doi:10.1017/S1431927614003109
Microsc. Microanal. 20 (Suppl 3), 2014

Investigation of Effect of Electron Irradiation on Ionic Liquid Using Electron Holography

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Ionic liquid (IL) has various attractive features and attract a great attention as new functional materials for applications. Recently, it has been reported that ILs were applied in scanning electron microscopic (SEM) observation because they do not vaporized even in vacuum condition [1]. Moreover, they can be also used as solvents and supporting films of nanoparticles for transmission electron microscopic (TEM) observation. Technique using ILs is useful for new electron microscopic observation and is expected to be applied widely in various filed. Before utilizing them for electron microscope applications, we need to examine their charging effect under electron irradiation. We employed electron holography [2] to characterize their charging effect. Electron holography is a unique technique to directly observe electromagnetic fields and quantitatively analyze the electrostatic potential distribution with high spatial and phase resolution. In the present study, we investigated the changes of the electrostatic potential around ILs under electron irradiation and its surface state change from liquid to solid.

We used an IL of 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF_4) (KANTO CHEMICAL Co., Inc.). IL droplet was mounted on a platinum (Pt) wire with 50 μm in diameter fabricated using a focused ion beam (FIB)-SEM (NB5000, Hitachi High-Technologies Co.) as shown in Fig. 1(a). The IL droplet was subjected to electron irradiation during *in situ* observation. Secondary electrons and/or x-rays emitted from the irradiated Pt wire could affect the electrostatic potential of the IL. We placed the wire within the shadow of the condenser aperture (mask), as shown Fig. 1(b), which enabled us to investigate the charging effect of the IL itself induced by the electron irradiation. After irradiation for 180 min., we directly confirmed the IL surface state by using a fine tungsten probe in the FIB-SEM. The electron holographic observation was performed using a Hitachi HF-3300X TEM (Hitachi High-Technologies Co.) equipped with a cold field-emission gun operated at 300 kV. Holograms were acquired using a slow-scan charge-coupled-device (CCD) camera with 4096x4096 pixels (UltraScan™ 4000, Gatan Inc.). ELFIN/ViewField ver. 2.0.0 software (ELF Co.) was used for simulating the electrostatic potential analysis. The simulations were performed on the basis of Maxwell's equations.

Figure 2(a) shows the temporal changes in the reconstructed phase images for 300 keV electron irradiation with a flux of $2x10^{17}$ e/m^2s. These images represent the electrostatic potential distribution outside of the IL droplet. The electrostatic potential distribution around the IL can be observed even at the initial observation. The density of the contour lines in the reconstructed phase images increased with irradiation time. That result indicates that the IL charging due to electron irradiation increases with time. Figure 2(b) shows the simulated phase images when the electrostatic potential of the IL surface was assumed to be 0.09 V, 0.14 V, and 0.21 V. The simulation results agree rather well with the experimental ones. Using these simulation results, we could convert the phase shift measured in experimental phase images into electrostatic potential of the IL surface. After electron irradiation of 180 minutes, TEM observation can be performed well because the amount of charge is so small. However, it was found that the IL surface changed from liquid to a solid state. It is reasonable that the solidification of the IL is related to an increase in the electrostatic potential due to the charging effect. Electron holography provides an indication of the IL phase change associated with the charging effect during electron irradiation.

In conclusion, *in situ* observation with electron holography successfully revealed the temporal change in the IL electrostatic potential distribution with a transform from liquid to a solid state due to electron irradiation. It is useful tool for evaluating the properties of ILs and broadening their functionalities toward application.

References:

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[3]The authors acknowledge to Dr. E. Nakazawa and Dr. T. Sato of Hitachi High-Technologies Co. for providing the ionic liquid samples and giving their fruitful comments. This research was supported by the grant from the Japan Society for the Promotion of Science (JSPS) through the “Funding Program for World-Leading innovative R&D on Science and Technology (FIRST program),” initiated by the Council for Science and Technology Policy (CSTP).

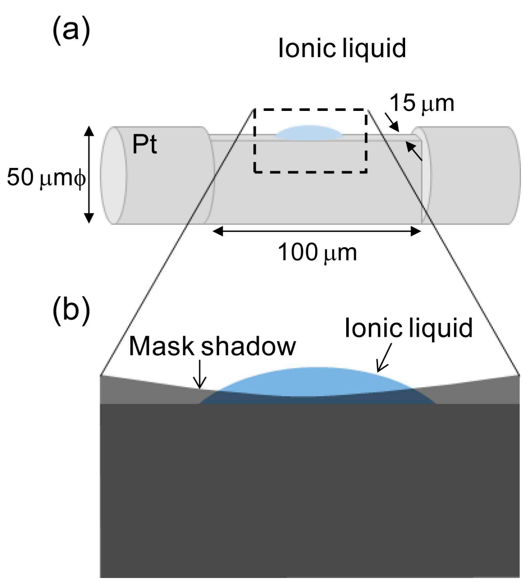

Figure 1. Schematic illustrations of (a) experimental setting and (b) TEM observation.

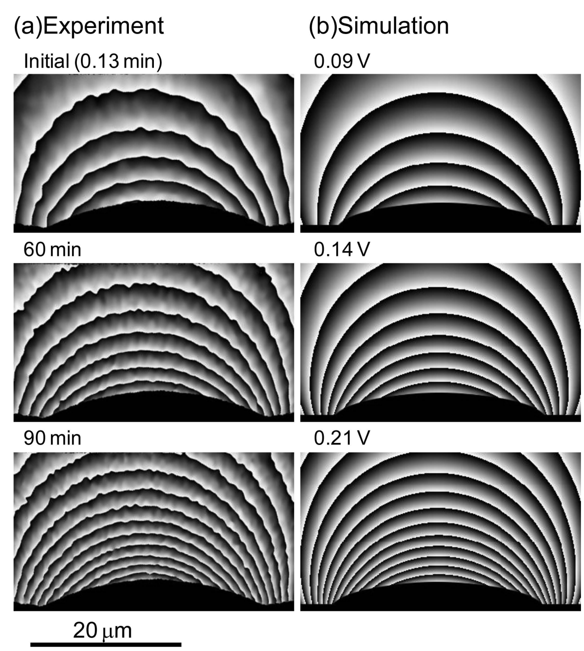

Figure 2. (a) Temporal changes in reconstructed phase images for 300 keV electrons irradiation with a flux of 2×10^{17} e/m^{2}s for 0.13 minutes, 60 minutes, and 90 minutes. (b) Simulation of reconstructed phase images assuming the electric potential of ionic liquid at 0.09 V, 0.14 V, and 0.21 V. Phase was wrapped by modulo operation in with divisor of 2π. Each phase gradient from black to black indicate phase shift of 2π.

https://doi.org/10.1017/S1431927614003109 Published online by Cambridge University Press