CO1-1 First Neutron Diffraction Results of Fluoride-ion Battery Materials on VCND

K. Mori[1] and F. Fujisaki[2]

[1]*Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS)*
[2]*Office of Society-Academia Collaboration for Innovation, Kyoto University*

INTRODUCTION: The all-solid-state rechargeable battery is a key technology for large-scale applications such as electric vehicles, plug-in hybrid vehicles, and electrical energy-storage systems in future smart grids. The use of solid electrolytes is critical for improving the battery performance parameters: energy density, power capacity, lifespan, and reliability. In the last decade, fluoride-ion batteries (FIBs) have attracted much attention as alternative candidates for lithium-ion batteries, nickel-metal hydride batteries, sodium-ion batteries, and so on. However, no standard choice for FIB materials has been established. For the realization of all-solid-state FIBs, it is very important to explore new fluoride-based solid electrodes and electrolytes. In this work, we performed structural studies for fluoride-ion battery materials such as Cu nanoparticle with BaF_2 (hereafter referred to as nano-Cu + BaF_2), AlF_3 nanoparticle (hereafter referred to as nano- nano-AlF_3), AlF_3 nanoparticle with Li (hereafter referred to as nano-AlF_3 + Li), using the VCND on the B-3 beam port of KUR.

EXPERIMENTS: Powder samples of the "nano-Cu + BaF_2", the "nano-AlF_3", and the "nano-AlF_3 + Li" were put into a cylindrical vanadium-nickel-alloy holder (diameter: 6 mm, thickness: 0.1 mm) under a high-purity argon atmosphere. ND experiments were performed using the VCND, as shown in Fig. 1. The neutron wavelength, λ, which is monochromatized by the (220) plane of a Cu single crystal (i.e., Cu monochromator), is 1.0 Å. Their ND data were collected in the 2θ range of 10–115 ° at room temperature. In addition, their X-ray diffraction (XRD) data were recorded on an X-ray diffractometer with Cu$K\alpha$ radiation (λ = 1.54 Å; SmartLab, Rigaku Co.) at room temperature.

RESULTS: The ND data of the "nano-Cu + BaF_2", the "nano-AlF_3", and the "nano-AlF_3 + Li" were shown in Fig. 2(a). Obviously, Bragg reflections were clearly observed in the higher 2θ range of ND data, compared with XRD data (see Fig. 2(b)). It is most likely that the ND data enable us to offer the precise atomic positions and thermal factors of F^- ions, since the scattering amplitude (or coherent scattering length) of F is as large as those of other elements. Further analysis (e.g. Rietveld analysis) is now in progress to determine their structures.

The authors acknowledge Mr. Tanaka of Kyoto University for his help with the sample preparation.

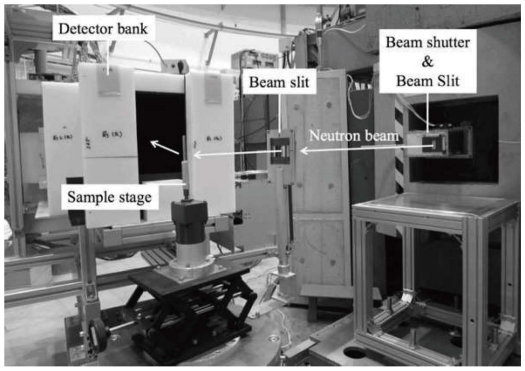
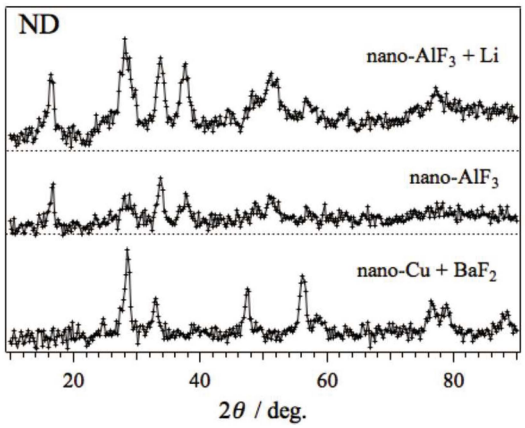


Fig. 1. Versatile compact neutron diffractometer (VCND) installed at the B-3 beam port of Kyoto University Research Reactor (KUR).

(a)



(b)

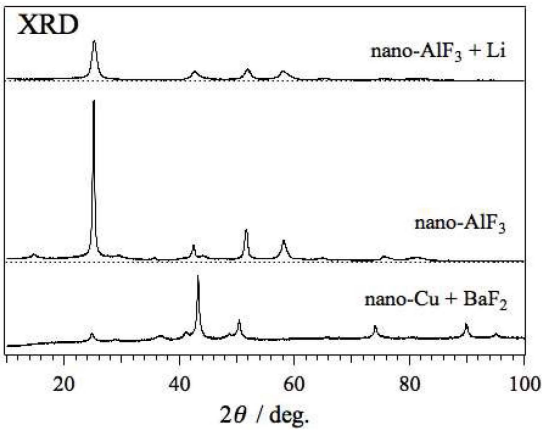


Fig. 2. (a) Neutron diffraction data of Cu nanoparticle with BaF_2 (nano-Cu + BaF_2), AlF_3 nanoparticle (nano-AlF_3), AlF_3 nanoparticle with Li (nano-AlF_3 + Li) collected at the VCND. (b) X-ray diffraction data of the "nano-Cu + BaF_2", the "nano-AlF_3", and the "nano-AlF_3 + Li" collected at the X-ray diffractometer with Cu$K\alpha$ radiation.

CO1-2 Current Status of Versatile Compact Neutron Diffractometer (VCND) on the B–3 Beam Port of KUR, 2019

K. Mori, R. Okumura, H. Yoshino, M. Kanayama, S. Sato[1], K. Iwase[2], Y. Oba[3], H. Hiraka[4], F. Fujisaki[5], F. Kobayashi[6], and T. Emoto[6]

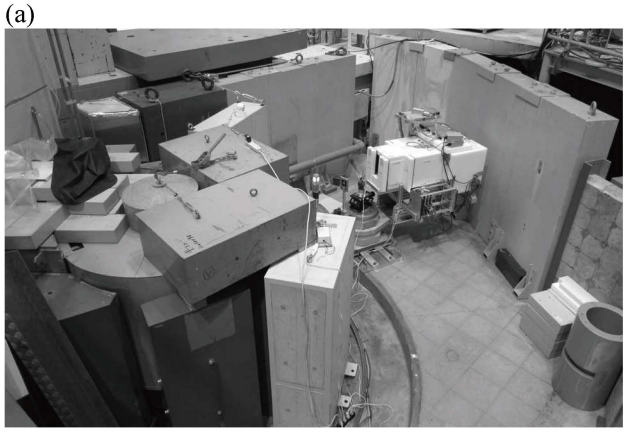
Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS)
[1]*High Energy Accelerator Research Organization (KEK)*
[2]*Department of Materials and Engineering, Ibaraki University*
[3]*Materials Sciences Research Center, Japan Atomic Energy Agency (JAEA)*
[4]*Neutron Science Center, Korea Atomic Energy Research Institute*
[5]*Office of Society-Academia Collaboration for Innovation, Kyoto University*
[6]*Graduate School of Engineering, Kyoto University*

INTRODUCTION: Neutron diffraction is a powerful tool to precisely determine the positions of light elements (e.g., hydrogen and lithium) in solids. This is the main reason why neutron powder diffractometers are critical for structural investigations of energy storage materials, for example, rechargeable lithium-ion batteries and hydrogen absorbing alloys. The B–3 beam port of Kyoto University Research Reactor (KUR) had long been used as a four-circle single-crystal neutron diffractometer (4CND). For the last decade, however, the 4CND was so old that its research activity on neutron science was quite low. Now, the versatile compact neutron diffractometer (VCND) is installed on the B-3 beam port of KUR.

SPECIFICATIONS: Figure 1 shows the current state of the VCND. The neutron wavelength, λ, which is monochromatized by the (220) plane of a Cu single crystal (i.e., Cu monochromator), is 1.0 Å. To cover the detector area of $6\,° \leq 2\theta \leq 130\,°$, twenty-five ^{3}He tube detectors (1/2 inch in diameter) are used, where 2θ is the scattering angle. A detector bank including twenty-five ^{3}He tube detectors is placed on the arm of the HUBER-440 goniometer. The distance from the Cu monochromator to the sample is approximately 2 m, and the distance from the sample to the detector is 1.2 m.

CRYSTAL STRUCTURE ANALYSIS: Strontium fluoride (SrF_2) is a key material for the solid electrolytes of all-solid-state fluoride-ion batteries. The crystal structure of SrF_2 is well-known as the fluorite-type structure, comprising a metal site and a fluorine site: Sr(0, 0, 0) in the 4*a* site and F(1/4, 1/4, 1/4) in the 8*c* site (Wyckoff notation in space group $Fm\bar{3}m$). To assess the ability of the VCND, we performed the ND experiment using SrF_2 powder. Figure 2 shows the ND data of SrF_2 at room temperature. In the figure, a good fit was obtained between the observed and calculated intensities. The lattice constant, *a*, was estimated to be 5.85(15) Å.

(a)



(b)

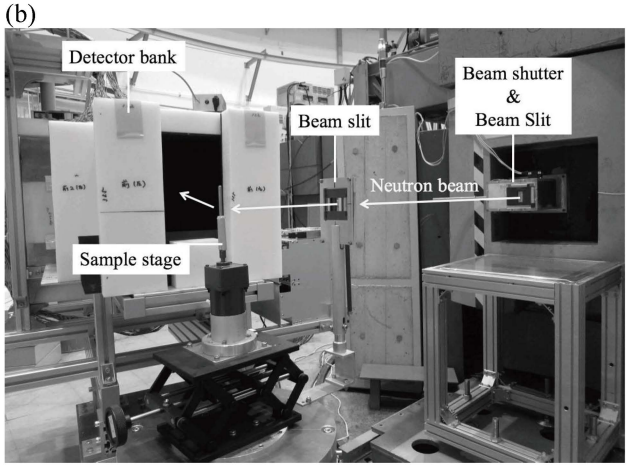


Fig. 1. Versatile compact neutron diffractometer (VCND) installed at the B-3 beam port of Kyoto University Research Reactor (KUR): (a) bird's-eye-view photograph and (b) partial view (around the sample stage) of the VCND.

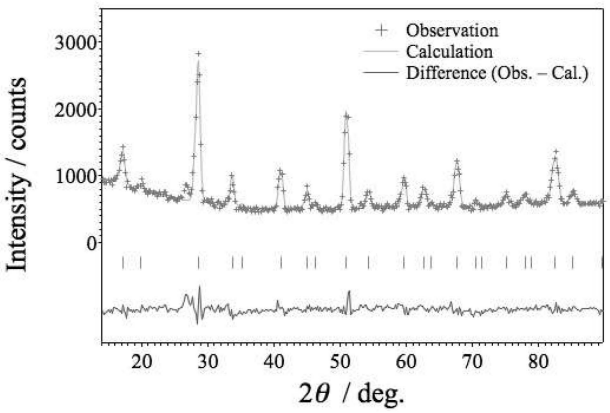


Fig. 2. The crystal structure refinement of SrF_2 using neutron diffraction data collected at the VCND.

CO1-3 Neutron scattering study on microstructure of vitrified radioactive wastes

K. Kaneko, R. Motokawa, Y. Oba, K. Mori[1] and R. Okumura[1]

Materials Sciences Research Center, Japan Atomic Energy Agency
[1]Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION:

The vitrification technique with borosilicate glass is used to immobilize high-level radioactive liquid wastes, which is produced during the reprocessing of nuclear fuels[1]. The high-level wastes is mixed with the borosilicate glass and melted, that results in forming an oxide. In order to have a long-term stability, details of this vitrification process are important. Among the constituents, molybdate tends to precipitate that lowers durability[2]. The segregation of platinoids also cause issues on fabrication[3].

In order to fabricate stable vitrified radioactive waste, microscopic insights into the structure are required. Neutron diffraction is suitable to structure of the glass as it can access to high-Q range. In addition, thanks to its high transmission, the vitrified waste can be investigated without crashing into a powder form. The latter could be essential to obtain an actual form of the waste.

Since the research reactor JRR-3 has not been in operation for roughly 10 years, the B-3 diffractometer offers an unique opportunity to perform neutron diffraction with the monochromatic beam. As a first step, we performed neutron diffraction experiments to check feasibility to study the vitrified nuclear waste using the simulated waste.

EXPERIMENTS:

The borosilicate glass samples with and without simulated radioactive wastes were prepared to have cylindrical form with several diameters ranging from 6 mm to 20 mm. In order to reduce neutron absorption of boron, one of the main constituent of the glass, enriched ^{11}B was used.

Neutron diffraction experiments were performed on the versatile compact diffractometer installed at the B-3 beam port. Neutrons with a wavelength of 1Å are provided by a Cu monochromator. An array of the ^{3}He detectors which covers 25° in the scattering angle allows efficient measurements. The sample was mounted on the continuous rotation stage which increases homogeneity.

RESULTS:

Figure 1 shows a representative neutron diffraction pattern of the borosilicate glass for vitrification without the simulated radioactive waste measured on the B-3. The inset of the figure displays the neutron transmission image for the same sample taken by the CCD camera. This

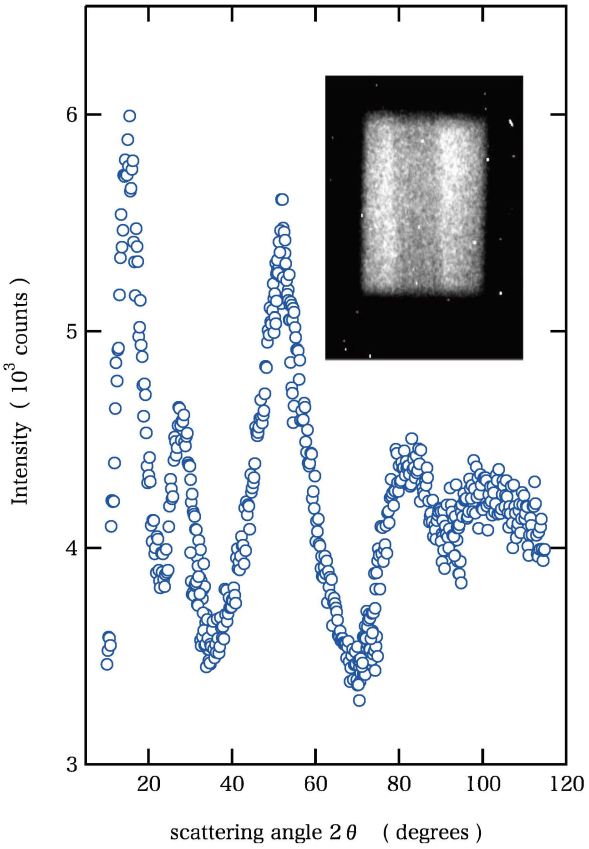


Fig. 1. Neutron diffraction patter of the borosilicate glass for vitrification without simulated radioactive waste recorded on the B-3 diffractometer. The inset shows a neutron transmission image for the same sample.

image proves that a sufficient transmission was obtained owing to the ^{11}B enrichment, The suppression of the neutron absorption leads to obtain a clear neutron diffraction pattern shown in the figure, which was taken for a few hours at 5MW. In addition to first sharp diffraction peak around 15°, the higher-order peaks were clearly observed around 27°, 52° and 83° as well. This high quality data with the high S/N ration should be sufficient for quantitative analysis and is in progress.

The present result demonstrates that the B-3 diffractometer is suitable for the study on the vitrified radioactive waste. We plan to extend our study on the simulated radioacitive waste with different compositions and fabrication conditions in order to reveal its impact on the structure in a microscopic scale.

REFERENCES:

[1] G. Roth, S. Weisenburger, Nucl. Eng. Des. **202**, 197e207 (2000).
[2] S. Morgan *et al.*, Mater. Res. Soc. Symp. Proc. **807**, 151e156 (2003).
[3] H. Mitamura *et al.*, Nucl. Chem. Waste Manag. **4**, 245e251 (1983).

CO1-4 Development of neutron spin flipper with large beam acceptance

M. Kitaguchi, H. Okabe[1], K. Morikawa[1], T. Oda[2] and M. Hino[2]

KMI, Nagoya University
[1]Department of Physics, Nagoya University
[2]Institute for Integrated Radiation and Nuclear Science, Kyoto University

INTRODUCTION: The recent values of neutron lifetime deviate far beyond the systematic errors claimed in the past and require the further improvement for the neutron the lifetime puzzle. We are continuing neutron lifetime measurement at the polarized beam branch of the NOP beamline installed at the port BL05 in J-PARC. The system consists of a neutron chopper (SFC) and a gas chamber (TPC) for detecting the electrons from the neutron beta decays. The TPC contains small amount of ^{3}He. The rate of the ^{3}He(n,p)^{3}H reaction is measured by counting the protons. The neutron lifetime is measured as the ratio of the electron events to the proton events [1].
The large background via neutron-induced reactions is suppressed by introducing small neutron bunches into the TPC and selectively detecting decay electrons and reaction protons only when neutron bunches are traveling inside the sensitive volume and they were not transmitting through chamber windows and other materials on the beam path. The SFC is a spin-selective optics to switch the neutron beam using the combination of magnetic supermirrors and spin flippers[2]. Polarized neutrons are injected into the SFC. Controlling the timing of spin-flip makes neutron bunches at the exit of the SFC, which can be reflected by the magnetic mirrors successively. By employing the triple series reflection, the present version of the SFC chops the neutron beam with the intensity contrast of about 400. During the lifetime measurement, the bunch length is adjusted as about 50 cm, which is half of the length of TPC sensitive region for maximizing the signal statistics. The cross section of the output bunches is 2 cm ×2 cm. In order to reduce the statistical uncertainties for the lifetime measurement to the order of 1 s, the incident neutron flux into the TPC must be increased. Although the new mirrors have been already assembled to accept large cross section of the neutron beam, large scale of spin flippers are also required. New mirrors and flippers with the beam acceptance of 4 cm ×4 cm can transfer neutrons with the intensity of 9 times larger than that before upgrade.
We have developed the precision simulation of neutron spin behavior to design the flipper. Composed magnetic field of the static field and the radio frequency field for the resonance spin-flip affects the spin-flip probability. To avoid the effect, the asymmetrical shape of the flipper coil was designed (Figure 1).

EXPERIMENTS: The experiments were performed at cold neutron beamline CN3 in KUR. Figure 2 shows the experimental setup. Disk chopper provided pulsed neutrons. Magnetic supermirrors were used for neutron polarizer and analyzer. The position and time-of-flight from the chopper to the detector were measured. The behavior of the spin of each neutron was investigated by scanning the position and magnetic field of the flipper coil.

RESULTS: The dependence of spin flipping probability for neutron beam position was clearly observed. It was consistent with the simulation. The probability achieved 0.95 for the required area of the acceptance (Figure 3). This type of the flipper is suitable for the new SFC. It will be installed into NOP beamline.

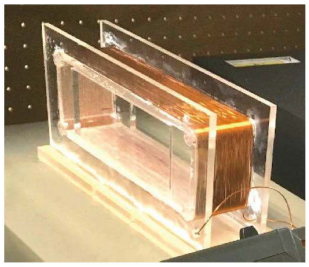


Fig. 1. New flipper coil with large acceptance.

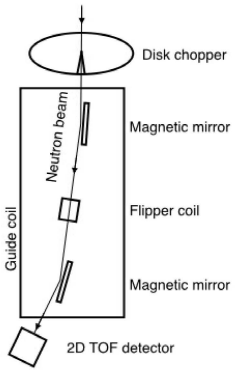


Fig. 2. Experimental setup with polarized neutron beam at CN3. beamline.

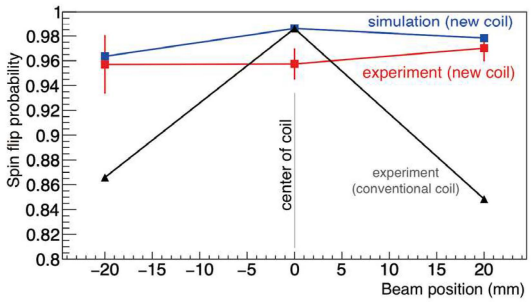


Fig. 3. Position dependence of spin flip probability.

REFERENCES:

[1] K.Mishima *et al.,* Nucl. Instrum. Methods A600 (2009) 342.
[2] K. Taketani *et al.*, Nucl. Instr. and Meth. A634 (2011) S134–S137.

CO1-5 Development of *m*=6.5 neutron spuermirror on ellipsoidal metal substrate

M. Hino[1], T.Hosobata[2], T.Oda[1], Y.Yamagata[2], H.Endo[3], N.L.Yamada[3], F. Funama[4], H.Yoshinaga[1], Y. Kawabata[1]

[1]*Institute for Integrated Radiation and Nuclear Science, Kyoto University (KURNS), Japan*
[2] *RAP, RIKEN, Japan*
[3] *IMSS, KEK, Japan*
[4]*Dept., Nucl. Eng., Kyoto University, Japan*

INTRODUCTION: Progress of neutron optical devices is very significant. We have established fabrication method for aspherical focusing supermirror with metal substrate [1-3]. The metallic substrate is robust and ductile, to which able to fabricate steeply curved surface with high form accuracy. It is also applicable to use under high radiation irradiation and high-temperature filed, even at a place close to the neutron target and moderator. Furthermore, it is possible to fabricate a large focusing mirror by combining multiple segmented mirrors with mechanical fastening entailing the usage of screw holes and fixture tabs. We have solved the problem of required surface roughness for neutron mirror. The roughness should be smaller than 0.3 nm for high-*m* supermirror coating. Here *m* is the maximum critical angle of the mirror in units of critical angle of natural nickel. By using electroless nickel-phosphorus (Ni-P) plating, we overcame the problem and are establishing fabrication process for aspherical focusing supermirror. There is still a problem of peeling off for high-*m* supermirror coating on metal substrate with steep curvature. In this study, we reported an improvement of higher-*m* NiC/Ti(SiC) ellipsoidal supermirror. Here the (SiC) means thin interlayers in which thickness are less than 1 nm. The NiC layers were sandwiched by the SiC thin inter-layers in to reduce compressive stress of layer and to improve interface roughness possibly.

EXPERIMENTS: We fabricated ellipsoidal metallic substrates with the Ni-P plating, based on the technology using ultrahigh precision cutting with correction processing, followed by mechanical precision polishing. The first precise manufacturing was conducted at a CNC machine for development of neutron optical devices at workshop of the KURNS. The ultra-precise manufacturing, polishing and cleaning of the metallic substrate were conducted at RIKEN. The supermirror coating was conducted with ion beam sputtering machine at the KURNS (KUR-IBS) [4]. The neutron experiments were conducted at CN-3 beam line at the KURNS and the BL16 (SOFIA) beam port at J-PARC MLF. We have succeeded in fabricated a couple of NiC/Ti ellipsoidal supermirrors in which length of 900mm. The semi-major and semi-minor axes of the ellipsoidal supermirror were 1250 mm and 65.4 mm, respectively. The acceptable angle of the minor axis arc of the ellipsoidal supermirror is 20 degree [5]. We have fabricated *m*=6.5 NiC/Ti supermirrors in which total number of layers was 8900, where the half of the layers were SiC interlayers.

RESULTS: Figure 1 shows reflectivity profiles of neutrons by the *m*=6.5 NiC/Ti (SiC) supermirror fabricated by the KUR-IBS. As shown in Fig. 1 (a), the profile by the supermirror on metal substrate was almost same with that on a well-polished silicon wafer. There is no big difference for the reflectivity profiles on each metal elements which corresponds to upstream, center, downstream parts shown in Fig.1(b). By using the new layer structure, we have realized *m*=6.5 supermirror, which is difficult even on a flat surface, on a curved surface with a steep curvature. Here the required number of periodic layers of high-*m* supermirror increases with the proportional of m^4, in which principle is well known as Porod's law. The number of effective periodic layers of the supermirror was 4450 and it was not much enough number for *m*=6.5 supermirror. It is also still preliminary measurement and we will report more detail in our future work.

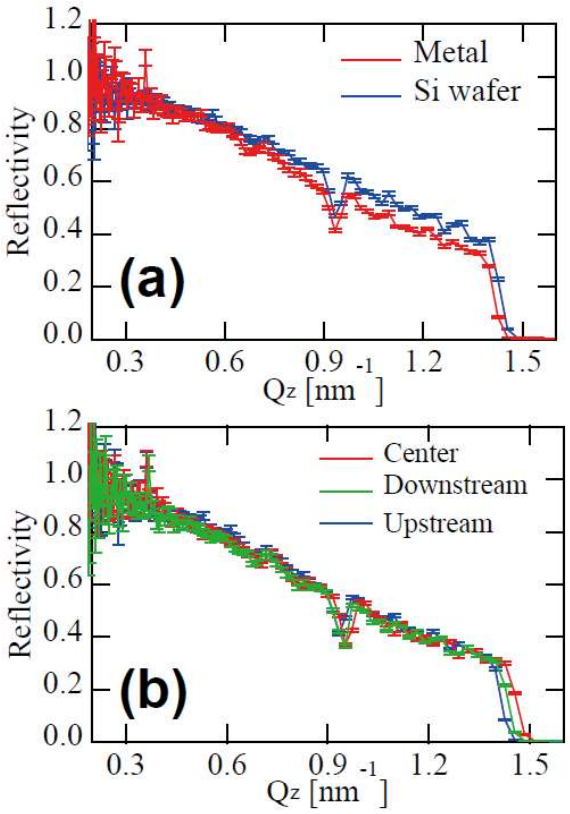


Fig. 1. Neutron reflectivity of m=6.5 NiC/Ti (SiC) supermirror deposited simultaneously on (a) metal substrate and silicon wafer. (b) Those on different metal elements (upstream, center downstream parts).

REFERENCES:

[1] J.Guo, *et al.*, Optics Express 22(2014) 063108.
[2] T.Hosobata, *et al.*, Optics Express 25(2017) 20012.
[3] T.Hosobata, *et al.*, Optics Express 27(2019)26807.
[4] M.Hino, *et al.*, Nucl. Instr. and Meth., **797**(2015) 265.
[5] T.Hosobata, *et al.*, JPS Conf. Proc. 22, 011010 (2018).

CO1-6 Development of high spatial resolution cold/ultracold neutron detector using nuclear emulsion

N. Naganawa, M. Hino[1], K. Hirota[2], H. Kawahara[2], M. Kitaguchi[3], K. Mishima[4], N. Muto[2], A. Umemoto[2]

Institute of Materials and Systems for Sustainability
[1]Institute for Integrated Radiation and Nuclear Science, Kyoto University
[2]Graduate School of Science, Nagoya University
[3]Kobayashi-Maskawa Institute for the Origin of Particles and the Universe
[4]High Energy Accelerator Research Organization, KEK

INTRODUCTION: Experiments measuring position distributions of ultracold neutrons under the earth's gravitation [1-3] have been carried out to study gravitation or short-range forces. For those purposes, ultracold neutron (UCN) detectors with high spatial resolution are useful. Conventional best detectors had resolutions of 1-2 μm [4,5]. To improve the ability to study gravitation, we successfully developed a detector with spatial resolution of less than 100 nm [6] using fine-grained nuclear emulsion [7]. It was fabricated by sputtering a converter layer with a structure of $^{10}B_4C$(50 nm)-NiC-C on a side of silicon wafer at KURRI using the ion beam sputtering system (KUR-IBS) and applying the fine-grained nuclear emulsion with the thickness of 10 μm on the layer. The detector can also be used in neutron imaging. In order to obtain position distributions of neutrons with a high accuracy of submicron, a method to connect images between microscopic views with high accuracy is necessary. We developed a method using microscopic marks formed on silicon substrates for the purpose. In this experiment, we sputtered a converter layer with a structure of $^{10}B_4C$-NiC-C on silicon wafers with those marks, applied fine-grained nuclear emulsion on them, exposed one of them to cold neutrons at J-PARC, and checked the stability of sputtered layer and the emulsion layer. The rest of the samples were used in an experiment measuring position distributions of UCNs under the earth's gravitation at Institut Laue-Langevin (ILL).

EXPERIMENTS: The detectors were fabricated as follows. The microscopic marks for fine alignment with their diameter of 1 μm, a pitch of 50 μm, and a depth of 0.5 μm were formed on areas of 10 mm by 70 mm on single sides of silicon wafers by electron beam lithography at Nanofabrication Platform in Nagoya University. After that, wafers were cut into the size of 20 mm by 90 mm and washed. Next, layers of $^{10}B_4C$(200 nm)-NiC(60 nm)-C(20 nm) were formed on those wafers at KURRI using KUR-IBS. After that, fine-grained nuclear emulsion gel was applied on those wafers with final thickness of 10 μm at Lab. F, Physics Department, Nagoya University. A detector was exposed to cold neutrons of 1000 m/s at BL05, MLF, J-PARC. The exposure density was approximately 2.7×10^7 neutrons/cm^2. After the exposure, it was developed and checked on stabilities of sputtered layer and adhesion between the layer of the emulsion. Observation of tracks was also done with epi-illumination optical microscope at Nagoya University.

RESULTS: Stability of sputtered layer was confirmed to be enough that the layer did not separate from silicon substrate after the application of fine-grained nuclear emulsion and development. Adhesion between the layer and the emulsion layer was also strong enough that the emulsion layer did not separate from the sputtered layer during the development. Tracks of alpha particles and ^{7}Li nuclei from neutron absorption by ^{10}B in the converter layer were clearly seen as shown in Fig. 1 with an expected density. Marks for fine alignment were also clearly seen as shown in the same figure.

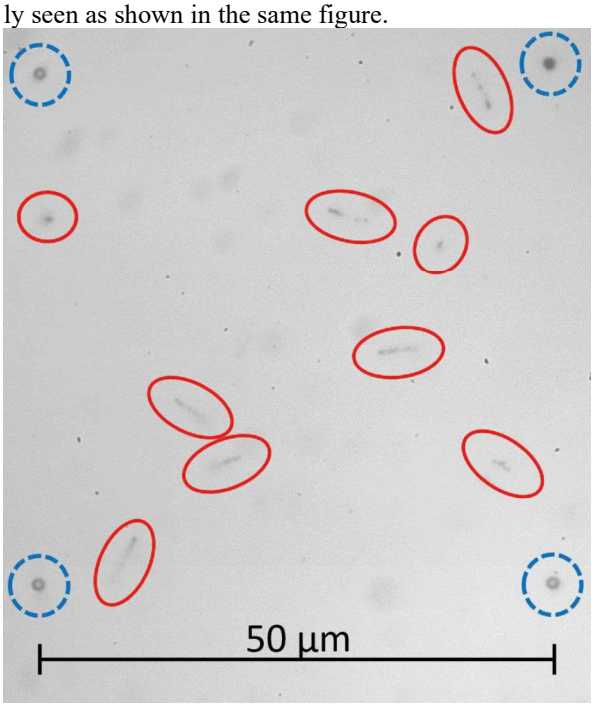


Fig. 1. Microscopic image of the detector after development. Observed tracks are surrounded by red ellipses. Marks for fine alignment are surrounded by dashed blue circles. Tracks and marks were clearly seen after development.

Thus, stability and functionality of the detector was confirmed, and the rest of the detectors were used in an experiment for measuring position distributions of quantized UCNs under the earth's gravitational field at PF2, ILL, whose analysis is going on.

REFERENCES:

[1] V. V. Nesvizhevsky *et al.*, Nature,**415** (2002) 297.
[2] H. Abele *et al.*, Nucl. Phys. A 827, 593c-595c (2009).
[3] G. Ichikawa *et al.*, Phys. Rev. Lett., 112, 071101 (2014).
[4] V.V. Nesvizhevsky *et al.*, Nucl. Instrum. Methods Phys. Res. A 440, 754-759 (2000).
[5] T. Jenke *et al.*, Nucl. Instrum. Methods Phys. Res. A, 732, 1-8 (2013).
[6] N. Naganawa et al., Eur. Phys. J. C, 78 (2018)959.
[7] T.Asada *et al.*, Prog. Thor. Exp. Phys., 2017 (2017) 063H01.