Influence of Deuterium Gas Permeation on Surface Elemental Change of [88]Sr Ion-Implanted Pd and Pd/CaO Multi-layer System

T. Hioki[1], J. Gao[1], N. Takahashi[1], S. Hibi[1], A. Murase[1], T. Motohiro[1] and J. Kasagi[2]

[1] *Toyota Central Research and Development Laboratories Inc., Japan*
[2] *Laboratory for Nuclear Science, Tohoku University, Japan*

Abstract

The selected nuclear transmutation [88]Sr $\rightarrow$ [96]Mo reported by Iwamura et al. was studied by combining [88]Sr$^+$ ion implantation with time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements of the isotopic abundance ratio for Mo. For both the Sr ion implanted Pd and Pd/CaO multilayer foils, Mo was clearly observed after D_2 gas permeation, when the foils were subsequently heat-treated in air in order to remove S which condensed at the surface during the permeation treatment. For the Sr implanted Pd, the isotopic abundance ratio for the observed Mo was similar to that of natural Mo. For the Sr implanted multilayer foil, a strong peak at a mass close to [96]Mo was observed, although the peak was contaminated with an unknown peak, probably from GaAl or Ca_2O. An analysis of the TOF-SIMS data cannot be used to rule out the possibility of existence of "excess [96]Mo" exceeding the amount of [96]Mo of nature. To obtain a definite conclusion, further studies on the mechanism of the appearance of natural Mo and the origin and the behavior of the unknown peak are required.

1. Introduction

Nuclear transmutation with deuterium gas permeation through a Pd/CaO multilayer foil was first reported by Iwamura et al.[1] Using X-ray photoelectron spectroscopy (XPS), they demonstrated that Sr and Cs deposited on the surface of the multilayer foil changes to Mo and Pr, respectively, with D_2 gas permeation for a period of a week or so at a temperature as low as 343 K. The isotopic abundance ratio for the induced Mo was quite different from that for natural Mo; this observation with secondary ion mass spectrometry has suggested that the change is caused by a nuclear process. Using the D_2 gas permeation method, they have further found that Ba changes to Sm.[2]

It has been assumed that these results will be easily replicated in different laboratories. However, only a limited number of replication experiments have been reported so far.[3-5] One of the difficulties is to reproduce the high D_2 gas flow rate.[6] A D_2 gas flow rate through Pd is sensitive to the state of surface. Therefore, appropriate pretreatments of Pd as well as clean experimental environment are required to produce a high D_2 flow rate. We have reported that commercially available Pd foils are often contaminated with S [7] and a segregation of the S impurity on the surface during D_2 gas permeation results in a lowering of the flow rate.[8]

Furthermore, if S is on the surface, it is difficult to examine the generation of Mo by using XPS, because a S_{2s} peak in the XPS spectrum overlaps with Mo_{3d} peaks.[7]

In this study, both pure Pd foils and Pd foils with five Pd/CaO layers were implanted with 65-keV $^{88}Sr^+$ ions, these foils were subjected to D_2 gas permeation treatments at 343 K, and XPS and TOF-SIMS measurements were performed to examine the change of surface elements before and after D_2 gas permeation.

2. Experimental

2.1. Sample Preparation

Pd foils of 50 μm (purity: 99.97%) and 100 μm (99.95%) in thickness were obtained from Nilaco Corporation for substrates of the complex foils. Three types of sample were prepared as summarized in Table 1. Sample #3, for example, was prepared as follows. An as-purchased foil was first ultrasonically cleaned with ethanol and heat-treated in vacuum (5×10^{-5} Pa) at 1223 K for 5 hours and subsequently in air at 873 K for 10 minutes. Layers of CaO and Pd were piled up alternately on the substrate foil, using the RF sputter deposition method. The structure of the multilayer was the same as reported by Iwamura et al.: 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) / Pd (100 μm). Then ^{88}Sr was implanted in the multilayer foil with 65-keV $^{88}Sr^+$ ion bombardment, with a dose of 1×10^{16} ions/cm^2. Subsequently the foil was treated in air at 573 K for 10 minutes in order to remove carbonaceous materials deposited during the ion implantation. The sample was then subjected to D_2 gas permeation treatments at 343 K for 230 h.

Table 1. Procedures for sample preparation

	#1 (Sr-implanted Pd)	#2 (Pd)	#3 (Sr-implanted multilayer system)
Pretreatments	·50μmPd : ultrasonic cleaning with ethanol	·50μmPd : ultrasonic cleaning with ethanol ·1273K×10min in air	·100μmPd : ultrasonic cleaning with ethanol ·1223K×5h in vacuum ·873K×10min in air
Multilayer formation	——	——	·Pd(40nm)/ 4×[CaO(2nm)/Pd(18nm)]/ CaO(2nm)/Pd(100μm)
Ion implantation	·65keV $^{88}Sr^+$ 1×10^{16}/cm^2	——	·65keV $^{88}Sr^+$ 1×10^{16}/cm^2 ·573K×10min in air
Heat treatments	·1223K×5h in vacuum ·873K×10min in air	——	——
D_2 permeation	·260h at 343K, 200kPa	·70h at 343K, 200kPa	·230h at 343K, 200kPa
Heat treatment after D_2 permeation	·1273K×10min in air	·1273K×10min in air	·1273K×10min in air

2.2 Elemental Analysis

The XPS method was employed to examine the change of surface elements with D_2 gas permeation. The system used was ULVAC-PHI, Inc. model Quantera SXM (20 kV, 100 W). The X-ray used to excite the photoelectrons was the monochromatic Al-K_α line (1.438 keV). The size of the incident X-ray beam was 100×1500 μm^2. A TOF-SIMS (ULVAC-PHI, Inc. model TRIFT II) was used to measure isotopic abundance ratios. The primary ion was ^{69}Ga$^+$ (15 keV, 2 nA) generated from an enriched ^{69}Ga metal. The pulse width and frequency were 12 ns and 10 kHz, respectively. The raster area was 50×50 μm^2 and the analysis time 120 s.

3. Results and Discussion

3.1. Depth profile of ion implanted Sr

The depth profile of the implanted Sr was measured by XPS for a Pd foil bombarded by a 65-keV ^{88}Sr$^+$ beam with a dose of 3×10^{16}/cm^2. The data showed that the concentration of Sr is almost constant from the surface to 8 nm inside the foil, and below that gradually decreases with the depth. The concentration at the surface was about 5 at%. The depth profile was examined by a simulation using TRIM code. However, the simulation indicated that the profile has a marked peak at 13 nm from the surface and the concentration at the surface is about 1/5 of the peak concentration. This disagreement suggests that redistribution of the implanted Sr occurs during the ion implantation. From these data, the concentration of Sr at the surface for the samples #1 and #3 was roughly estimated to be about 1 at%.

3.2. ^{88}Sr$^+$-implanted Pd

Figure 1 shows obtained XPS spectra for the sample #1. The curve A is the one before D_2 permeation; neither Mo nor S exists on the surface. The curve B is after the D_2 permeation. Two peaks are clearly observed at 227.5 eV and 233.0 eV; this indicates the existence of a sulfate and a sulfide.[9] Sulfur is often contaminated in Pd as an impurity. Although its concentration is less than 1 ppm, it concentrates and forms sulfuric compounds at the surface during D_2 permeation. In order to remove the sulfuric compounds, the sample was subsequently annealed in air at 1273 K for 10 min. The curve C is the spectrum obtained after the D_2 permeation and the subsequent annealing. It shows two peaks at 232.4 eV and 235.5 eV. The energy difference is 3.1eV, which agrees well with that between Mo$_{3d5/2}$ and Mo$_{3d3/2}$.[9] The intensity ratio is about 1.5, which also agrees with that for Mo$_{3d5/2}$/Mo$_{3d3/2}$. Therefore, the two peaks correspond to Mo$_{3d5/2}$ and Mo$_{3d3/2}$, respectively. The observed binding energy for Mo$_{3d5/2}$ indicates that the chemical state of Mo is MoO3.[9] The oxidation is probably caused by the annealing in air after the permeation. Thus the appearance of Mo after D_2 permeation was clearly observed. Similarly, the appearance of Mo was confirmed for two other samples prepared following the same procedure as #1.

The TOF-SIMS spectrum for the observed Mo is shown in Fig. 2. All of the isotopes of Mo are observed and the isotopic abundance ratio is similar to that of natural Mo, as seen in Fig. 3.

We considered the possibility that the natural Mo comes from impurities in the Pd bulk, and these impurities concentrate on the surface during D_2 permeation. To examine this idea, the XPS measurement was performed for the sample #2. However, no Mo peak is observed, as

shown in Fig. 4. Thus, the cause of the natural Mo on the surface of the Sr implanted Pd foil is presently not clear.
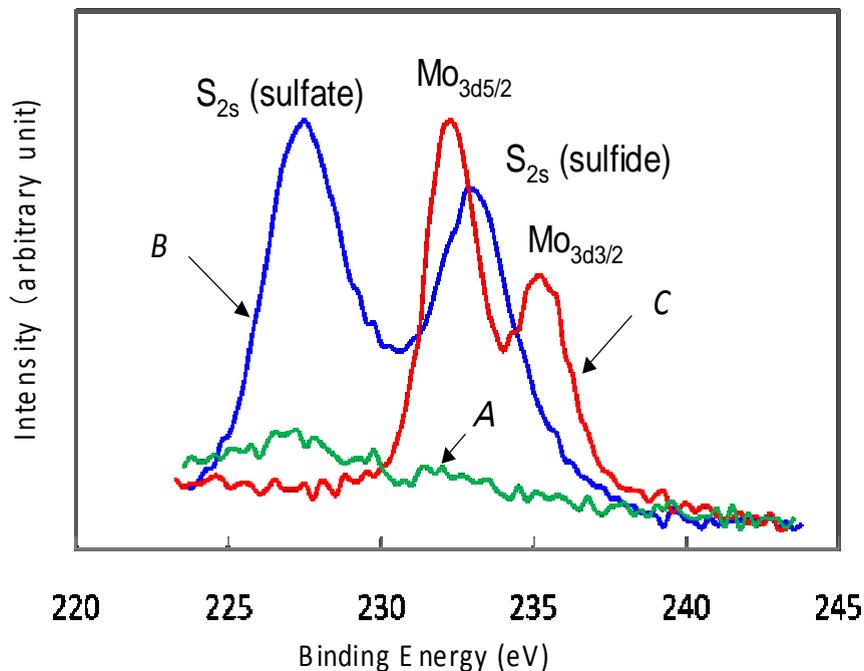

Figure 1. XPS spectra around Mo3d for sample #1; A: before permeation, B: after permeation, C: after permeation followed by annealing in air.
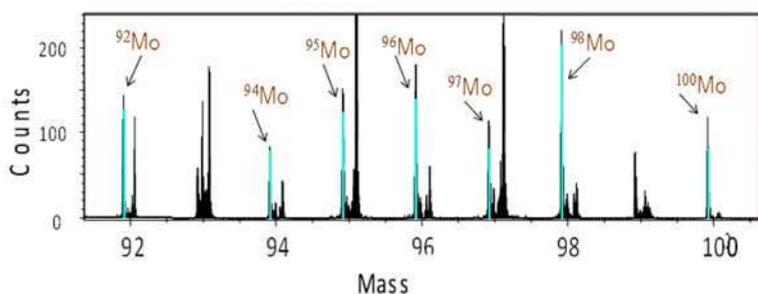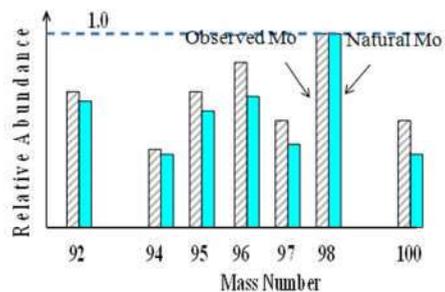

Figure 2. TOF-SIMS spectrum for sample #1.
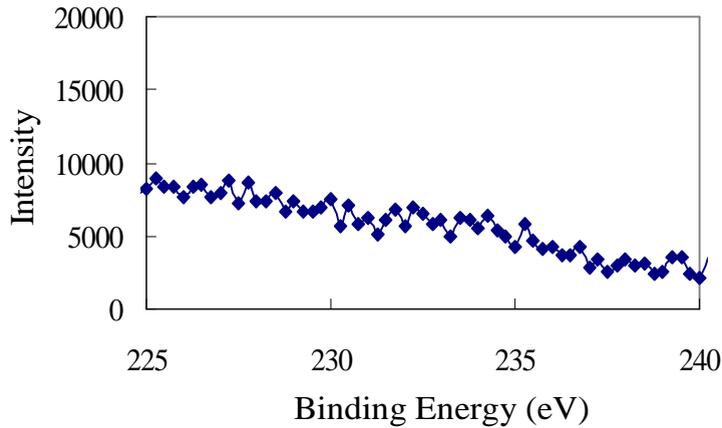
Figure 3. Isotopic abundance ratio

Figure 4. XPS spectrum around Mo$_{3d}$ for sample #2 after permeation followed by annealing in air.

3.3. ^{88}Sr$^+$- implanted Pd/CaO multilayer foil

For sample #3, Mo peaks are again clearly observed in the XPS spectrum when the sample is annealed in air after the permeation, as shown in Fig. 5.
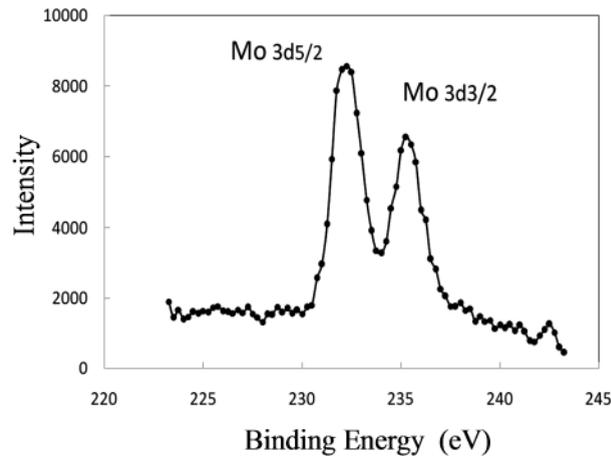

Figure 5. XPS spectrum around Mo$_{3d}$ for sample #3 after permeation followed by annealing in air.

Figure 6 shows TOF-SIMS spectra of the sample #3 after the permeation. On the surface of #3, the existence of ^{88}Sr is confirmed by a peak at Mass = 88 in Fig. 6-a, and all the isotopes of Mo appear as shown in Fig. 6-b. Inside sample #3, however, a stronger peak is observed at the mass of ^{96}Mo as is shown in Fig. 6-c, which show the spectrum after the 60-sec sputtering of Ga ions which removes a surface layer of about 2-3 nm in depth. As seen in Fig. 6-c, the peak at the mass of ^{96}Mo is strongest among the isotopes of Mo and the spectrum is similar to that reported by Iwamura et al. [1]
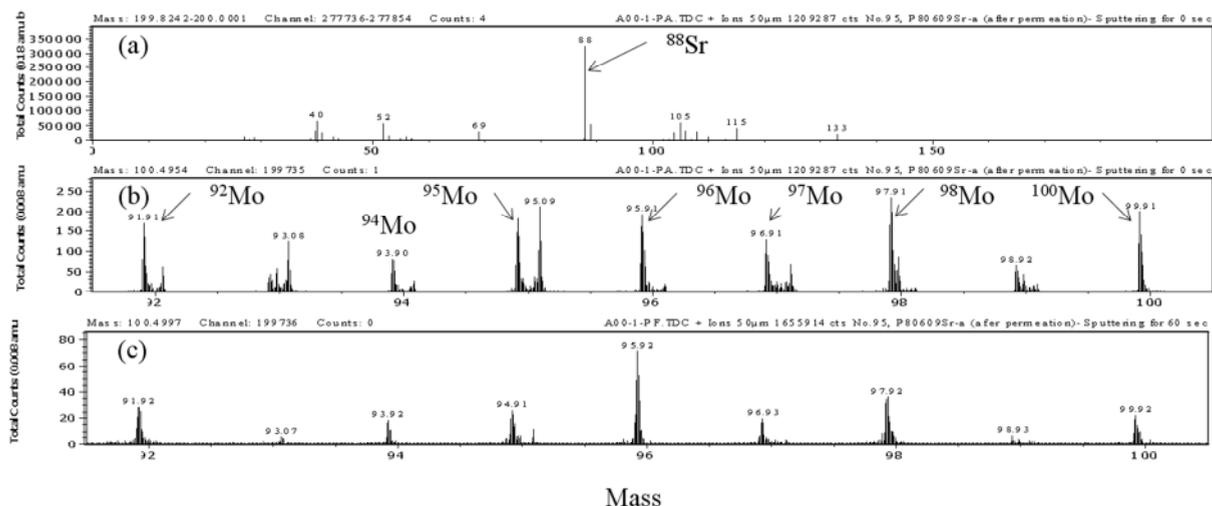
Figure 6. TOF-SIMS spectra for sample #3; (a) wide scan spectrum at surface; (b) spectrum around Mo at surface, (c) spectrum around Mo after sputtering for 60 s.

Figure 7 shows the spectra before D_2 permeation. They were taken for the area where Sr^+ ions had not been implanted. On the surface, neither Sr nor Mo isotopes are observed as shown in Figs. 7-a and 7-b, respectively. However, when the outermost surface layer is removed by sputtering for 60 sec, a peak at a mass close to [96]Mo is observed, as shown in Fig. 7-c. The peak cannot be due to natural [96]Mo, because no other Mo isotopes are seen, especially not the most abundant isotope [98]Mo. We refer to this peak as [96]X. Candidate materials for X are GaAl and Ca_2O as shown in Table 2.
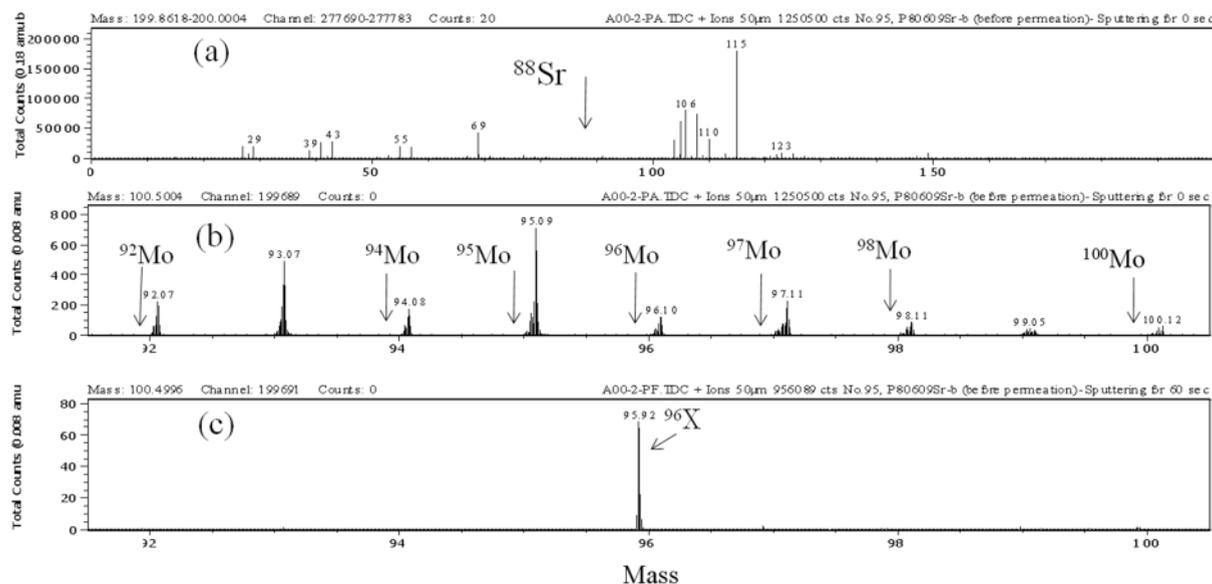

Figure 7. TOF-SIMS spectra for sample #3 (un-implanted area) before permeation; (a) wide scan spectrum at surface; (b) spectrum around Mo at surface, (c) spectrum around Mo after sputtering for 60 s.

Table 2. Candidates for X

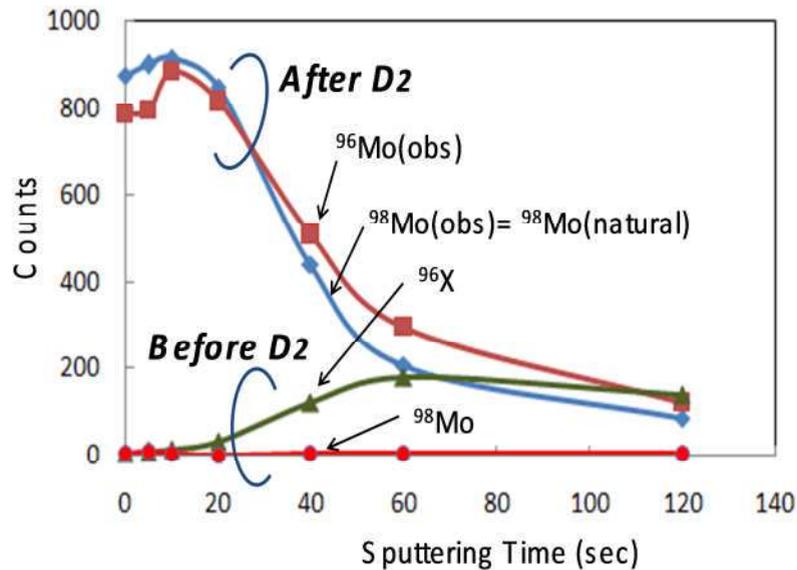| Molecule	Mass	Source Material
Ca_2O	95.920	Ca ⇔ CaO/Pd multilayer
GaAl	95.907	Ga ⇔ $^{69}Ga^+$: Primary ion for SIMS
		Al ⇔ impurity in Pd
^{96}Mo	95.905	

Figure 8. TOF-SIMS counts vs. sputtering time (depth).

Figure 8 shows total counts of each peak in TOF-SIMS spectra as a function of sputtering time before and after the D_2 permeation. It is noted that the intensity of ^{96}X is very small before the permeation, especially when the sputtering time is small, and after the permeation, the intensity of ^{96}Mo is larger than or comparable to that of ^{98}Mo. The natural isotopic abundance of ^{96}Mo is 69% of ^{98}Mo. Thus the intensity of ^{98}Mo should always be larger than that of ^{96}Mo, if the intensity of ^{96}Mo is only due to ^{96}Mo of nature. Therefore, we assume that the observed intensity of ^{96}Mo is the sum of those of ^{96}Mo of nature, ^{96}X, and excess ^{96}Mo, i.e.,

$$^{96}Mo(observed) = {}^{96}Mo(natural) + {}^{96}X + {}^{96}Mo(excess) \qquad (1)$$

where $^{96}Mo(natural) = 0.69 \times {}^{98}Mo(natural) = 0.69 \times {}^{98}Mo(observed)$, because the observed ^{98}Mo is natural, as shown in Fig. 8. We estimate the intensity of $^{96}Mo(excess)$ as shown in Fig. 9, assuming further that the intensity of ^{96}X has the same time dependence as the curve shown in Fig. 8 and is equal to that of $^{96}Mo(observed)$ at a sputtering time of 120 s. The intensity of

excess ^{96}Mo is about 1/4 of ^{96}Mo of nature, and it exists only in the surface layer within 6 nm. Because the total concentration of Mo is estimated to be about 0.3 at% from the XPS measurement, the concentration of excess ^{96}Mo is of order 0.01 at %. It should be stressed, here, that the intensity of the excess ^{96}Mo depends strongly on the behavior of the unknown peak ^{96}X. Therefore, a definite conclusion on the nuclear transmutation ^{88}Sr→^{96}Mo cannot be made without clarifying the origin of the ^{96}X.

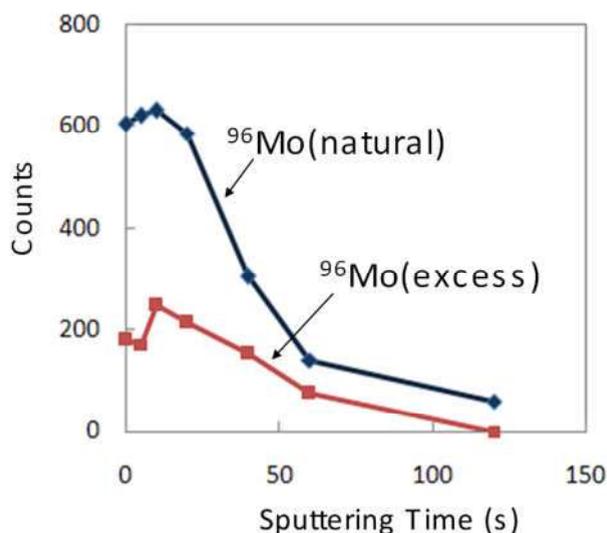**Figure 9. ^{96}Mo(excess) and ^{96}Mo(natural) versus sputtering time (depth).**

4. Summary

For both ^{88}Sr ion implanted-Pd and ^{88}Sr ion implanted-Pd/CaO multilayer foils, segregation of S onto the surface during D_2 permeation at 343 K was observed. When S on the surface was removed by annealing in air, Mo was clearly observed by XPS measurement.

For the ^{88}Sr ion implanted Pd foil, the TOF-SIMS analysis showed that the isotopic abundance ratio of observed Mo was similar to that of natural Mo. For the multilayer sample, however, the peak at the mass of ^{96}Mo was stronger than ^{98}Mo (or comparable to it). At the mass of ^{96}Mo, an unknown peak ^{96}X, probably arising from GaAl, or Ca_2O, was also found. An analysis of the peak intensity as a function of sputtering time cannot be used to rule out the possible existence of excess ^{96}Mo that exceeds the amount of ^{96}Mo in nature.

Further studies on the behavior of the unknown peak or trials to eliminate ^{96}X are required to confirm the existence of excess ^{96}Mo.

Acknowledgments

References

1. Y. Iwamura, et al., Jpn. J. Appl. Phys.41, (2002) pp. 4642-4648.

2. Y. Iwamura, et al., *Proc. ICCF11*, Marseilles, France, 31 October-5 November (2004) pp. 339-350.
3. T. Higashiyama, et al., *Proc. ICCF10*, Cambridge, USA, 24-29 August (2003) pp. 447-454.
4. A. Kitamura, et al., *Proc. ICCF12*, Yokohama, Japan, 27 November-2 December (2005) pp. 272-277.
5. F. Celani, et al., *Proc. ICCF10*, Cambridge, USA, 24 -29 August (2003) pp. 379-397.
6. Y. Iwamura, et al., *Proc. ICCF10*, Cambridge, USA, 24 -29 August (2003) pp. 435-446.
7. T. Hioki, et al, *Proc.ICCF13*, Sochi, Russia, 25 June-1 July (2007) in press.
8. J. Gao, et al., submitted to J. Vac. Sci. Tech.
9. J. F. Moulder, et al., *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, 1992.