Development of a new neutron mirror made of deuterated Diamond-like carbon

Dai SAKURAI, Junsei CHIBA, Takashi INO, Nobunori KAKUSHO, Naokatsu KANEKO, Ryo KATAYAMA, Masaaki KITAGUCHI, Kenji MISHIMA, (Deceased) Suguru MUTO, Kazuhide OZEKI, Yoshichika SEKI, Hirohiko M SHIMIZU, Satoru YAMASHITA, Tamaki YOSHIOKA, Daiki NISHIMURA

Faculty of Science and Technology, Tokyo University of Science, Noda 278-8510, Japan
Department of Physics, Nagoya University, Nagoya 464-8602, Japan
High Energy Accelerator Research Organization, Tsukuba 305-080, Japan
International Center for Elementary Particle Physics, The University of Tokyo, Tokyo 113-0033, Japan
School of Science, The University of Tokyo, Tokyo 113-0033, Japan
Research Center for Advanced Particle Physics, Kyushu University, Fukuoka 812-8581, Japan
School of Science, Ibaraki University, Hitachi 316-8511, Japan
Institute of Physical and Chemical Research, Wako 351-0198, Japan
Center of Experimental Studies, Nagoya University, Nagoya 464-8602, Japan
E-mail: j6212608@ed.tus.ac.jp

Abstract.
We developed a new neutron mirror made of Diamond-like carbon (DLC). DLC is a film of amorphous carbon that has characteristics of both diamond and graphite. We produced DLC mirrors by ionization deposition method which is one of the chemical vapor deposition (CVD). Generally, DLC made by CVD contains a few tens of percentages of hydrogen. It decreases the Fermi potential of the DLC coating because hydrogen has negative Fermi potential. In order to increase the Fermi potential of the coating, we deuterated the DLC by using deuterated benzene as the source gas. The characteristics of the deuterated DLC(DDLC) coating was evaluated by RBS, ERDA, x-ray reflectivity, AFM. As a result, DDLC coating has 243neV due to deuteration, which is the same level as Ni. The RMS of height of the DDLC was 0.6nm so that the DDLC coating can be applied for a focusing mirror or specular transportation of pulsed neutron. Besides, we also developed Hydrogen/Deuterium DLC multiple layer mirror. So far, 4 layers mirror has been succeeded.

1. Introduction
With the development of various neutron mirrors, neutron application is spreading in particle physics and even industrial society. Therefore, better performance of the neutron mirror is getting more important. Generally, it is said that good neutron mirror has high Fermi potential and low off specular reflectivity. The Fermi potential determined the limit of neutron reflection energy and how much amount of neutrons can be collected. The off-specular reflectivity determined how controllable neutron beam is. Ni alloy is well-used as a neutron mirror because of high Fermi potential and low off-specular reflectivity, for example, NiC, NiV. Other typical
Figure 1. Schematic view of ionized evaporation method. The deposition mechanism is that (a) benzene or deuterated benzene is flowed in the chamber, (b) source gas is ionized by reacting the electron generated from a filament, (c) sputtering ionized benzene to substrate by voltage, $V_b$. Ar gas is used to make substrate’s surface smooth before the deposition of DLC layer.

materials are Fe for a magnetic mirror, Be and Diamond-Like Carbon (DLC) for an alternative to Ni mirror. However, Be is difficult to handle because of poisonous nature. On the other hand, as the technology of making a film of DLC has recently been developing, DLC is gradually getting attention as a new neutron mirror.

The critical energy of the reflection of neutrons is given by the Fermi $V_F$ potential of the material, which is written as

$$V_F = \frac{2\pi \hbar^2}{m_n} \sum_i N_i b_i$$

where $\hbar$ is plank constant divided by $2\pi$, $m_n$ is the neutron mass, $N_i$ is the number density of the elements in the material and $b_i$ is their scattering lengths. Ni mirror has 243meV in this parameter, which is well-known as $m = 1$. The diamond is known as the best potential in all materials. Therefore, it is said that DLC is possible to be a mirror with a large Fermi potential. DLC is a film of amorphous carbon that has characteristics of both diamond and graphite. It can be classified by its three components, which are diamond, graphite and hydrogen. At recent work[1], hydrogen free DLC is selected for a neutron guide. This is because hydrogen has a negative factor of it. However, if all hydrogen is replaced by deuterium, its Fermi potential could be large enough to be applicable because deuterium has a positive potential and the small absorption cross-section for neutrons. We report about fabrication and evaluation of our new DLC (DDLC) neutron mirror, comparing with previous researches[2][3].

2. Fabrication

Techniques for producing diamond coatings have changed dramatically over the last few years. It is now possible to coat large areas with a diamond-like material by means of chemical vapor deposition (CVD).[4] We selected an ionized evaporation method to make a film of DLC, which
is classified as a means of CVD. A reason to select this method is to be able to coat on a large and curve area. Another reason is that it is possible to make DDLC and HDLC multiple layer mirror, if hydrogen benzene and deuterium benzene are used. Hydrocarbon gas, benzene, is used for the source material. DDLC has been deposited by using deuterated benzene as source gas to replace hydrogen in the layer. Figure.1 is schematic view of ionized evaporation method. The deposition mechanism is that (a) benzene or deuterated benzen is flowed in the chamber, (b) source gas is ionized by reacting the electron generated from a filament, (c) supettering ionized benzene to substrate by voltage, $V_b$. Ar gas is used to make substrate's surface smooth before the deposition of DLC layer. Silicon wafers with 3 inch diameter for a substrate. Surface of the wafer was sputtered by argon gas to make its surface smooth before the deposition of DLC layer. The parameters to deposit DLC are voltage to substrate, pressure of source gas, and temperature in the chamber. We produced DLC mirrors with changing these parameters for optimization. The range of parameters were 0 to 3.0kV for substrate voltage $V_b$, 0.001 to 0.1Pa for the pressure of the source gas, and 200$^\circ$C to 400$^\circ$C for the temperature in the chamber.

3. Evaluation of the DDLC mirrors
The characteristics of DDLC as a neutron mirror was evaluated by Rutherford Backscattering Spectrometry (RBS), Elastic Recoil Data Analysis (ERDA), X-Ray Reflectivity (XRR), Atomic Force Microscope (AFM) and Neutron Reflectivity (NR) measurements at J-PARC BL16 SOFIA. From now we report results of these measurements respectively.

3.1. Neutron Reflectivity
Neutron reflectivity (NR) was measured at neutron reflectometer in J-PARC BL16 SOFIA [5]. This is the direct measurement for the Fermi potential. The wavelength of the incident neutron is 0.2 - 0.9nm. By changing two slits, it is able to select the range of neutron beam at a film. The result of typical neutron reflectivity is shown in Figure.2(left). The solid line in this figure is the calculated reflectivity of a layer with the thickness of 75nm and the critical Fermi potential of 243 neV. The filled circle is the reflectivity data of DDLC, the open circle is of HDLC. As shown in this figure, the Fermi potential of DDLC is increased by deuterated, compared with HDLC. Figure.2(right) shows that the correlation between film-forming condition and neutron reflectivity, where high pressure is 0.1Pa, the filled circle, low pressure is 0.01Pa, the open circle. The best condition for the Fermi potential was 0.5kV for the substrate voltage. There was no temperature in the chamber dependence between 200$^\circ$C to 400$^\circ$C. Therefore, temperature in chamber is set at about 300$^\circ$C. On the other hands, Fermi potential of DDLC is high when pressure condition is low.

3.2. Measurement of mass density and chemical compositions
As further evaluations, mass density and chemical compositions were measured by XRR in RIKEN [6] and RBS/ERDA at Tsukuba university [7].
XRR is a method to measure electron number density and thickness of a film from a spectrum of x-ray reflection. When X-rays are applied to a material’s surface, a portion of x-rays is reflected at every interface. Interference of these partially reflected x-ray beams creates a reflectometry pattern. By analyzing it, the parameters are determined. The source of x-ray is CuK$\alpha$ with wavelength of 1.54A. The two slits set to measure the same position, which was measured by the NR. The evaluation of thickness in XRR is consistent with NR within 3%. RBS/ERDA is a method to measure chemical composition of a film. It is possible to determine the chemical composition and amount of the targets by measuring counts of scattered ions caused by He ions irradiation on the sample. Figure.3 is schematic view of RBS/ERDA. Two detector were used; a forward Silicon Semiconductor Detector (SSD) detects the hydrogen and deuterium. A backward SSD detects the He scattered by carbon and silicon. The energy of incident beam, He+, was
Figure 2. Above figure shows the result of neutron reflectivity measurement (right) neutron reflectivity of D-DLC, compared with H-DLC, (left) correlation between Fermi potential and film-forming condition. (right): closed circle is DLC made from Deuterated benzene, we called DDLC, open circle is DLC made from benzene, HDLC, and dashed line is calculated line by two parameters, Fermi potential: 243neV and film thickness: 75nm. Obviously, the total reflection range of DDLC is much larger than HDLC. (left): open circle is deposited by high pressure condition, 0.1Pa. On the other hand, closed circle is deposited by low pressure, 0.01Pa.

Figure 3. Schematic view of RBS/ERDA. The incident angle of accelerated He is 15°. The setting angles of forward SSD are 30°, whereas backward are 150°. A mylar sheet of 12 μm is set before forward SSD to eliminated recoiled He. 2.5MeV, and the beam size is 20mm diameter. The incident angle of accelerated He is 15°. The setting angles of forward SSD are 30°, whereas backward are 150°. A mylar sheet of 12 μm is set before forward SSD to eliminated recoiled He. Though the cross section of He/H and He/D is still uncertain[8], a high molecule polyethylene and deuterated polyethylene are used as a standard sample for a calibration. For analysis RBS/ERDA, SIMNRA program[9] which is the simulation program of RBS/ERDA is used to obtain the components of DDLC. More detail is shown in Ref.[7].

Figure 4 shows the result of relation between (right) Deuterium components and film-forming condition, (left) density of film. The mass density of film was calculated by electron number density measured by XRR and chemical compositions measured by RBS/ERDA. There is a tendency in this figure that deuterium components and mass density of film is high with low pressure, which is reason why Fermi potential is high when pressure is low. For the sample of 243neV, the parameters are respectively, the mass of density is 2.07(8) g/cm³, the components are 43(4)% of deuterium and 3.3(6)% of hydrogen in DDLC. Additionally, DDLC still contents 1-5% of hydrogen components.
Figure 4. Above figure shows the relation between (right) Deuterium component in film, (left) density of film and film-forming condition.

Table 1. Typical data of various parameters in DDLC and HDLC

| material | C[\%] | D[\%] | H[\%] | \(\rho [g/cm^{-3}]\) | \(V_F [neV]\) |
|----------|-------|-------|-------|----------------|--------------|
| DDLC     | 65(2) | 31(2) | 3.8(5)| 2.07(8)        | 240(10)      |
| HDLC     | 64(3) | 0.8(1)| 35(3) | 2.18(4)        | 150(10)      |

3.3. Consistency of Fermi potential between neutron reflectivity and RBS/ERDA, XRR

From the equation (1), we get the equation

\[
V_F \approx b_C N_C + b_D N_D + b_H N_H
\]

\[
N_i = \rho_M R_i \times \frac{N_A}{A_i}
\]

where \(N_A\) is Avogadro constant, \(A_i\) is the atomic mass of \(i\) material, \(R_i\) is the material of chemical composition. NR is the direct measurement of Fermi potential, whereas XRR and RBS/ERDA have the relation with Fermi potential. Therefore, substituting two parameters, mass density and chemical compositions, for Eq.2, Fermi potential is calculated. Figure 5 shows that y axis is Fermi potential of NR measurement, x axis is Fermi potential calculated by \(\rho_M\), \(R_i\). The open circle is hydrogen DLC (HDLC) and closed circle is DDLC. In HDLC data, the value measured by NR tend to be larger than the value calculated by \(\rho_M\), \(R_i\), while DDLC data has opposite trend of it. There is the consistency with error of 8%. The error of cross section of H/He, D/He caused this error.

3.4. roughness of DDLC

There are two types of refection; one is a specular reflectivity whose incident angle is same as refection angle, the other is off specular reflectivity whose angle not. As a model recently studied[10], roughness causes off-specular reflectivity. As generally, roughness causes off-specular reflectivity. Therefore, firstly, we measured the surface roughness by AFM to evaluate it. The result shows that DDLC surface is very smooth, rms of height is 0.6(2) nm in DDLC, on the other hand, 0.3(1) nm in Si substrate in Fig.6, where b is rms of height. Therefore, low off-specular reflectivity of DDLC can be expected.
Figure 5. Consistency between neutron measurement and RBS/ERDA, XRR

Figure 6. Above figure shows a roughness of (left) Si substrate and (right) DDLC. The thickness of DDLC is 107 nm, the parameter of \( b \) is the height of Root Mean Square.

3.5. a multiple layers of DDLC/HDLC
As mentioned above, it is possible to produce a DDLC/HDLC multiple layer by changing the source gas between hydrated and deuterated benzene. A multiple layers is a method of exceeding the critical angle of total reflection. It provide reflections from multiple interfaces between different indexes of refraction. Therefore, on trial, we made the forth multiple layer. Figure 7 shows a spectrum of neutron reflectivity of DDLC/HDLC 4 layer (solid line) with a single layer mirror of DDLC (dotted line). There are some sign of multiple reflection at figure 7.

4. conclusion
We fabricated a DDLC coating for a new neutron mirror, and measured its characteristics. Fermi potentials measured by NR were 190-243 neV. The maximum Fermi potential of DDLC gained 10% from the previous report \cite{2} \cite{3}, which is the same as Fermi potential of NiC, 243 neV. The typical surface roughness of DDLC measured by AFM was 0.6 nm as a RMS of height. Therefore, low off-specular reflectivity of DDLC can be expected. The chemical composition was measured by RBS/ERDA. The typical components of hydrogen and deuterium was 3% and 43%, respectively. These results show that performance of DDLC as a neutron mirror is satisfactory. Therefore, DDLC will be useful for neutron guides with complicated shapes.
because DDLC can be deposited on any surface by CVD. In addition, we successfully made DDLC/HDLC multiple layer mirror.

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