



# Material properties of co-deposition formed on plasma facing materials in all-metal machine TRIAM-1M

M. Miyamoto <sup>a,\*</sup>, K. Tokunaga <sup>b</sup>, T. Fujiwara <sup>b</sup>, N. Yoshida <sup>b</sup>, TRIAM group<sup>b</sup>,  
Y. Morimoto <sup>c</sup>, T. Sugiyama <sup>c</sup>, K. Okuno <sup>c</sup>

<sup>a</sup> *Interdisciplinary Graduate School of Engineering Science, Science Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan*

<sup>b</sup> *Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

<sup>c</sup> *Radiochemistry Research Laboratory, Faculty of Science, Shizuoka University, 836 Oya, Shizuoka 422-8529, Japan*

## Abstract

To examine re-deposition of impurities on the plasma facing walls, material exposing experiments were carried out in TRIAM-1M under-long plus discharges. The exposed specimens and simulate specimens, which was made by physical vapor deposition in a low pressure oxygen atmosphere, were analyzed by means of X-ray photoelectron spectroscopy and thermal desorption spectroscopy. The deposition was composed mainly of Mo and O, and contained C and components of the vacuum vessel (304SS) slightly. The chemical state of deposited Mo was mixture of metal and oxide, and agrees with the one of simulate specimen implanted with deuterium ions, quantitatively. These results indicate that the co-deposited hydrogen and oxygen, affect the physicochemical properties of the depositions in TRIAM-1M. The retention properties of hydrogen isotope could be changed largely even if the least amount of deposition is formed on the surface.

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## 1. Introduction

In plasma confinement devices, plasma-facing materials (PFMs) are bombarded and heated up to high temperature by high fluences of energetic hydrogen ions and neutrals. This interaction causes erosion of PFMs and penetration of impurity atoms into the plasma. They will subsequently be deposited back onto the wall surface and form layers containing all elements used at the in-vessel wall. Such deposition-dominant surfaces have been observed in TRIAM-1M [1,2], high magnetic

field superconducting tokamak, as well as in many other tokamaks [3–7]. The formation of such deposition layer is anticipated to change the physical and chemical properties of the plasma-facing surface. Especially, change of hydrogen retention properties may have large impacts on fuel recycling and inventory under a long pulse operation. It is, therefore important to examine the properties of the deposited material formed on PFMs under actual tokamak plasma discharges.

In the present work, material properties of impurities deposition, such as chemical behavior and its effect on hydrogen retention, were studied by using the exposing specimen in TRIAM-1M and comparable vacuum-deposited materials. The composite elements and chemical states of the depositions were examined by means of X-ray photoelectron spectroscopy (XPS). Thermal desorption spectroscopy (TDS) were adopted for the

\* Corresponding author. Tel.: +81-92 583 7719; fax: +81-92 583 7690.

E-mail address: [mitsu@riam.kyushu-u.ac.jp](mailto:mitsu@riam.kyushu-u.ac.jp) (M. Miyamoto).

quantitative analysis of hydrogen retention in the depositions. The surface structures of the depositions, furthermore, were observed by scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Probe experiment and sample preparation

TRIAM-1M is a superconductive high field tokamak with a vessel made of 304SS, divertor plates of Mo and limiter of Mo. Non-metallic materials such as graphite have not used for in-vessel components. To examine the surface modification by impurities deposition, specimens mounted on the surface probe system [8] were exposed to discharges with the limiter configuration at the plasma facing side (P-side) and the electron drift side (E-side) in the scrape-off layer (SOL) as shown in Fig. 1. Silicon wafer specimens were used for this probe experiment because they have not used in TRIAM-1M, and metallic depositions formed on them could be analyzed easily. The duration of each discharge was about 1–2 min and reached in total 31 min. Typical plasma parameters were following:  $I_p = 25\text{--}28$  kA,  $n_e \sim 1 \times 10^{19}$  m<sup>-3</sup>,  $T_i = 1.5\text{--}2.1$  keV. The temperature of the probe head during discharges was almost constant at about 25 °C.

In addition, Mo depositions, Mo(O)/SS, were prepared by physical vapor deposition (PVD) in a low pressure oxygen atmosphere at  $p(\text{O}_2) = 5 \times 10^{-3}$  Pa in order to simulate the deposition in TRIAM-1M. The vacuum condition and deposition rate of Mo were adjusted to obtain a deposition ratio comparable to the TRIAM-1M case [1]. Bulk stainless steel 304SS specimens were used as substrates. The deposition thickness was measured by a thickness monitor during the vacuum deposition and controlled to be between 10 and 80 nm.

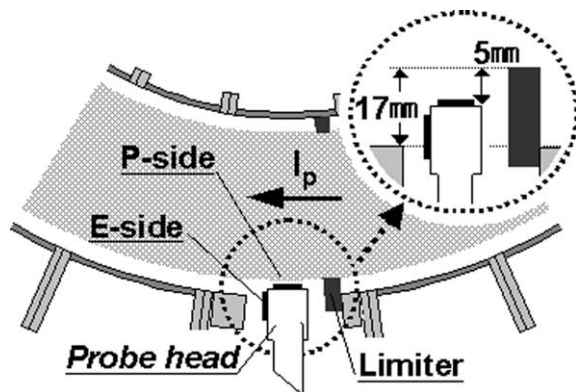


Fig. 1. The schematic view of the experimental set-up in TRIAM-1M.

### 2.2. XPS measurement

After the exposures, the specimens were taken out to the air to transfer to the XPS chamber. The composite elements and chemical states of the depositions on the silicon specimens were examined. The XPS system is composed of an electron hemispherical analyzer, a Mg-K<sub>α</sub> X-ray source and an argon ion gun for depth profiling and removing contaminant of top surface. The sputtering rate was estimated to be about  $1.7 \times 10^{-20}$  nm/ion, which had measured by using the Mo(O)/SS specimen whose thickness was known. In addition, the chemical shifts due to irradiation of co-deposited hydrogen were investigated by using Mo(O)/SS specimens implanted with 1 keV D<sub>2</sub><sup>+</sup> (500 eV D<sup>+</sup>) deuterium ions at RT. The ion irradiation and the XPS measurement were repeated sequentially until the ion fluence reached  $1.0 \times 10^{22}$  D/m<sup>2</sup>.

### 2.3. TDS measurement and SEM observation

TDS measurements were carried out for the quantitative analysis of hydrogen retention in the Mo depositions. The Mo(O)/SS specimens of various thickness were implanted with 6 keV D<sub>3</sub><sup>+</sup> (2 keV D<sup>+</sup>) deuterium ions at RT to a fluence of  $3 \times 10^{21}$  D/m<sup>2</sup>. After implantation, the thermal desorption of molecules composed of D<sub>2</sub>, DH, D<sub>2</sub>O and DHO was measured under heating with a ramping rate of 1 K/s by quadrupole mass spectroscopy (QMS). The signals were quantified by using the He calibrated leak bottle. The change of surface structure before and after the ion implantation and heating were observed with SEM.

## 3. Results and discussion

### 3.1. Chemical compositions of the deposition material

The peaks originated Mo, O and C as well as other impurities, such as Fe, Cr and Ni, which are components of the vacuum vessel (304SS), were detected as deposited elements in TRIAM-1M by the XPS measurement. In the measurements, only elements with *Z* above 3 can be detected, so hydrogen isotope cannot be detected. Fig. 2 shows the depth profile of the chemical compositions for the deposited material on Si specimen placed at the E-side with argon ion sputtering. As shown in the figure, the surface contamination layer was almost completely removed during the first 3 nm of ion sputtering. The average concentrations of the deposited elements in the middle of the layer were constant; Mo, O, C and Fe were 73, 14, 6.3 and 5.1 at.%, respectively. The tiny peaks originated from Cr and Ni were also detected, but these concentrations were less than 1 at.%. The thickness of the deposited layer was approximately 30 nm.

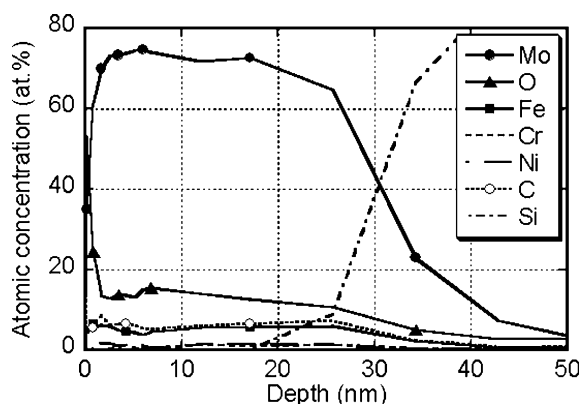


Fig. 2. The depth profile of the chemical compositions for the deposited material on Si substrate placed at the E-side in TRIAM-1M.

In the case of the specimen placed at P-side, the large Si 1s peak was detected without argon sputtering. This means scarcely any depositions formed at the P-side, because the range that can be analyzed by XPS is restricted to the near surface. This minimum net deposition of impurities at P-side seems to result from the lowest sticking rate and higher sputtering rate, because ionized particles drift along the magnetic field parallel to the P-side.

### 3.2. Chemical state of the deposition material

As in previous studies [1], it is already confirmed that the deposition formed in TRIAM-1M has the similar properties as the Mo(O)/SS specimen in the viewpoint of microstructures and thermal stabilities. Both have similar defective structures; the grain size was about 1 nm and crystal structure was not bcc but fcc. On the other hand, the chemical state of each deposition was not necessarily same.

In order to examine the chemical state of the deposited Mo, XPS Mo3d spectra were fitted by some symmetric Gaussian/Lorentzian functions. When Mo 3d spectra were fitted with the assumption that the deposited Mo exists as metallic Mo ( $\text{Mo}^0$ ),  $\text{MoO}_2$  ( $\text{Mo}^{4+}$ ) and  $\text{MoO}_3$  ( $\text{Mo}^{6+}$ ), Mo 3d spectra obtained in this study were recreated adequately. For this fitting procedure, a Shirley-type background subtraction was applied. The Mo  $3d_{5/2}$  peaks from  $\text{Mo}^0$ ,  $\text{Mo}^{4+}$  and  $\text{Mo}^{6+}$  at  $227.7 \pm 0.1$ ,  $229.3 \pm 0.1$  and  $232.4 \pm 0.1$  eV, respectively, were used according to Ref. [9]. One should note that these chemical bonds were distributed locally because the clear crystallographic structure of oxides were not observed [2] and the more than half of the constituting atoms is expected to locate on or near the grain boundaries.

Table 1 lists the comparison of the Mo chemical states before and after argon ion sputtering until a steady state was reached for the deposition in TRIAM-

Table 1  
Comparison of deposited Mo chemical states after and before argon ion sputtering

	Atomic concentrations (at.%)		
	Mo	$\text{MoO}_2$	$\text{MoO}_3$
<i>Top surface</i>			
TRIAM-deposition	26.8	6.9	66.3
Mo(O)/SS	0.0	33.0	67.0
<i>Middle of the layers</i>			
TRIAM-deposition	79.8	20.2	0.1
Mo(O)/SS	39.9	40.7	19.4

1M and the Mo(O)/SS. The oxidation states of both depositions at the top surface were similar qualitatively. More than half of Mo in these depositions oxidized into the most stable oxide  $\text{MoO}_3$  by exposing to air due to a large absorption capability of the defective surface. It seems that these drastic oxidation are characteristic phenomena of these depositions whose surfaces were consisted with fine crystal grains and many grain boundaries.

However, in the middle of the layers, the ratio of oxides for the Mo(O)/SS was much higher than that for depositions in TRIAM-1M. This difference was caused by co-deposited hydrogen during the discharges. The dependence of the Mo chemical state on deuterium ion fluence of 1.0 keV  $\text{D}_2^+$  is shown in Fig. 3. The ratio of metal Mo to Mo-oxide increased with the increasing the deuterium ion fluence. This change means deoxidization of Mo-oxide by deuterium irradiation. The ratio of Mo,  $\text{MoO}_2$  and  $\text{MoO}_3$  in the Mo(O)/SS implanted with 1 keV  $\text{D}_2^+$  deuterium ion to a fluence of  $1 \times 10^{22}$   $\text{D}/\text{m}^2$  was determined to be 81, 18 and 1 at.%, respectively. This ratio almost agrees with the one of the deposition formed in TRIAM-1M.

These results indicate that a large amount of hydrogen and oxygen co-deposit with Mo on the surface, and

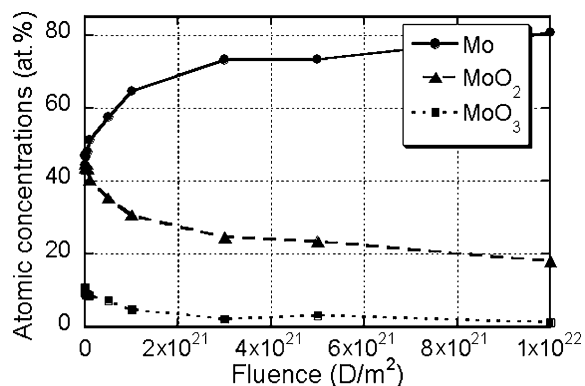


Fig. 3. The dependence of Mo chemical state on deuterium ion fluence of 1 keV  $\text{D}_2^+$  for Mo(O)/SS.

play an essential role in the physicochemical properties of the depositions formed in TRIAM-1M.

### 3.3. Deuterium retention in the deposition material

Fig. 4 shows thermal desorption spectra of  $D_2$  ( $m/e = 4$ ) and  $D_2O$  ( $m/e = 20$ ) obtained from the Mo(O)/SS specimens of various thickness implanted with 6 keV  $D_3^+$  at room temperature to a fluence of  $3 \times 10^{21} D/m^2$ . Data for bulk 304SS and Mo is also plotted in the figure for comparison. For each Mo(O)/SS, the large desorption peaks of  $D_2$  and  $D_2O$  were observed, and desorption occurs until high temperature even at 800 K.

In case of  $D_2$ , the largest desorption occurred for the Mo(O)/SS, whose thickness was 10 nm. This thickness was about equal to the projected range of 2 keV  $D^+$  ions, therefore the large amount of deuterium had been

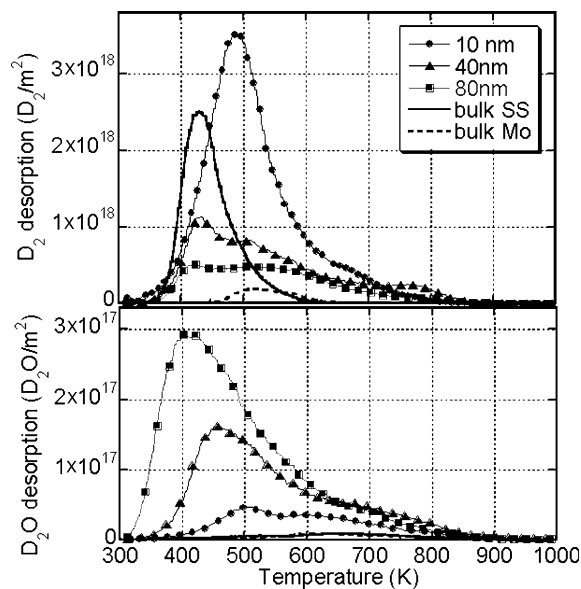


Fig. 4. Thermal desorption spectra of  $D_2$  and  $D_2O$  obtained from the Mo(O)/SS specimens of various thickness, Mo and 304SS specimens implanted with 6 keV  $D_3^+$  at room temperature to a fluence of  $3 \times 10^{21} D/m^2$ .

trapped in the interface of the deposition and the substrate as deuterium molecules. This interpretation of the trapping mechanism was supposed by the formation of blisters for only the Mo(O)/SS whose thickness was 10 nm as shown in Fig. 5(a). It was thought that the interface works as a diffusion barrier for deuterium implanted near the interface, so the large amount of deuterium was trapped in blisters through the recombination in the interface. These blisters were flaked after annealing for the TDS measurement up to 1100 K (Fig. 5(b)). The blistering and flaking were observed in TRIAM-1M, and considered to be a source of metallic dust [10]. On the other hand, with increasing in the thickness of deposition, the sudden decreasing of  $D_2$  desorption and relative increasing of  $D_2O$  desorption were observed. This implies that the most of deuterium were trapped in the deposition layer, which contains the large amount of oxygen, without being trapped in the interface.

Due to the strong trapping effect of the interface and the deposition, the total amount of desorbed deuterium for Mo(O)/SS specimens without regard to the thickness had reached 10 or more times of that for bulk Mo and was even larger than for stainless steel, which is known as a strong hydrogen trapping material. With these results, the retention of hydrogen isotopes can be changed largely, even if a small amount of deposition is formed on the PFMs.

In TRIAM-1M, large continuous wall pumping and temporal reduction of wall exhaust capability in the ultra-long discharges were reported [11]. A relation with the depositions continuously formed under discharges is expected.

## 4. Summary

The physicochemical properties and the hydrogen retention properties of depositions formed in TRIAM-1M have been determined. The major elements of the deposition were Mo and O. The components of the vacuum vessel (304SS) and C were also contained slightly in the deposition. The chemical state of the de-

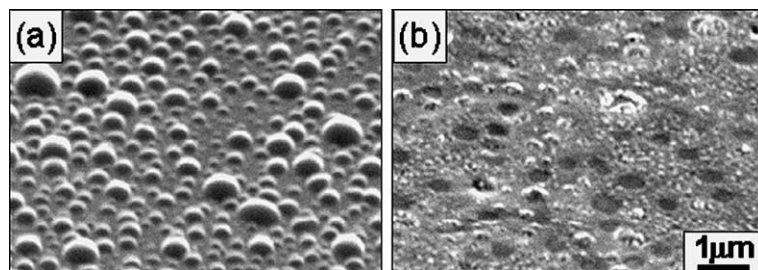


Fig. 5. The blisters of the Mo(O)/SS surface implanted with 6 keV  $D_3^+$  at room temperature to a fluence of  $3 \times 10^{21} D/m^2$  (a). These blisters were flaked after annealing for the TDS measurement (b).

posited Mo in TRIAM-1M was mixture of metal and oxide, but the ratio of oxides was much smaller than that for the Mo(O)/SS specimen. The cause of this smaller ratio was explained by that co-deposited hydrogen brought about deoxidization of Mo-oxides in the depositions. Adapting the affect of co-deposited hydrogen and oxygen, the vacuum deposited Mo had the same properties as the deposition in TRIAM-1M in the viewpoint of not only microstructure but also the chemical state. The depositions showed very large and strong trapping effect of hydrogen isotope even if a small amount of deposition is formed on the surface.

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