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Effect of substrate temperature on microstructure and deuterium retention of molybdenum co-deposition with oxygen

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Abstract

The formation of co-deposition has a large impact on plasma surface interactions. It has been reported that co-deposition of Mo and O changed the surface properties of the TRIAM-1M tokamak and affected the confinement of the plasma. In this work, the influence of the substrate temperature on the crystallographic structure and hydrogen retention of the Mo–O co-deposition was studied by means of transmission electron microscopy and thermal desorption spectroscopy. Microstructures and hydrogen retention of the depositions showed a remarkable substrate temperature dependence. The deposition formed at high temperatures (>673 K) was found to be Fe_2MoO_4, which is the oxide of deposited elements and substrate elements. For the deposition formed and implanted at high temperatures (>573 K), the retention of deuterium is negligibly small. These results indicate that the retention of the hydrogen isotope is expected to become quite small by optimizing the wall temperature, even if the peculiar material is formed on the plasma-facing surface.

1. Introduction

In plasma confinement devices, plasma-facing materials (PFMs) are bombarded and heated up to high temperatures by high fluences of energetic hydrogen ions and neutrals. This interaction causes erosion of PFMs and introduction of impurity atoms into the plasma which are subsequently deposited back onto the wall surface and form layers containing all elements used on the in-vessel wall. Such deposition-dominant surfaces have been observed in many tokamaks [1–5]. The formation of such deposition layers is anticipated to change the physical and chemical properties of the plasma-facing surface. Especially, the change of hydrogen retention properties may have large impacts on the fuel recycling and inventory under long pulse operation.

It was shown in previous studies [6,7] that the co-deposition of molybdenum (Mo) with small amounts of oxygen (O) formed in TRIAM-1M, a high magnetic field superconducting tokamak, had a defective structure and showed very large and strong deuterium retention. As PFMs will be used at high temperature in a future fusion reactor such as ITER, it is important to understand the relation between the properties of deposition and the wall temperature. In the present work, therefore, the influence of the substrate temperature on the crystallographic structure and hydrogen retention of the Mo–O co-deposition was studied by means of transmission electron microscopy (TEM) and thermal desorption spectroscopy (TDS).

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2. Experimental

2.1. Sample preparation

Mo depositions were prepared by physical vapor deposition in a low pressure oxygen atmosphere at $p(O_2) = 5 \times 10^{-3}$ Pa. The vacuum condition and deposition rate of Mo were adjusted to obtain a deposition ratio comparable to the TRIAM-1M case [6]. Pre-thinned or bulk stainless steel 304SS specimens were used as substrates. The substrate temperature during vacuum deposition was controlled between room temperature (RT) and 773 K. The deposition thickness was measured by a thickness monitor during the vacuum deposition and was regulated at about 50 nm for all specimens.

2.2. TEM observation and TDS measurements

The microstructure of the depositions formed at various substrate temperatures was examined by TEM. The electron diffraction images were used to examine the crystallographic structure. TDS measurements were carried out for the quantitative analysis of hydrogen retention in the Mo depositions. The depositions formed at various substrate temperatures were implanted with 6 keV-D_3^+ (2 keV-D^+) deuterium ions at RT to a fluence of 3×10^{21} D/m^2. It is likely that the majority of the implanted ions were stopped within the depositions, because their thickness of about 50 nm was larger than the projected range of 2 keV-D^+ ions (<30 nm). To simulate the high temperature use of PFMs, the formation of the depositions and the deuterium implantation were carried out in the range of RT to 673 K. After implantation, the thermal desorption of molecules composed of D_2, DH, D_2O and DHO was measured under heating with a ramping rate of 1 K/s by quadrupole mass spectrometry. The signals were quantified by using the He calibrated leak bottle.

3. Results and discussion

3.1. Microstructure of the depositions

Fig. 1 shows dark field images and corresponding electron diffraction patterns of the Mo depositions formed in oxygen atmosphere at various substrate temperatures. The images were obtained from a part of the first broad diffraction ring. Under this image condition, only the grains satisfying the Bragg condition are designated as a white contrast. Microstructures of the depositions showed a strong dependence on the substrate temperature. As reported in Ref. [6,7], the depositions formed at RT consisted of fine fcc crystal grains only around 1 nm in diameter, which are similar to that formed in TRIAM-1M [6]. An increase of the substrate temperature caused not only coarsing of the grains but also a change of the crystal structure. As a result of the

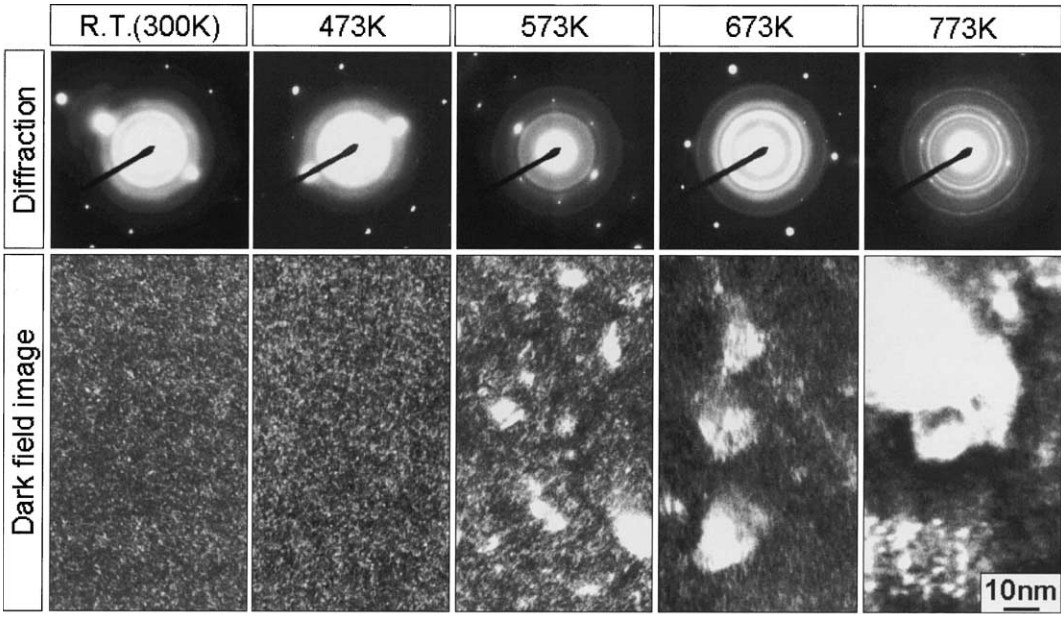

Fig. 1. Electron diffraction patterns and microstructures of the Mo depositions formed in oxygen atmosphere ($p(O_2) = 5 \times 10^{-3}$ Pa) at various substrate temperatures. Images with white contrasts show individual grains.

detailed XRD analysis, the patterns above 673 K, especially at 773 K, agreed with those of Fe_2MoO_4. This implies that a mixed-material layer was formed from deposited Mo and Fe, major components of the 304SS substrate, in the sub-surface layer of the specimen. This result indicates that interdiffusion and solid state reaction between deposition and substrate are also an important factor to determine the properties of the co-depositions at elevated temperature. Such phenomenon was observed in a carbon deposition layer on a beryllium plate, which formed Be_2C due to heating in vacuum [8].

The formation of mixed-material layers will bring about further modifications of the PFMs surface. As discussed in the following paragraph, the mixed material results in a large change of surface properties.

3.2. Deuterium retention in the Mo depositions

Fig. 2 shows thermal desorption spectra of D_2 ($m/e = 4$) and D_2O ($m/e = 20$) obtained from the deuterium ion irradiated Mo depositions, which were formed in an oxygen atmosphere at $p(O_2) = 5 \times 10^{-3}$ Pa on the 304SS substrate kept at various temperatures. Data for bulk Mo and 304SS are also plotted in the figure for comparison. Though the details depend on the substrate temperature, the total amount of the retained deuterium in co-deposited Mo is in general much higher than in bulk Mo. At least three desorption peaks of D_2 from the Mo co-deposition formed at RT are distinguished at around 440, 520 and 760 K. With increasing deposition temperature, the desorption above 600 K

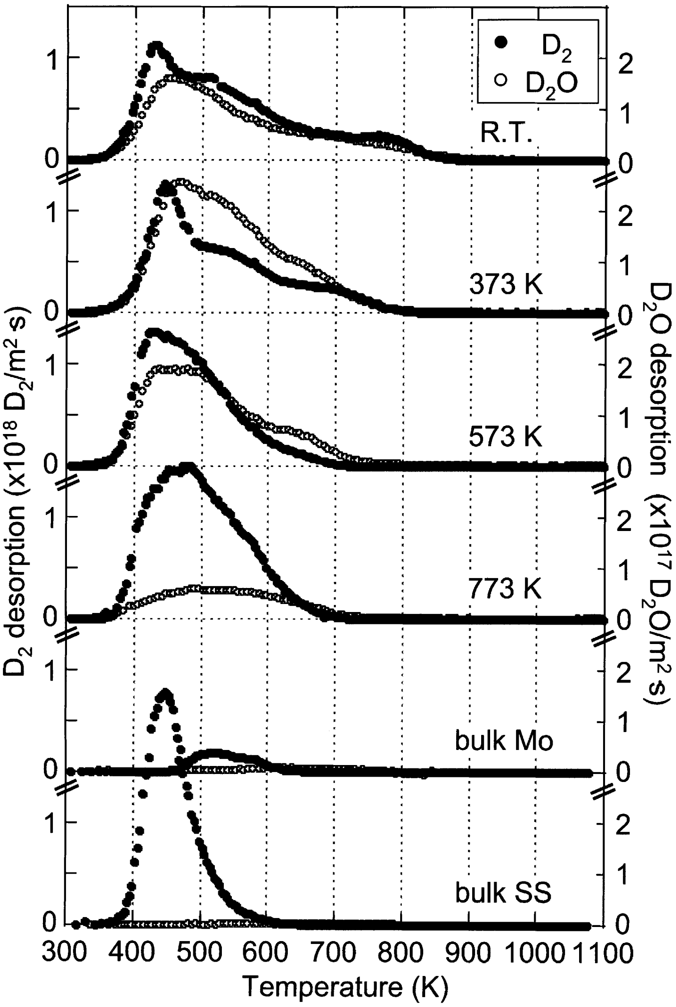

Fig. 2. Thermal desorption spectra of D_2 and D_2O obtained from the Mo depositions formed at various substrate temperatures, Mo and 304SS specimens implanted with 6 keV-D_3^+ at RT to a fluence of 3×10^{21} D/m^2.

decreased and most of the deuterium detrapped around 470 K. In the case of D_2O, a significant amount of desorption was observed for all Mo co-depositions but not for bulk Mo and 304SS. As shown in Fig. 2, the desorption processes of D_2O and D_2 showed similar tendency for each Mo deposition. This means that the desorption of D_2 had a close relation to the oxygen release from Mo depositions. It seems that the peaks at 520 and 760 K are caused by the existence of unstable oxygen, which has been absorbed on the defective surface consisted of fine crystal grains with a large absorption capability and involved in the deposited layer during vacuum deposition. However, at elevated temperatures, where Fe_2MoO_4 is formed, the amount of D_2O decreases because most of oxygen is tightly trapped as oxide. The peak of the high temperature Mo depositions observed around 470 K is detrapped from Fe_2MoO_4. These changes of deuterium trapping were observed at a rather low temperature even at 373 K and became distinct at high temperatures.

Table 1 shows the amounts of desorbed deuterium from Mo depositions formed at various temperatures and of bulk Mo and 304SS. Each datum is the sum of the desorbed deuterium as DH, D_2, DHO and D_2O molecules. In contrast to the small retention in bulk Mo, all of the Mo depositions show large retentions. It is worth to note that trapping of deuterium in each Mo deposition is even larger than in stainless steel, which is known as a strong hydrogen trapping material. As shown in Table 1, the ratio of deuterium desorbed as water (DHO or D_2O) decreased drastically for the Mo deposition at 773 K. This fact evidences that the amount of unstable oxygen is reduced by the formation of the stable oxide Fe_2MoO_4. On the other hand, the ratio of deuterium desorbed as DH or D_2 increased gradually with increasing temperature above 373 K due to the strong trapping effect of Fe_2MoO_4.

Table 1
Retained deuterium in the Mo depositions formed at various substrate temperatures, Mo and 304SS specimens implanted with 6 keV-D_3^+ at RT to a fluence of 3×10^{21} D/m^2

Specimen	Temp. (K)	Deuterium desorption ($\times 10^{20}$ D/m^2)		
		D_2 and DH	D_2O and DHO	Total
Mo deposition	RT	6.4	2.6	8.9
	373	5.3	3.3	8.5
	573	5.5	2.6	8.1
	773	6.3	1.1	7.4
Molybdenum		0.53	0.12	0.64
Stainless steel		4.2	0.16	4.4

Fig. 3 and Table 2 show the results of the TDS measurements when the formation of the depositions and the deuterium ion implantation were carried out at the same temperature in the range of RT to 673 K. As shown in the figure and table, the effect of temperature seems to be sensitive. Especially above 573 K, the retention of deuterium is negligibly small. With this result, the retention of hydrogen isotopes in the Mo depositions can be suppressed by keeping the wall temperature above 573 K, even if the peculiar material is formed on the surface.

The present work indicates that the microstructure and the hydrogen retention properties of the PFMs surface largely depend on the wall temperature where the co-deposition is formed. Taking into account the fact that the formation of mixed material is made up of deposited elements and substrate elements at elevated temperature, one should pay more attention to the combination of PFMs and their properties.

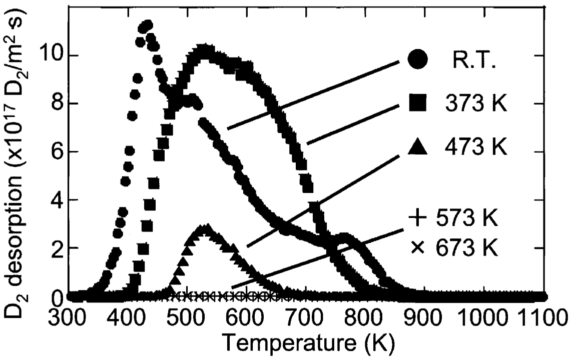

Fig. 3. Thermal desorption spectra of D_2 ($m/e = 4$) obtained from the Mo depositions implanted with 6 keV-D_3^+ at a fluence of 3×10^{21} D/m^2. The Mo depositions were formed and implanted at the same substrate temperature.

Table 2
Retained deuterium in Mo depositions implanted with 6 keV-D_3^+ at a fluence of 3×10^{21} D/m^2

Temp. (K)	Deuterium desorption ($\times 10^{20}$ D/m^2)		
	D_2 and DH	D_2O and DHO	Total
RT	6.4	2.6	8.9
373	6.2	0.82	7.0
473	0.91	0.41	1.3
573	0.04	0.14	0.18
673	0.05	0.15	0.20

The Mo depositions were formed and implanted at the same substrate temperature.

4. Summary

The influence of the substrate temperature on the crystallographic structure and hydrogen retention of the Mo deposition has been examined by means of TEM and TDS. The deposition above 673 K is Fe_2MoO_4 with large grain sizes, which is formed by interdiffusion and solid state reaction between deposition and substrate. Large desorption of D_2 and D_2O occurred from each Mo deposition, while desorption processes were different from each other due to the formation of the oxide. The retention of deuterium is negligibly small from the deposition formed and implanted above 573 K. These results indicate that the retention of hydrogen isotopes is expected to become quite small by optimizing the wall temperature, even if the peculiar material is formed on the plasma-facing surface.

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