



Research Article

Detection of Pr in Cs Ion-implanted Pd/CaO Multilayer Complexes with and without D₂ Gas Permeation

Naoko Takahashi,* Satoru Kosaka, Tatsumi Hioki and Tomoyoshi Motohiro

Toyota Central R&D Labs. Inc., Japan

Abstract

Iwamura-type nuclear transmutation, $^{133}\text{Cs} \rightarrow ^{141}\text{Pr}$, with D₂ permeation through Pd/CaO multilayer complexes, was examined. Using ICP-MS, the amounts of Pr were measured in the range 10^{10} atoms/cm². The amounts of Pr measured in D₂ permeated samples were larger than samples that were not permeated.

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Keywords: CaO/Pd multilayer complex, Cs→Pr, Deuterium permeation, Nuclear transmutation

1. Introduction

Iwamura et al. have published several reports claiming that nuclear transmutation occurs with D₂ gas permeation through Pd substrates covered with a Pd/CaO multilayer film (multilayer complexes) [1]. The elements to be transformed are deposited on to the surface of the multilayer complex by the electrochemical method or by ion implantation, and the complex is subjected to D₂ permeation at 343 K for a week or so. The selected nuclear transmutations reported so far are ^{88}Sr to ^{96}Mo , ^{133}Cs to ^{141}Pr and ^{138}Ba to ^{150}Sm [1,2].

Few replication attempts at other laboratories have succeeded. One of the difficulties in reproducing the results of the Iwamura group may be that the amounts of the transformed element are too small to be detected by surface elemental analysis such as XPS, which has often been used in Iwamura-type nuclear transmutation replication experiments [3,4].

In this study, we focused on the Cs to Pr transmutations. We investigated the performance of trace Pr detection by several analysis methods. We compared the detection sensitivity among Glow Discharge Mass Spectrometry (GD-MS), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using reference samples that were doped with different concentrations of Pr. We concluded that ICP-MS is the best technique for detecting small amounts of Pr. Using ICP-MS, we measured the amounts of Pr in samples with and without D₂ permeation treatment, and in some reference samples. Our goal was to discover whether the observed Pr is generated as a result of a nuclear reaction during the D₂ permeation process, or whether it is simply

*E-mail: nao-t@mosk.tytlabs.co.jp

chemical contamination. In this study, efforts were made to examine chemical contamination in the materials used and in the process of sample preparation, e.g., surface concentration of impurities in Pd during the D₂ permeation process.

2. Experimental

2.1. Materials

Substrates of Pd (purity: 99.95%) 100 μm thick were obtained from Tanaka Kikinzoku Kogyo. The as-purchased substrates were heat-treated in vacuum (5×10^{-5} Pa) at 1173 K for 15 h and subsequently in the air at 873 K for 10 min to remove impurity atoms. With this pre-treatment, S impurities in the Pd substrates were greatly reduced [5]. The D₂ gas for permeation treatments with purity of more than 99.995% was obtained from Takachiho Chemical Industrial Co. Ltd. The impurity concentrations listed by the supplier were less than 5 ppm for oxygen, nitrogen and water, and less than 1 ppm for carbon monoxide, carbon dioxide and total hydrocarbons.

2.2. Sample preparation

A multilayer film of Pd/CaO was formed on the Pd substrates by pulsed laser deposition (PLD). The multilayer complex was similar to the ones used by Iwamura et al., i.e., Pd (40 nm), CaO (2 nm), Pd (18 nm), CaO (2 nm), Pd (18 nm), CaO (2 nm), Pd (18 nm), CaO (2 nm), Pd (18 nm), CaO (2 nm), and Pd substrate (100 μm).

Cs atoms were implanted in the multilayer complex at 65 keV to a dose of 1.5×10^{15} atoms/cm². The range of the implanted Cs was estimated to be 11.8 nm. The Pd substrates were then heat-treated in air at 573 K for 10 min to remove carbonaceous materials deposited during the ion implantation.

The deposition of Cs on the top of the multilayer film was also carried out with the electrochemical method in the same manner as reported in the original paper by Iwamura et al. [1].

The samples were then subjected to D₂ gas permeation treatments at 343 K or 423 K for a period of 150–250 h. The deuterium gas was supplied to the up-stream side (the multilayer film side) of the sample via a reservoir tank of about 1 L, which was connected with a 6 MPa cylinder (D₂: 200 L) through a pressure regulator. Table 1 shows a list of the samples prepared in this study.

2.3. ICP-MS

The ICP-MS instrument used was an Agilent 7700X. The samples were dissolved partially or totally by nitric acid or aqua regia. Most samples were partially dissolved. The depth of dissolution was about 100 nm.

In order to evaluate the detection limit of the ICP-MS analysis, we prepared reference samples, i.e., Si wafers and Pd substrates with the CaO/Pd multilayer complexes, which were implanted with Pr ions at doses of 10^{12} , 10^{13} , and 10^{14} atoms/cm².

3. Results and Discussion

3.1. Structure of multilayer complex

An X-ray diffraction pattern using Cu ($K\alpha$) radiation was made to confirm the structure of the multilayer complex of the samples. Figure 1 shows the pattern for a Si wafer on which the multilayer structure was formed with the PLD technique.

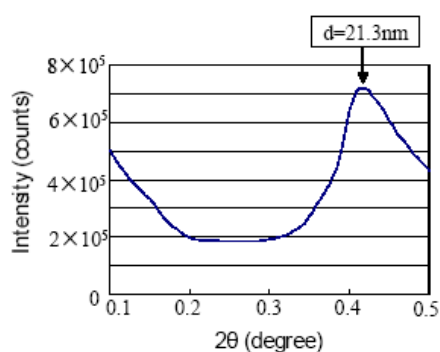
A peak is seen at very low angles indicating a super lattice structure with a spacing of 21.3 nm, which is close to the planned spacing of 20 nm. The PLD conditions, under which the multilayer film on the Si wafer was formed, were also used to form multilayer film on Pd substrates.

Table 1. Samples prepared for ICP-MS analysis (–: no data)

Sample No.	Multilayer	Cs deposition	D ₂ permeation	Max. upstream D ₂ pressure (atm)	Premeation Temp. (°C)	Average D ₂ flux (sccm)	Total permeated D ₂ (L)
1	Yes	Electro-chemical	Yes	5	70	0.77	18.7
2	Yes	Electro-chemical	Yes	9	70	1.6	45.4
3	Yes	Electro-chemical	Yes	5	150	1.6	34
4	Yes	Electro-chemical	Yes	2	70	0.71	14.3
5	Yes	Electro-chemical	Yes	9	150	3.6	111
6	Yes	Ion implantation	Yes	9	150	5.3	43
7	Yes	Ion implantation	Yes	9	150	2.6	74
8	Yes	Ion implantation	Yes	9	150	–	–
9	Yes	No	Yes	9	150	2	27
10	No	No	Yes	9	150	–	–
11	No	No	Yes	9	150	–	–
12	Yes	Ion implantation	No				
13	Yes	Ion implantation	No				
14	No	No	Yes				
15	No	No	Yes				
16	No	No	No				

3.2. Deuterium permeation

According to Iwamura et al. [6], the conversion rate of Cs to Pr increases with increasing D₂ gas permeation flux. The D₂ flux is sensitive to the surface conditions of the sample. Furthermore, it is generally observed that the permeation

**Figure 1.** Low angle X-ray diffraction pattern for the multilayer structure prepared on a Si wafer by PLD.

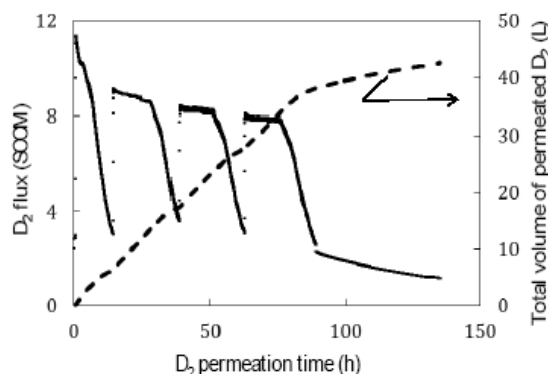


Figure 2. Permeation flux and total permeated D₂ volume vs. time for sample #6.

flux is relatively higher at the beginning of permeation but it decreases as permeation continues [7]. Therefore, it is not easy to keep a high D₂ flux during the whole duration of a D₂ permeation test.

Figure 2 shows an example of D₂ flux as a function of permeation time. As seen in Fig. 2, when the reservoir tank and the upstream side was filled up to about 900 kPa and kept at that pressure, the permeation flux was very high; about 8 sccm or more. The abrupt decreases of the flux sometimes seen in Fig. 2 were caused when the supply of D₂ to the tank was stopped. Under such condition, the D₂ pressure in the upstream side decreases with time and so does the permeation flux.

In Table 1, the average permeation flux and total permeated D₂ volume are shown for each sample.

3.3. Calibration of ICP-MS to detect Pr

In Fig. 3, the amounts of Pr measured by ICP-MS analysis were plotted as a function of the given doses of Pr ion implantation for the two series of samples. The amounts of Pr measured by ICP-MS is in close agreement with the ion implantation doses for both the Si wafer samples and CaO/Pd multilayer samples. It is seen that ICP-MS is capable of accurately detecting amounts of Pr as small as 1×10^{11} atoms/cm² in the samples of CaO/Pd multilayer complex as well as in high purity Si wafers. Figure 3 also indicates that contamination is low; nearly all of the Pr atoms in the multilayer complexes were implanted. The contamination level is estimated to be at most 10^{11} atoms/cm².

3.4. Amount of Pr in deuterium permeated samples

Figure 4 compares the amount of Pr measured by the ICP-MS technique for samples #1–#11. The results for the amount of Cs are also shown.

In Fig. 4, all the samples were treated with deuterium permeation. The samples #1–#8 are deposited with Cs either by electrochemical method or by ion implantation, while #9, #10, and #11 are samples without Cs deposition. Samples #10 and #11 are Pd substrates treated only with D₂ permeation.

It is seen in Fig. 4 that significant amounts of Pr are detected in the three samples #6, #7, and #8. In samples #2 and #4, amounts of Pr far exceeding 1×10^{11} atoms/cm² are also detected. From this figure, it is suggested that Pr is not detected in the samples which are not deposited with Cs before D₂ permeation treatment (#9, #10, and #11). This seems to be consistent with the idea that Pr emerges as a result of nuclear transmutation from Cs.

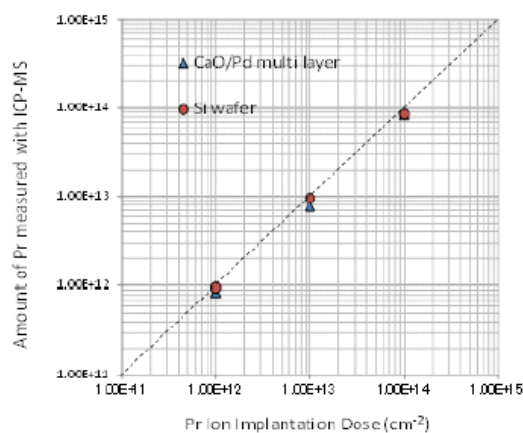


Figure 3. The amount of Pr measured by ICP-MS vs. ion implantation dose.

The samples #1–#5 are deposited with Cs by the electrochemical method. In these samples, however, as seen in Fig. 4, the amounts of Cs detected after D₂ permeation treatments are much smaller compared to the samples deposited with Cs by ion implantation. The detected amounts of Cs in samples #6–#8 are comparable with the ion implantation dose of 1.5×10^{15} atoms/cm². The electrochemical method seems to be unable to control the amount of Cs to be deposited.

If we assume that the Pr atoms detected in samples #6–#8 are converted from Cs atoms, the conversion rates, Pr/Cs, are in the order of 0.1% as shown in Table 2. The conversion rates are 1 to 2 orders of magnitude smaller than those reported by Iwamura et al.

Table 2 suggests that the conversion efficiency is more correlated with the total volume of permeated D₂, rather than the average D₂ flux.

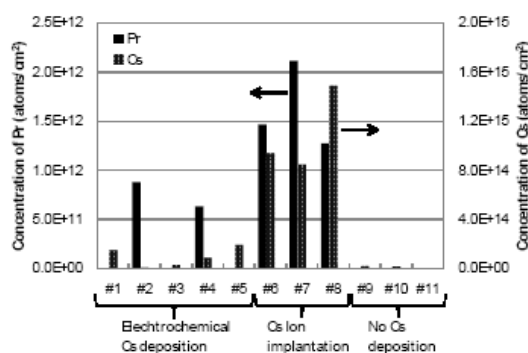


Figure 4. The detected amounts of Pr and Cs in the samples with D₂ permeation treatments.

Table 2. Conversion rate and permeation conditions

Sample No.	Pr/Cs (%)	Average D ₂ flux (sccm)	Total permeated D ₂ (L)
6	0.16	5.3	43
7	0.25	2.6	74
8	0.086	–	–

3.5. Amount of Pr in samples that were not permeated

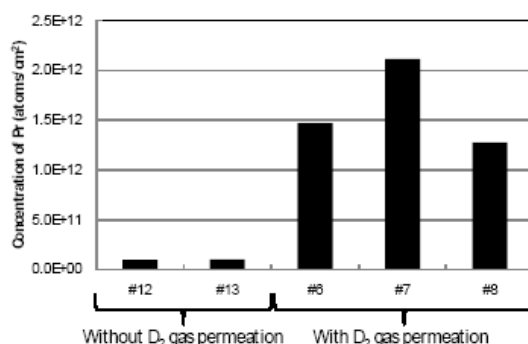
To confirm the effect of deuterium permeation on the emergence of Pr, the ICP-MS analyses were performed on control samples #12 and #13. These multilayer samples are deposited with Cs by ion implantation but not subjected to D₂ permeation treatment. The results are shown in Fig. 5. For comparison, the data for samples #6, #7, and #8 is shown. These were deposited with Cs by ion implantation and subjected to D₂ permeation.

As seen in Fig. 5, small amounts of Pr are detected in the control samples: 0.98×10^{11} atoms/cm² and 1.0×10^{11} atoms/cm² in #12 and #13, respectively. Such small amounts of Pr can be expected in the impurities in an ordinary environment. The amounts of Pr detected in the D₂ permeated samples are more than one order of magnitude larger than those detected in the control samples.

3.6. Amount of Pr in Pd substrates

In order to determine the amount of Pr contained in the Pd substrates, 3 Pd samples (#14 and #15) in the as-purchased state were analyzed with ICP-MS. These samples are totally dissolved. The results are shown in Fig. 6. For comparison, the result of #6–#8 is also shown.

As shown in the figure, Pd substrates contained small amount of Pr: 2.3×10^{10} atoms/cm², 9.0×10^{10} atoms/cm² and 7.9×10^{10} atoms/cm² for #14, #15, and #16, respectively. Therefore, the contamination of Pr in Pd substrates is at most 1.0×10^{11} atoms/cm². We conclude that the amounts of Pr detected in the samples #6–#8 are more than one order of magnitude larger than the total amount of Pr impurities in the Pd substrates used in the present study.

**Figure 5.** Comparison of the amounts of Pr in samples with and without D₂ permeation.

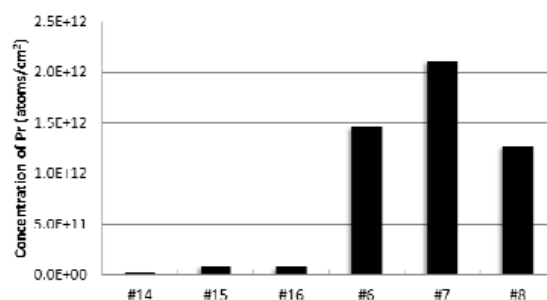


Figure 6. The amount of Pr in Pd substrates #14–#16. The result of #6–#8 is included for comparison.

4. Conclusions

Using ICP-MS, we measured the concentration of Pr in the range of 1.0×10^{10} atoms/cm². The amounts of Pr in the D₂ permeated samples were one order of magnitude larger than those in the control samples not permeated with D₂. We detected approximately 1.0×10^{12} atoms/cm² of Pr in the D₂ permeated Pd/CaO multilayer samples with ion-implanted Cs atoms. On the other hand, in the control samples, the amount of Pr was at most 1.0×10^{11} atoms/cm². If we assume that the Pr atoms detected were converted from Cs atoms, the conversion rates, Pr/Cs, were in the order of 0.1%. This value is much smaller than these reported by the Iwamura group.

Acknowledgment

We would like to thank T. Nishi, H. Azuma, S. Hibi for their discussions and support in the experiments. We are also grateful to N. Nakamura of Toyota Motor Corporation for discussions and encouragement.

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