Advanced Neutron Reflectometer for Investigation on Dynamic/Static Structures of Soft-Interfaces in J-PARC

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Abstract. A novel neutron reflectometer with horizontal geometry will be established at BL16 in Materials and Life Science Experimental Facility (MLF) of Japan Proton Accelerator Research Complex (J-PARC) as a successor of a reflectometer ARISA-II. ARISA-II corresponding to a single neutron beam downward at 2.22 deg has achieved off-specular and time-resolved reflectivity measurements. The novel reflectometer is designed so as to receive two tilted neutron beams (2.22 & 5.71 deg), which gives us an opportunity in investigation on a free liquid surface. The reflectometer can provide a micro-sized beam by slit collimation and obtain a fair reflectivity with small sample area. Also, T0 chopper and neutron focusing mirror are newly introduced. The T0 chopper can suppress the background due to fast neutrons. The focusing mirror produces further reduction of measurement time not only for specular reflection by focusing neutrons on a sample, but also grazing incidence small-angle neutron scattering (GISANS) measurements by focusing on a detector.

1. Introduction

Neutron reflectometry is a powerful method for investigations on interfaces composed of soft materials so-called Soft-Interfaces, since neutrons can distinguish soft materials with and without deuteration [1]. The method allows us to measure the reflection from buried interfaces such liquid/solid, because of high transmittance of neutrons inside materials. Also, white pulsed neutron can cover wide range of scattering vector ($q$) at the same time, owing to time-of-flight method, which is applicable in time-resolved measurements to measure the dynamics of Soft-Interfaces [2].

ARISA-II is a horizontal-type neutron reflectometer installed at BL16 in Materials and Life Science Experimental Facility (MLF), J-PARC, Japan. For free interfaces, such as water surface, two downward beam lines with 2.22 and 5.71 deg relative to horizontal are introduced. ARISA-II was open for users from 2009, and made the fruits as a scientific publication [3, 4]. However, ARISA-II can receive only a 2.22 deg beam line because this reflectometer is reutilizing old ARISA reflectometer at KENS facility in KEK, Japan, [5] which does not have the enough strokes to change the vertical positions of sample and detector for both beam lines. This did not meet the demand on measurements with high $q$ range for free liquid surfaces. Additionally, the minimum beam size of ARISA was relatively large (~0.1 mm), in which the footprint on sample is over 30 mm at incident
angle of 0.3 deg with \( q \) resolution of 3%. In the point of efficiency on sample preparations, further reduction of sample area, hopefully less than 10 mm \( \times \) 10 mm, is preferred.

We are developing an advanced neutron reflectometer with horizontal geometry as a successor of ARISA-II in order to overcome the disadvantages of ARISA-II and realize the reflectometer with higher performance. In this paper, we describe about the present state of ARISA-II and discuss on the specification of the novel neutron reflectometer with introduction of new attempts for further upgrades.

2. Instrumental Outline of ARISA-II

Figure 1 shows the schematic drawing of ARISA-II. Pulsed neutron beam at 25 Hz came through a guide tube with 3Q, super mirror. The beam passed through a disk chopper to determine wavelength band of incident neutrons as 2.0 – 8.8 Å. After the disk chopper, iron collimator was installed for reduction of unnecessary fast neutrons which give rise to an increase of background. Before a sample, the beam was finely collimated by a pair of slits (S1 and S2) with sintered B,C blades. The samples were placed on a stage with horizontal geometry. The reflected neutrons went through the third slit and the reflection angle and time-of-flight of each neutron were counted by a 2-dimensional scintillation detector with \(^6\)LiF/ZnS (OHYO KOKEN, Japan) and position-sensitive photomultiplier tube (HAMAMATSHU, Japan). The beam divergence, sample position, incident and reflection angles were precisely controlled by a computer to keep an angle resolution. The reflection intensity was normalized by incident beam intensity and converted to the reflectivity depending on scattering vector \( q \).

3. Results of Soft-Interfaces.

Figure 2 represents the time-resolved specular neutron reflectivity (NR) profiles of a poly(3-(N-2-methacyroyloxyethyl-N,N-dimethyl)ammonatopranesulfonate) (PMAPS) brush on a quartz substrate in contact with D\(_2\)O. The PMAPS brush was synthesized by atomic transfer radical polymerization [6]. The first reflectivity curve was collected in 30 min after the immersion in a D\(_2\)O medium, and each reflectivity curve was obtained at scan duration of 300 seconds. The figure shows that weak fringes resulted from a brush structure in D\(_2\)O [4] were successfully obtained and the brush structure became stable within 30 min after the immersion of D\(_2\)O. The profiles indicate that a fair reflectivity profile with a statistical error of reflectivity (\( \Delta R/R \) < 15 %) can be obtained from liquid/solid interfaces in minute order within \( q_z = 0.03 \) Å\(^{-1}\), where structural change of a film with thickness over 200 Å can be detectable. It should be noted that this experiment was performed at proton beam power of 120 kW (neutron flux evaluated by Monte Carlo simulation is \( 2.4 \times 10^5 \) neutrons/s in this experiment). Since the J-PARC accelerator is planning to be 1MW, the time resolved measurements in about 40 sec as a scan slicing will be possible in the future. The measurements are applicable for interfacial dynamics of soft materials with dimension over 200 Å taking place in minute order.

Since ARISA-II utilized a 2-dimensional scintillation detector with the 100mm effective area in a diameter and 1 mm spatial resolution, off-specular reflectivity besides the specular reflection was...
measured. Figure 3 shows NR profile obtained from a stacking of dipalmitoylphosphatidylcholine (DPPC) bilayers on a Si wafer with ARISA-II. As seen in the figure, the Bragg peaks resulted from lamellar structure of the DPPC bilayers were clearly observed at $q_z = 0.11$ and 0.22 Å$^{-1}$. Besides the Bragg peaks, the clear streaks in $q_x$ direction were observed, where $q_x$ is a momentum in direction of beam’s travel among axes parallel to the film plane. The streaks of off-specular reflection was extended over $q_x = 6 \mu m^{-1}$. This indicates the presence of in-plane structures with long-length correlation, that is, the surface fluctuation of the multilayer as shown in a previous study [7]. In principle, grazing incidence small-angle neutron scattering (GISANS) measurements can be also realized by collimating the neutron beam in vertical direction.

4. Instrumental upgrades

For further upgrades, we are planning to replace old ARISA system as well as install new components. As presented in the proceeding result section, ARISA-II showed a good performance on specular and off-specular reflectivity measurement with the 2.22 degree beam line. To utilize the 5.71 degree beam line, a new reflectometer system with slits, sample and detector stages will be replaced to adjust their vertical positions with longer strokes. As simple calculation, an incident neutron with $\lambda = 2.0$ Å at 5.71 deg obtains $q$ value 0.56 Å$^{-1}$ in a specular condition. The use of this beam will enable us to perform high $q$ scans, which are of great use in the measurements on a liquid surface, especially in structural estimation of a monolayer or thin film with a few nanometers in thickness on a liquid surface (e.g. Langmuir or Gibbs film).

As well as the expansion of the vertical strokes, the fine silt collimation will be installed to realize the reflectivity measurements with smaller samples. The new slits are designed so that closest slit width in vertical direction is down to 10 µm, and the footprint on a sample will be reduced in 3 mm, about one tenth of that of ARISA-II, with a few percentages of $q$ resolution. Here, a slit system with positioning sensors with high resistivity against radiation and repetitive reproducibility of less than 0.5µm (High-accuracy MT-touch Sensor, Metrol Co., Ltd.) was examined to obtain a slit width of 10 µm. Since typical sample size in the latest frontiers is around 10 mm × 10 mm, this is a great advantage to investigate new materials with small amount by a neutron reflectometer.

The replacement of old ARISA can realize reflectivity measurements in high-$q$ region and with small samples. However, these measurements require long time due to low reflectivity and small beam size. To reduce the measurement time, we plan to introduce a focusing mirror (500 mm × 100 mm) with an ellipsoidal shape between the slits. By focusing the incident neutrons, on a sample, we can utilize high-flux neutron with large beam divergence, and it bring us the further reduction of measurement time and sample area. On the test measurements at ARISA-II, we succeeded in focusing neutron with 1 mm width at sample position, and the neutron flux at focusing position was about 10 times as much as a natural beam when aperture slit width was 0.4 mm [8]. Here we should keep it in mind that increase in beam flux is accompanied by worse angle resolution, because the beam flux is
proportional to the product of its size and divergence according to Liouville’s theorem. On the other hand, detector-focusing geometry allows us to obtain high intensity with keeping an angular resolution because the beam size at a sample can be enlarged. This is applicable for GISANS measurements by focusing in horizontal direction at the detector.

Furthermore, we are going to implement a double frame mode in the TOF system, that is, screening of the neutrons so that the frequency of neutron pulse (25 Hz) decreases into half (to 12.5 Hz) by adjusting the frequency of the disk chopper rotation after the neutrons coming in the beam line. The double frame mode is an attempt to expand the neutron’s wavelength available for NR measurements into double, which the reflectivity with doubled $q$ range can be obtained with an incident angle, although the duration time is also doubled. The double frame mode is of great use in the time-resolved NR measurements with wide $q$ range. Our examination of the double frame mode on ARISA-II showed that it worked successfully and wavelength available was extended in double (from 2.0-8.8 Å to 2.0-17.6 Å). However, the disk chopper was made of aluminum plate coated by gadolinium paint which could not stop high energy neutrons generated at 25 Hz which cause a rise of background noise. To stop the fast neutrons, a T0 chopper made by Inconel block is going to be installed in back of the disk chopper.

5. Conclusions

In the present state of ARISA-II at BL-16 in MLF/J-PARC, it has achieved the off-specular reflection measurement and time resolved NR measurements as well as specular NR measurements from Soft-Interfaces. The time resolved NR measurements are brought by increment of the proton beam power, which provide us reduction of measurement time.

On the basis of the specification of ARISA-II, an advanced neutron reflectometer will be newly introduced at the beam line. The new reflectometer with enlarged vertical strokes of components is able to receive two downward beams (2.22 and 5.71 deg) for high $q$ measurement (up to 0.56 Å$^{-1}$) on a liquid surface. The slit collimation is also improved to correspond to the smaller sample area down to 10 mm $\times$ 10 mm. Also, the T0 chopper and neutron focusing mirror are put into practical use in the new machine. The T0 chopper is able to stop the extremely fast neutrons which cause background noise. The sample focusing mirror brings us the further reduction of measurement time and sample area. The detector focusing mirror with a 2-dimensional detector can provide us high intensity with keeping an angular resolution in the GISANS measurement as an advanced measurement.

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