MLF Experimental Report	提出日 Date of Report 2017/4/21
課題番号 Project No. 2016A0263 実験課題名 Title of experiment Moisture Accumulates and Aggregation Structure at the Buried Polymer/Metal Interface 実験責任者名 Name of principal investigator 藤井義久 Yoshihisa Fujii 所属 Affiliation 三重大学 Department of Chemistry for Materials, Mie University	装置責任者 Name of responsible person 山田悟史 Norifumi Yamada 装置名 Name of Instrument/（BL No.） SOFIA / BL16 実施日 Date of Experiment 2016/4/1– 2017/01/31

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.

epoxy adhesive
(DENATITE 2204, Nagase Chemtex Corp., Osaka, Japan)
curing condition: 30 °C for 24 hours

Deuterated water (D_2O)

sputtered Copper (Cu)

Silicon substrate (Si)

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.

Experimental method

The adhesive epoxy resin layer was coated onto thick silicon blocks with sputtered copper layer. The silicon block with the size of 40 mm × 40 mm × 7 mm was used after piranha treatment to remove any organic contaminants. Then, the ca. 50-nm thick copper layer was deposited by sputtered method on the Si substrate. Finally, the epoxy adhesive (DENATITE 2204, Nagase Chemtex Corp., Osaka, Japan, curing condition: 30 °C for 24 hours) was coated on Si with Cu layer.

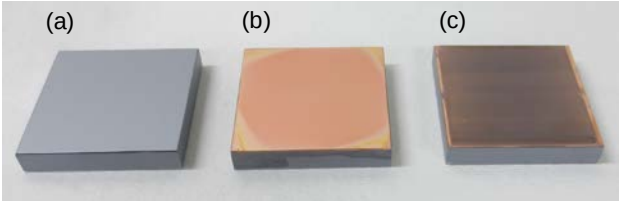

Figure 1. Photo image of each samples. (a)Si, (b)Si with Cu layer, and (c) adhesive coated on Si with Cu layer.

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

The thickness of the adhesive layer is controlled to be approximately 46 μm which is definitely “not” suitable for NR measurements but close to the using state with an actual adhesive that is actually used. To evaluate the intrinsic swollen structures of these samples, films are aged in deuterium oxide (D_2O) for a given time. Density profiles of the films along the direction normal to the surface in contact with deuterated liquids are examined by NR measurements. The neutron beams are guided into the film from the silicon side, and the reflected beam is detected under the specular condition.

Figure 2 (a, d) show the reflectivity curves as a function of the scattering vector ($q = (4\pi/\lambda)\sin\theta$, where λ and θ are the wave length and the incident angles of the neutron beams, respectively) for Cu, denatite and denatite in D_2O. The open symbols denote the experimental data, and the solid curves were fit curves calculated from the scattering length density (b/V) profiles in Figure 2 (b). Since the solid curves in panel (a) are in good agreement with the experimental data, it is most likely that the model (b/V) profiles drawn panel (b) in Figure 2 would reflect the density profiles of the films. The (b/V) values for sputtered Cu layer was 6.43×10^{-4} nm^{-2} which was slightly lower than that of the bulk Cu metal (6.54×10^{-4} nm^{-2}). This difference indicates that the density of sputtered Cu layer was lower than that of Cu metal.

The reflectivity curves marked as red and blue open symbols in Figure 2 (d) obtained from epoxy adhesive in air and in water, respectively. What is so surprising is that a clear difference exists among both curves, nevertheless the adhesive layers were extremely thick which is not suitable for reflectometry at all.

It might be concluded that this reason is inserting the copper layer enhance the (b/V) change near the copper and adhesive interface. To discuss more details, the new fitting model will be proposed in near future.

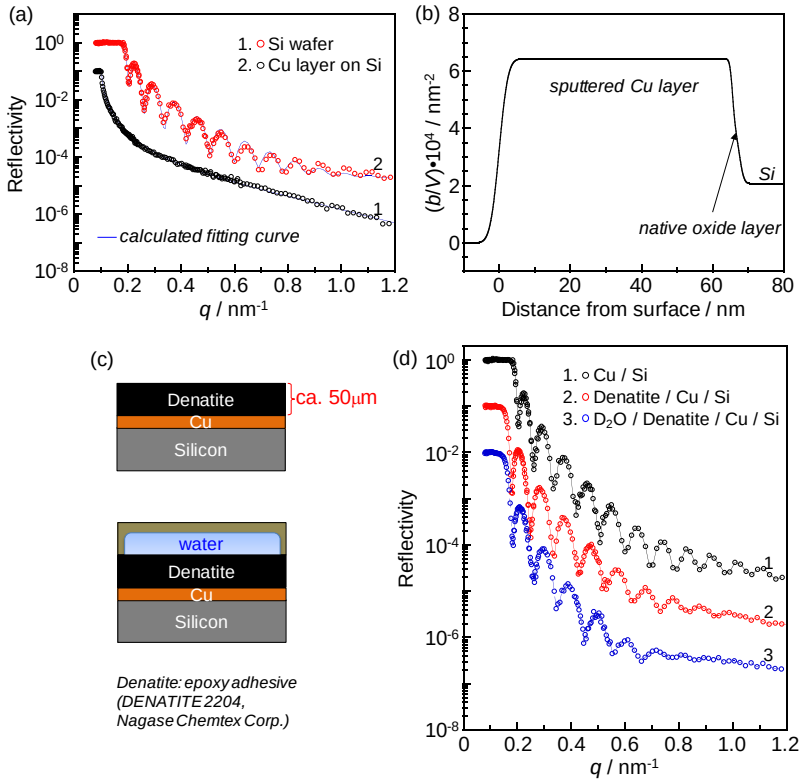

Figure 2. Neutron reflectivity for (a) Si and Cu layer on Si. Open symbols depict experimental data, and solid lines represent the reflectivity calculated on the basis of the scattering length density (b/V) profiles (b), respectively. (c) Schematic illustration of the model used for the film. (d) Neutron reflectivity for Cu, denatite and denatite in D_2O