J. Condensed Matter Nucl. Sci. 10 (2013) 63–71

Research Article

Recent Advances in Deuterium Permeation Transmutation Experiments

Y. Iwamura [*], T. Itoh and N. Yamazaki

Advanced Technology Research Center, Mitsubishi Heavy Industries Ltd., Yokohama 220-0012, Japan

H. Yonemura

High Energy Accelerator Research Organizations (KEK), Tsukuba 305-0801, Japan

K. Fukutani

Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan

D. Sekiba

Research Facility Center for Science and Technology, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan

Abstract

We have been investigating low-energy nuclear transmutation reactions observed in the nano-structured Pd/CaO multilayer complex induced by deuterium permeation through it. A micro-beam Nuclear Reaction Analysis (NRA) system, by means of a resonant nuclear reaction ^{1}H(^{15}N,$\alpha\gamma$)^{12}C, has been developed for the purpose of the 3D mapping of the hydrogen distribution in the Pd multilayer complex. Using this system, we observed hydrogen density of Pd/CaO multilayer is higher than that of normal Pd. Preliminary experimental results were obtained, which suggested that implanted W was transmuted into Os or Pt.
© 2013 ISCMNS. All rights reserved. ISSN 2227-3123

Keywords: Deuterium, Multilayer, Nano-structure, Permeation, Pd, Transmutation

1. Introduction

Low-energy nuclear transmutation reactions have been observed in the nano-structured Pd multilayer complex, which are composed of Pd and CaO thin film and Pd substrate, induced by deuterium permeation through the Pd multilayer complex [1–5]. Transmutation reactions of Cs into Pr, Ba into Sm and Sr into Mo were observed. Especially, transmutation of Cs into Pr has been confirmed by "in-situ" measurements using X-ray fluorescence spectrometry

*E-mail: yasuhiro_iwamura@mhi.co.jp

© 2013 ISCMNS. All rights reserved. ISSN 2227-3123

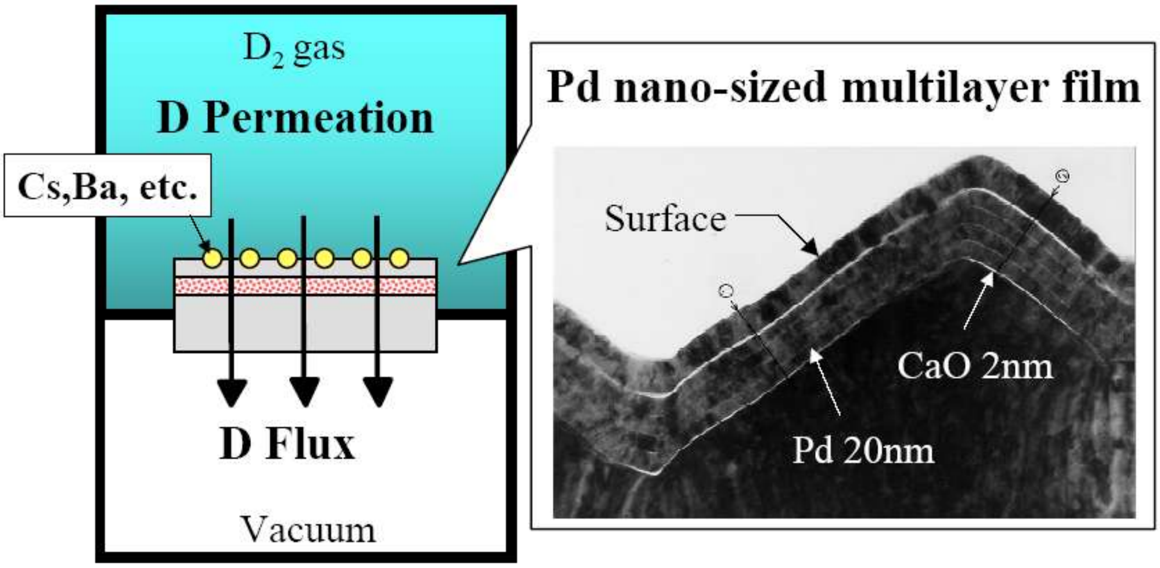

Figure 1. Experimental method for permeation-induced nuclear transmutation.

(XRF) at SPring-8 in Japan [2,3]. Experimental data that indicates the presence of transmutation has been accumulated and experimental conditions for inducing low-energy transmutation reactions are gradually becoming clear, although systematic experimental study is still insufficient. Similar experiments have been performed by some researchers and positive results have been obtained [5–7].

Figure 1 shows schematic of our experimental method. Our approach can be characterized by the permeation of D_2 gas through the nano-structured Pd complex and the addition of an element that is specifically targeted to be transmuted. Permeation of deuterium is attained by exposing one side of the Pd multilayer thin film to D_2 gas while maintaining the other side under vacuum conditions. The sample is a Pd complex composed of bulk Pd on the bottom, alternating CaO and Pd layers, and a Pd thin film on top. After fabricating a Pd complex, Cs, Ba, W or other element is deposited on the surface of the top thin Pd layer. The added elements can be transmuted. From a different point of view, we can provide a deuterium flux through the Pd multilayer thin film on which an element is placed as a target to be transmuted.

Reactions observed so far in our group are shown in Fig. 2. Based on these experimental results, alkali elements seem to be transmutable by our method. In other words, chemically active elements that can easily emit electrons might be transmutable. And the obtained experimental results so far suggest that a certain rule seems to exist. We can notice that 2d, 4d or 6d looks like reacting with deposited elements. Multi-body reactions like 2d, 4d and 6d require sufficient number of d. Therefore, we can see that sufficient deuterium density would be important to induce transmutation reactions.

Table1 shows the correlation between intermediate material in Pd multilayer film and transmutation results. If we replaced CaO with MgO, we did not obtain any positive transmutation products; we could not observe any transmutation reactions. It means that MgO cannot work instead of CaO. Three cases out of the three experiments using MgO show no Pr by ICP-MS measurements, although D_2 gas Flow rates were enough (2–3 sccm) in all cases. However, if we replaced

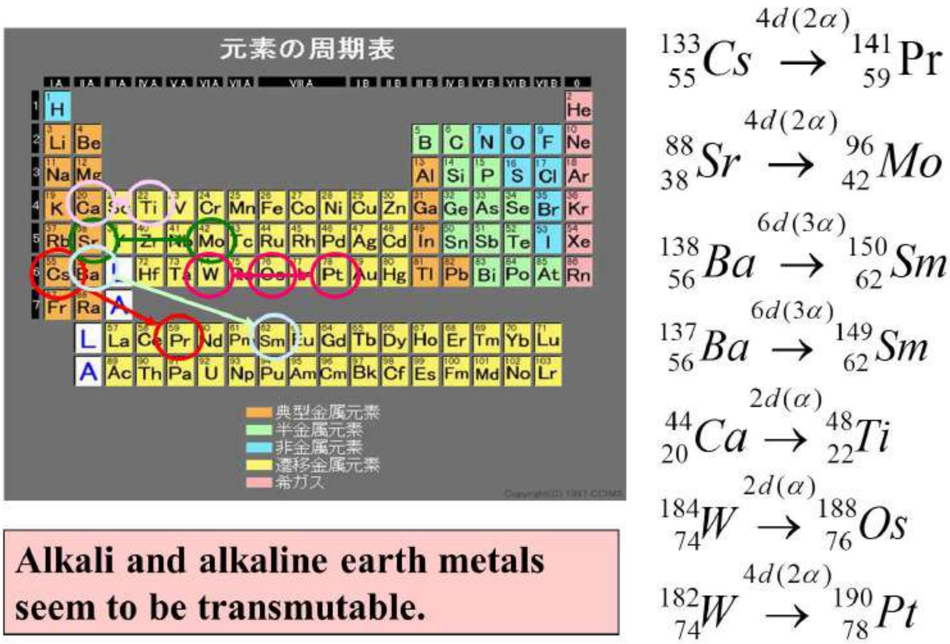

Figure 2. Typical nuclear transmutation reactions observed so far at Mitsubishi Heavy Industries (MHI).

CaO with Y_2O_3, we could observe transmutation reactions from Cs to Pr. Y_2O_3 works like CaO. Work functions for MgO, Y_2O_3 and CaO are shown in Table 1. Although it is difficult to make conclusive results, the existence of low work function of intermediate material might have some effects to induce transmutation.

The permeation induced transmutation technology would be expected as an innovative nuclear transmutation method for radioactive waste and a new energy source. However, it is necessary to increase the amount of transmutation products for commercialization.

The author is now assuming that the following two conditions are important to increase up transmutation products based on the above considerations.

(1) Local deuterium density is sufficiently high.
(2) A characteristic electronic structure for inducing nuclear transmutation should be formed.

Based on these assumptions, we performed local hydrogen density measurement using resonant nuclear reaction and first principal calculation for investigation electronic structure of the Pd–H cluster.

Table 1. Correlation between intermediate material in Pd multi-layer film and transmutation results.

Intermediate material	Work function (eV)	Results for analysis after permeation
MgO	3.3	No Pr (3 cases)
Y_2O_3	2.2	Pr detected (>10 cases)
CaO	1.2	Pr detected (>100 cases)

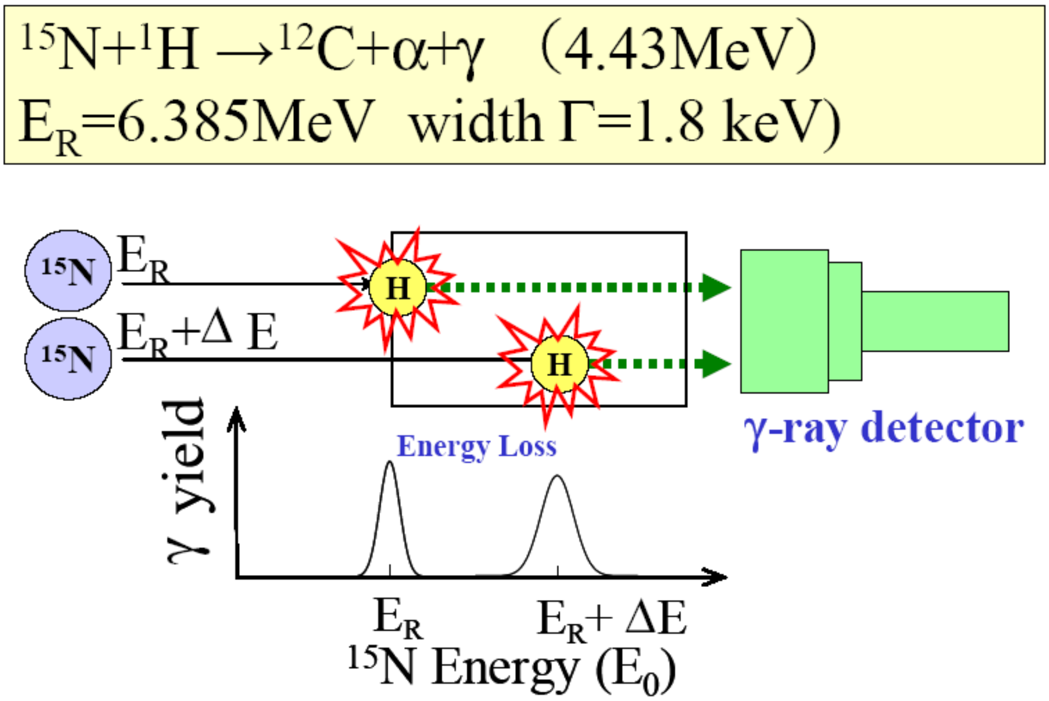

Figure 3. Principle of the resonant nuclear reaction for the analysis of hydrogen density depth profile.

2. Hydrogen Density Measurement using a Resonant Nuclear Reactions

The resonant nuclear reaction $^{1}H(^{15}N, \alpha\gamma)^{12}C$ is widely used for hydrogen distribution analysis [9–11]. This reaction has a very narrow resonance of 1.8 keV at ^{15}N energy of 6.385 MeV, which allows for high-resolution depth profiling shown in Fig. 3. In order to obtain depth profile of hydrogen, energy of ^{15}N and its stopping power in the sample has to be known. The energetic emitted γ-ray is proportional to the concentration at the respective depth of hydrogen in the sample. The H concentration profile is then obtained by scanning the ^{15}N incident beam energy. No resonant nuclear reaction for deuteron is known that have a narrow resonance width equal to 1.8 keV. Then we are trying to measure hydrogen distribution instead of deuterium in our Pd/CaO multilayer thin film during permeation.

Usually hydrogen distribution analysis can be performed under vacuum condition because a ^{15}N beam interacts with air and attenuates. However, it is necessary to measure hydrogen distribution under H_2 gas environment for our case. The authors have developed 3D hydrogen mapping technique in solids under atmospheric environment using a CREST program of Japan Science Technology Agency (JST).

The experiments were performed at the Van de Graaff Tandem accelerator in Micro-Analysis Laboratory of the University of Tokyo. Figure 4 shows schematic of the experimental set-up and photograph of the experimental set-up is shown in Fig. 5. The ^{15}N beam coming from the vacuum side irradiates the Pd/CaO multilayer sample through the SiN membrane, which separates the vacuum from the gas atmosphere of the sample chamber. While the upstream chamber is kept at a vacuum of 10^{-6} Pa, the downstream chamber can be filled with hydrogen or other gases of up to 2×10^{5} Pa.

The right side of Fig. 4 is the enlarged figure of the sample holder of the left side. H_2 gas is filled outside of the permeation unit. The permeation unit can be heated by the heater since transmutation experiments are conducted at 60–80°C.

Two 4-inch-BGO scintillators mounted 30 mm from the sample outside the vacuum are used for γ-ray detection. The yield of γ-ray at 4.4 MeV due to the nuclear reaction is normalized to the Rutherford backscattering spectroscopy (RBS) signal from the gold layer on the SiN membrane, which is proportional to the ^{15}N beam current. The accelerator set-up, i.e. the beam energy and lens/deflector parameters, and data acquisition, i.e. γ-ray detection, RBS measurement, beam current reading and sample positioning, are computer-controlled by a Labview-based software, which enables us to perform automatic beam-energy scan and NRA measurements and detector geometry.

Typical size and current of the ^{15}N beam at the target were 200 μm in diameter and 20 nA, respectively. A SiN membrane grown by low-pressure chemical vapor deposition with a size of 1.1 mm^2 and a thickness of 100 nm (Silson Ltd., UK) were used for beam extraction into an ambient condition.

Several depth profiles of hydrogen density during H_2 gas permeation have been taken by our groups. However, due to the limitation of the ^{15}N beam time and the time for experiments, we cannot obtain reasonable and consistent depth profiles up to now. I would like to stress that the all the depth profiles of Pd/CaO/Pd and pure Pd were different from each other. We could not arrange the experimental condition (pressure and temperature) similar to the transmutation experimental condition (1 atm and 70°C) due to the lack of heater capacity or strength of SiN membrane.We are improving the permeation unit and have plans to measure hydrogen density distribution under various conditions(temperature, time, layer, pressure, etc.) to understand hydrogen behavior in our nano-structured Pd multilayer thin film in the near future.

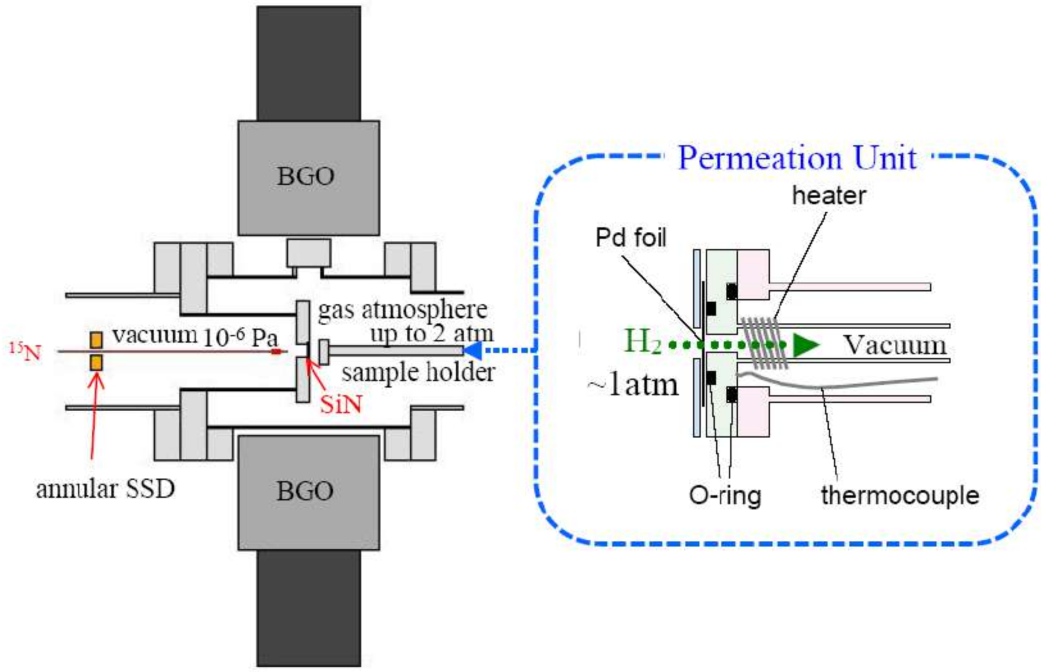

Figure 4. Schematic of the experimental setup for measurement of hydrogen density distribution during permeation.

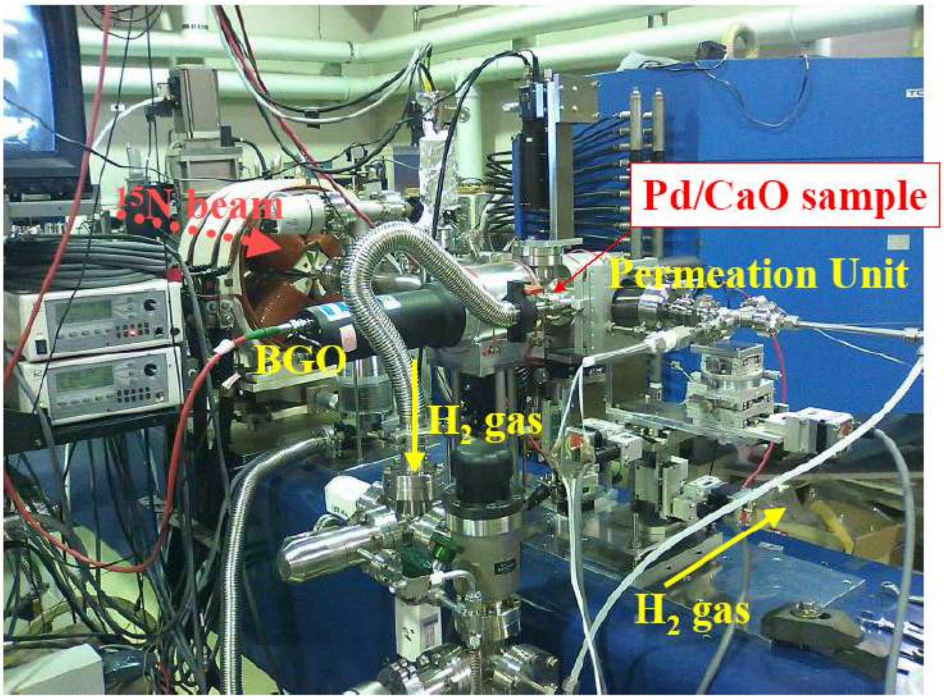

Figure 5. Photograph of the experimental set-up.

3. Experimental Results on W Transmutation

Recently, W (tungsten) transmutation experiments were tried using our permeation technique aiming production of Pt or Os. Experimental procedure for a W transmutation experiment is shown in Fig. 6.

Preparation of the multilayer Pd thin film is as follows. A Pd plate (with purity up to 99.99%; Tanaka Kikinzoku Kogyo K.K.) was washed with acetone and annealed in vacuum. A Pd was washed with acetone and annealed in vacuum ($<10^{-5}$ Pa) at 900°C for 10 h. It was then cooled to room temperature in furnace and washed with aqua regia to remove impurities on the surface of the Pd plate. The surface of the plate was covered by layers of CaO and Pd, which were obtained by five times alternately sputtering 2-nm-thick CaO and 20-nm-thick Pd layers. Then a 40-nm-thick Pd layer was sputtered on the surface. These processes are basically same as before [1,2].

Tungsten (W) ion implantation (63 kV, 2.5×10^{14}/cm^2) was applied to the fabricated Pd/CaO multilayer films and then permeation experiments were performed several times. D_2gas is supplied at 1–1.5 atm on the Pd film side of the test piece and dissolves in D atoms at the surface. The D atoms intrude into the Pd thin film and diffuse through the Pd complex and then reach the surface of the bulk side, where they combine and are released as D_2 molecules. The Pd multilayer thin film is heated to 70°C. After one or two week deuterium diffusion through the Pd complex, the D_2 is evacuated. The sample is removed from the chamber and its surface is analyzed by secondary ion mass spectrometry (SIMS). In this study, we analyzed the Pd complex after an experiment using SIMS to investigate the isotopic compositions of the detected elements. Only surface isotopic compositions were analyzed; we did not measure their depth profiles. SIMS analysis was performed by Probion Analysis Inc., France.

Figure 7 shows the SIMS analysis using Cs^+ ions, in which mass spectra were compared between permeated

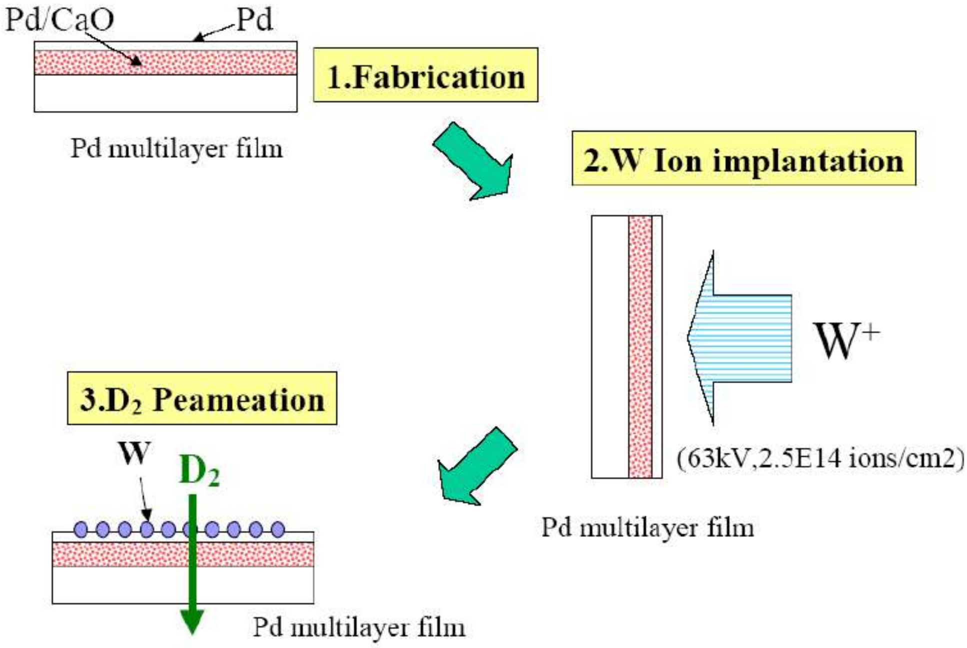

Figure 6. Experimental procedure of W transmutation experiment.

samples and no permeated one. No permeated sample has implanted W and Pt mass numbers. Pt is the major impurity in Pd. Observed spectra have natural W and Pt mass distributions. On the contrary, mass distributions for permeated samples are anomalous. Significant increases for mass 190 should be noticed, although no mass counts of 190 for the No permeated sample. The increase for the two permeated samples cannot be attributed to natural contaminants from Os or Pt. We cannot see any mass 189 in Fig. 7 and then expect no contribution to mass 190 by natural Os. Contribution to mass 190 by impurity Pt should be smaller than mass 192 based on the natural mass distribution of Pt. Effects of compound species were also considered intensively as shown in Table 2. However, the increase of mass 190 could not be explained consistently with isotope distributions of each element.

Based on these discussions, we consider that the observed increase of mass 190 for permeated samples must be explained by the transmutation of implanted W. However, addition of evidences using elemental analysis such as XRF is desirable as a next step research.

Table 2. Possible compounds for mass 190.

^{186}W (28.6%) D_2	^{160}Gd (21.9%) ^{28} Si D
^{188} Os D	^{110}Pd ^{78}Se (23.8%) D
^{176}Yb (12.7%) ^{12}CD	^{108}Pd ^{80}Se (49.6%) D
^{172}Yb (21.9%)^{16}OD	^{106}Pd ^{82}Se (8.73%) D

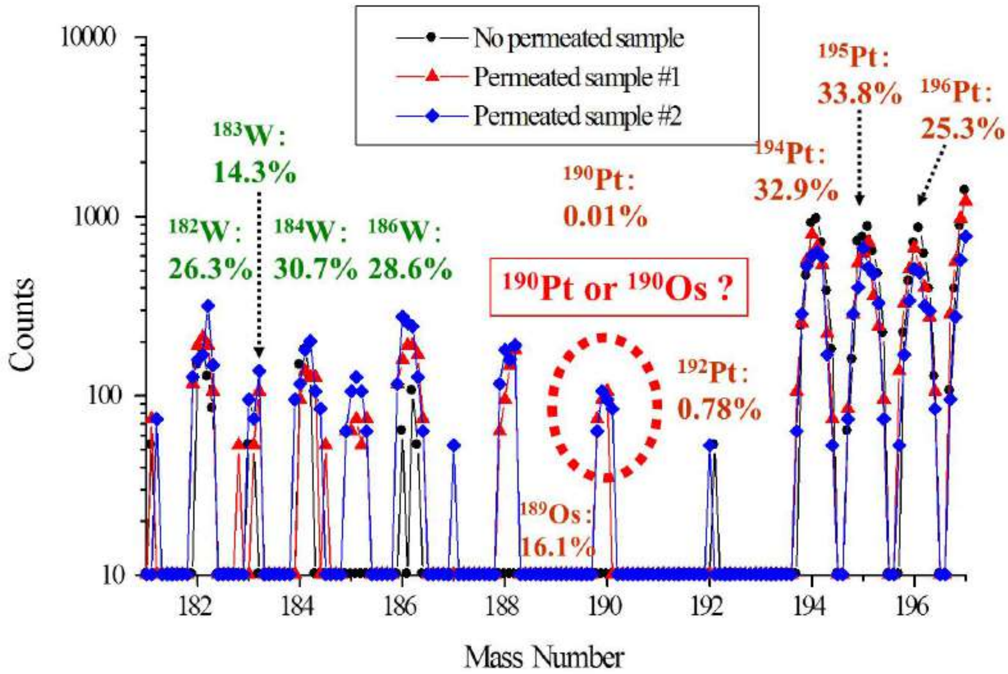

Figure 7. SIMS spectra for D_2 permeated samples and no permeated sample.

4. Concluding Remarks

We assume that the following two conditions are important to induce nuclear transmutation reactions in the permeation experiments.

(1) Local deuterium density is sufficiently high.
(2) A characteristic electronic structure for inducing nuclear transmutation should be formed.

Based on these assumptions, we performed local hydrogen density measurement using resonant nuclear reaction and first principal calculation for investigation electronic structure of the Pd–H cluster. The hydrogen density measurement experiments suggested that hydrogen density of Pd/CaO multilayer seems higher than that of pure Pd. The first-principles computation suggested that high hydrogen density state (H/Pd = 1) in Pd–Cs–H cluster was more stable than low hydrogen density state (H/Pd = 0.33).

Tungsten transmutation experiments were tried using our permeation transmutation method.Significant increases for mass 190 in SIMS were observed, which suggested that W was transmuted into Os or Pt.

Acknowledgements

The authors would like acknowledge Dr. C. Nishimura, Prof. A.Takahashi, Prof. J. Kasagi, Dr. Hioki, Prof. M. Melich, Dr. K. Grabowski, Dr. F. Clelani, Prof. H. Yamada and Prof. S. Narita for their supports and valuable discussions. This work is supported by Japan Science Technology Agency (JST) CREST Program, and Thermal & Electric Energy Technology Foundation (TEET).

References

[1] Y. Iwamura, M. Sakano and T. Itoh, Elemental analysis of Pd complexes: Effects of D_2 gas permeation, *Japanese J. App. Phys.* **41** (2002) 4642–4650.

[2] Y. Iwamura, T. Itoh, N. Yamazaki, J. Kasagi, Y. Terada, T. Ishikawa, D. Sekiba, H. Yonemuraand and K. Fukutani, Observation of low energy nuclear transmutation reactions induced by deuterium permeation through multilayer Pd and CaO thin film, *J. Condensed Matter Nucl. Sci* .**4** (2011)132–144.

[3] Y. Iwamura, T. Itoh, M. Sakano, S.Kuribayashi, Y. Terada and T. Ishikawa, Observation of surface distribution of products by X-ray fluorescence spectrometry during D_2 gas permeation through Pd complexes, *Proc. ICCF 12,* A. Takahashi et al. (Eds.), World Scientific, New Jersey (2006), pp. 178–187.

[4] Y. Iwamura, T. Itoh, M. Sakano , S. Sakai and S. Kuribayashi, Low energy nuclear transmutation in condensed matter induced by D_2 gas permeation through pd complexes: Correlation between deuterium flux and nuclear products, *Proc. ICCF 10,* P.H. Hagelstein and S. Chubb (Eds.), World Scientific, New Jersey (2006), pp. 435–446.

[5] Y. Iwamura, T. Itoh, M. Sakano, S.Kuribayashi, Y. Terada, T. Ishikawa and J. Kasagi, Observation of nuclear transmutation reactions induced by D_2 gas permeation through Pd complexes, *Proc. ICCF 11*, J.-P. Biberian (Ed.), World Scientific, New Jersey (2004), pp. 339–350.

[6] T. Higashiyama, M. Sakano, H. Miyamaru and A. Takahashi, Replication of MHI transmutation experiment by D_2 gas permeation through Pd complex, *Proceedings of 10th International Conference on Condensed Matter Nuclear Science*, P.H. Hagelstein et al. (Eds.), *Condensed Matter Nuclear Science*, World Scientific, New Jersey (2006), pp. 447–454.

[7] H. Yamada et al., Producing transmutation elements on plain Pd-foil by permeation of highly pressurized deuterium gas, *Proc. ICCF 12*, A. Takahashi et al. (Eds.), *Condensed Matter Nuclear Science*, World Scientific, New Jersey (2006), pp. 196–205.

[8] N. Takahashiet et al., Verification of MHI transmutation, No. 8 Spring-8 Industrial Application Conference, Sep.8–Sep.9, 2011, Kobe, Japan (in Japanese).

[9] H. Yonemura, Y. Kitaoka, D. Sekiba, H. Matsuzaki, S. Ogura, M. Matsumoto, Y. Iwamura, T. Ito, T. Narusawa and K. Fukutani, Depth profiling of hydrogen under an atmospheric pressure, *Nucl. Instr. Methods Phys. Res.* B **269** (2011) 632–635.

[10] H. Yonemura, D. Sekiba, Y. Kitaoka, S. Ogura, M. Wilde, T. Narusawa, T. Nebiki, Y. Iwamura, T. Ito, H. Matsuzaki and K. Fukutani, Development of $H(^{15}N, \gamma\alpha)^{12}C$ nuclear reactionanalysis method at atmosphere with glass capillary, *J. Vac. Soc. Jpn*. **52** (2009) 145.

[11] D. Sekiba, H. Yonemura, T. Nebiki, M. Wilde, S. Ogura, H. Yamashita, M. Matsumoto, J. Kasagi, Y. Iwamura, T. Itoh, H. Matsuzaki, T. Narusawa and K. Fukutani, Development of micro-beam NRA for 3D-mappingof hydrogen distribution in solids: Application of taperedglass capillary to 6 MeV 15 N ion, *Nucl. Instr. Methods Phys. Res.* B **266** (2008) 4027–4036.