Sample Preparation Technique with Electric Nano-Shield Films for In-Situ Electron Holography of Battery Materials

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Electron holography is one of the phase imaging TEM techniques to quantitatively observe electric and magnetic potential distributions, and has been widely used for functional materials. One of the authors applied the electron holography to all-solid-state Li-ion batteries [1,2], in order to visualize the local potential changes under the battery reactions in a TEM. The potential values in the positive electrode and the negative electrode changed as the charge/discharge processes proceeded. *In situ* spatially-resolved EELS measurement was also applied to visualize the Li distribution in the negative electrode, and the Li profile was similar to the potential observed by the electron holography [3]. However, there is still a point that the explanation is not enough yet, that is the micron-order width of electric double layer at the electrode/solid-electrolyte interfaces. One of us have inspected the detail using a simple capacitor model and have reported that the electric field 3-dimensionally leaked from the biased TEM sample covered the real potential distribution formed in the battery [4]. This probably influences on all phase imaging techniques, not only electron holography but also recent techniques using STEM. Here, we propose a unique sample preparation technique to shield the leaking field from biased TEM samples and show the effect on the phase measurement [5].

We prepared a model sample, Cu/solid-electrolyte/Cu. A 50-µm-thick $Li_{1+x+y}Al_x(Ti, Ge)_{2-x}Si_yP_{3-y}O_{12}$ (LASGTP) sheet was used as the solid-electrolyte. Using an FIB system, we prepared the TEM sample to apply the voltage in a TEM. In this case, when an external voltage is applied between the Cu electrodes, the leaking field spreads 3-dimensionally as illustrated in Fig. 1(a), as a result, the electrons are modulated by not only the potential inside the sample but also the leaking potential outside the sample. To supress the leakage, we coated thin AlO_x insulator and carbon films (nano-shield films) on the TEM sample, and then the carbon film was grounded as shown in Fig. 1(b). Note that the carbon film does not contact with the biased Cu electrode, thus we can apply the voltage to the Cu/LASGTP/Cu sample inside the nano-shield films. We performed the electron holography with applying 2V to one-side of the Cu electrodes. Figures 2(a) and 2(b) show the reconstructed phase images around the grounded-Cu/LASGTP interfaces without and with the nano-shield films, respectively, where the other side of the Cu was biased. In Fig. 2(b), the finer potential distribution due to the inner potential change of the materials was observed in the Cu and LASGTP. The nano-shield films suppressed 99% of the leakage from the sample. The films would contribute to precise analysis of the phase measurement under the biased condition.

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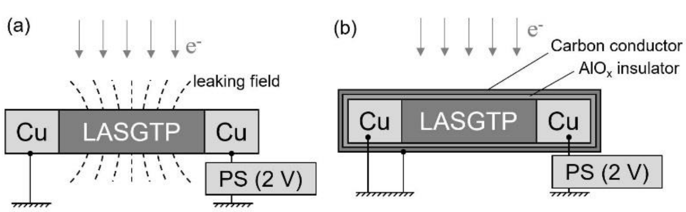

Fig. 1 Illustrations of cross-sectional Cu/LASGTP/Cu sample (a) without and (b) with the nano-shielding films.

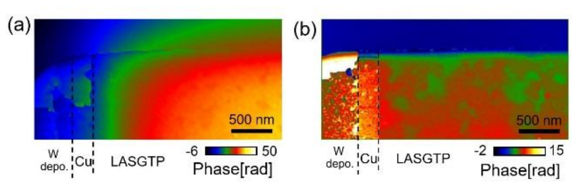

Fig. 2 Reconstructed phase images around the Cu/LASGTP interfaces (a) without and (b) with the nano-shielding films.