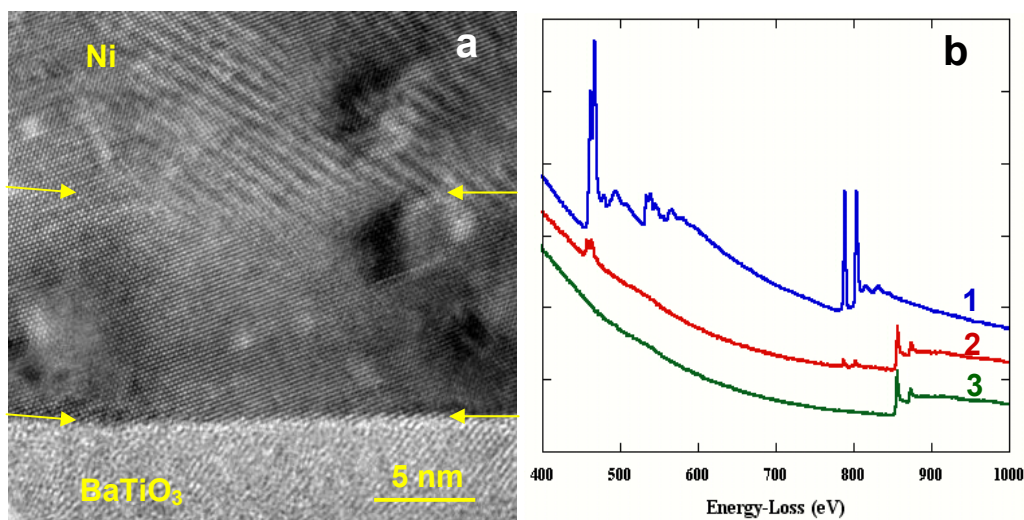


Figure 1. (a) HRTEM image of Ni and BaTiO₃ showing the formation of interfacial layer, (b) EEL spectra obtained from BaTiO₃, interfacial layer, and Ni. Ni in the interfacial layer is of metallic.

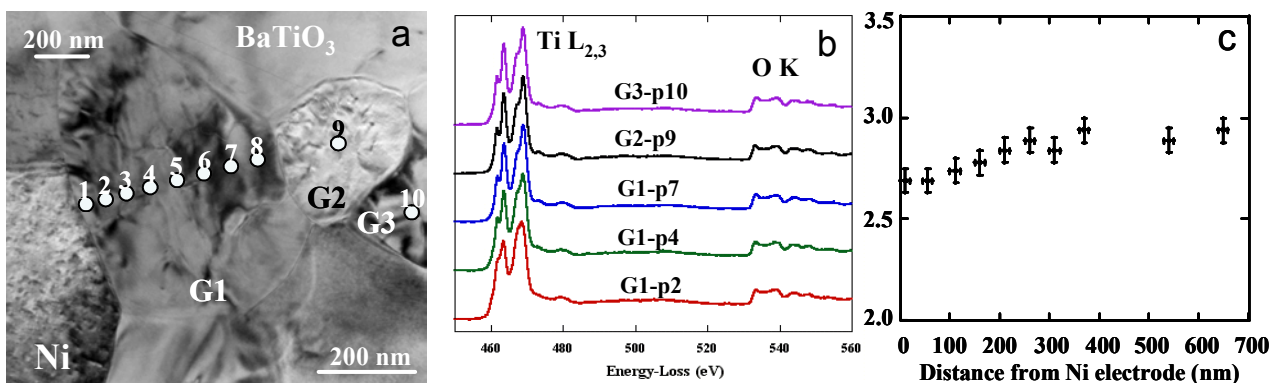


Figure 2. (a) Bright field image of BaTiO₃ grains adjacent to a Ni electrode. (b) EEL spectra obtained from different positions in the BaTiO₃ grains. (c) The calculated stoichiometry ($3-\delta$) as a function of distance from the Ni electrode.

Acknowledgments

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References:

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