MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2015A0105 実験課題名 Title of experiment Porosity Control of Porous Diamond-like Carbon Membranes 実験責任者名 Name of principal investigator 藤井 義久 所属 Affiliation (国)物質・材料研究機構	装置責任者 Name of responsible person 山田悟史 装置名 Name of Instrument/(BL No.) SOFIA / BL16 実施日 Date of Experiment 2015/4/1- 2016/04/30

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.

Name of samples: porous diamond-like carbon (DLC)

Chemical formula: $C_xH_yN_z$

Figure 1 shows the photo image of our porous diamond-like carbon (DLC) membrane floated on water.

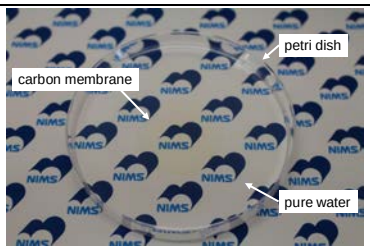

Figure 1. DLC membrane floated on water.

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

Diamond-like carbon DLC membranes are prepared from various precursor gases onto thick silicon blocks with a size of 40 mm × 40 mm × 7 mm by CVD method. The thickness of the membranes in a dried state is controlled to be approximately 60 nm which is appropriate for NR measurements. To evaluate the intrinsic swollen structures of these porous DLC, membranes are aged in deuterium oxide (D_2O) for a given time, which is sufficiently enough to induce contrast change by sorption of deuterated liquids. 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.

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

Results

Figure 2(a, c) show the reflectivity curves as a function of the scattering vector (q = (4π/λ)sinθ, where λ and θ are the wave length and the incident angles of the neutron beams, respectively) for porous DLC films in air (a) and under deuterated water (c). 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) and (d). Since the solid curves in panel (a) and (c) are in good agreement with the experimental data, it is most likely that the model (b/V) profiles drawn panel (b) and (d) in Figure 2 would reflect the density profiles of the films. The (b/V) values for silicon (Si), and native oxide layer (SiO_x) were 2.07×10^{-4} and 4.10×10^{-4}, respectively. The fitting parameters are summarized in Table below. It is noteworthy that the (b/V) value of the DLC film in water was higher than that of the film in air, indicating that water molecules with higher (b/V) value deeply penetrated into the film. Then, the water content of the film was calculated on the basis of (b/V) difference between DLC films measured in air and under water. Surprisingly, the water content in the interior region, namely, the constant density region, of the film was almost 50 vol %. Since the porous film contained water molecules after being immersed in the water, it became slightly thicker than before. However, the thickness increasing from 56.3 to 61.2 nm was only 9%. If the film is in fact swollen by water molecules, the thickness must be increased to conserve the mass of DLC film. It is plausible to assume that above mentioned difference is originated from the pore with sub-nanometer scale if we consider that our DLC film contains the porous structure. Therefore, on the basis of neutron reflectivity measurements, the initial volume fraction of the pore was estimated as almost 40 %. We also evaluated the refractive index of these porous DLC films by using ellipsometry. The value of refractive index of our porous DLC film was reasonable when we take into account the effects of sub-nanometer pores.

In this experiments, we revealed the evidence of the existence of pores and estimated the volume fraction of pores. The filtration properties of these porous DLC films will be discussed in conjugated with above mentioned results.

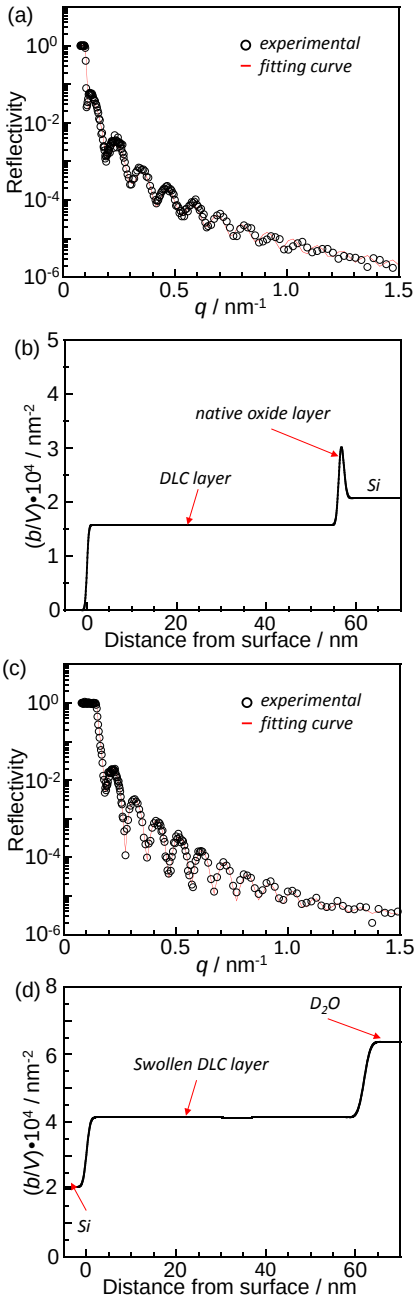

Figure 2. Neutron reflectivity for DLC film in (a) air and (c) deuterated water. Open symbols depict experimental data, and solid lines represent the reflectivity calculated on the basis of the scattering length density (b/V) profiles, respectively.

Table. Parameters Used to Fit Obtained Reflectivity

Curves	in Air		in water	
	thickness / nm	(b/V)•10⁴ / nm^{-2}	thickness / nm	(b/V)•10⁴ / nm^{-2}
Air	-	0	-	6.38
DLC	56.3	1.58	61.2	4.13
SiOx	7.45	4.10	7.45	4.10
Si	-	2.07	-	2.07