MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2015A0054 実験課題名 Title of experiment Neutron reflectivity measurements on the ionic multilayer structures at ionic liquid surface 実験責任者名 Name of principal investigator Naoya Nishi 所属 Affiliation Kyoto University	装置責任者 Name of responsible person Norifumi Yamada 装置名 Name of Instrument/（BL No.） BL16 実施日 Date of Experiment 2016.4.23 9:00 - 4.26 9:00

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Four ionic liquids were used as samples:

[C4mim][FSA] ($C_8H_{15}F_2N_3O_4S_2$, liquid)

[C4mim$_{0.4}$Li$_{0.6}$][FSA] (($C_8H_{15}N_2)_{0.4}Li_{0.6}F_2NO_4S_2$, liquid)

[THTDP][C4C4N] ($C_{40}H_{68}F_{18}NO_4PS_2$, liquid)

[THTDP][PFPB] ($C_{56}H_{68}BF_{20}P$, liquid)

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Nb film on the polished surface of a Si substrate was used as conductive electrode film. The surface of the electrode film was covered by an ionic liquid (IL). The IL was sandwiched by the electrode film and another electrode film formed on the rough (as-sliced) surface of a Si wafer, the latter of which acts as a counter electrode. Two sheets of PTFE membrane are also sandwiched as a spacer and a Ag foil was inserted between the sheets as a reference electrode. Neutron beams were irradiated from the edge of the Si substrate to the Si/Nb/IL interface. The reflected neutron beams from the interface were measured.

Before going to the buried Si/Nb/IL interface that we are interested in, we measured neutron reflectivity at Si/Nb/air interface in order to investigate the characteristics of the Nb film. The reflectivity profiles (logR vs Q plot where R is the reflectivity and Q is the surface normal component of the scattering vector) showed fringes whose period reflects the thickness of the Nb film (36 nm). The profiles were well fitted with the two-box model. The fitting result indicates that the scattering length density (SLD) increases at the surface of the film with a thickness of 8 nm, suggesting that the Nb film is oxidized at the surface.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

For the results of the buried Si/Nb/IL interface in this document, we focus on [THTDP][PFPB], an IL that showed the most pronounced behavior.

For the buried Si/Nb/[THTDP][PFPB] interface, the reflectivity profiles also showed fringes but the shape of the profiles depended on the electrode potential. With more positive potentials, the fringes became deeper. This change in the fringe depth reflects the change in the local concentrations of the IL-ions at Nb/IL interface.

Each reflectivity profile was fitted with a box model containing an interfacial layer where the concentrations of IL-ions and therefore SLD are different from those in bulk. From the fitting, it was found that anions (cations) are accumulated to the positively-charged (negatively-charged) electrode interface. Furthermore, the thickness of the interfacial layer depends on the potentials. At negatively-charged potentials when cations are accumulated, the layer thickness is the same as average diameters of the IL-cation and IL-anion, meaning that cation-rich ionic monolayer is formed at the interface. On the other hand, at positively-charged potentials, the layer is rather thick and composed of 2 to 4 anion-rich ionic layers depending on the potentials. This difference between the behavior of the IL-cation and the IL-anion at the interface is probably caused by the nature of the ions; THTDP is a soft cation having flexible four alkyl chains whereas PFPB anion is a hard anion with rigid perfluorophenyl moieties.