

## Oxygen Plasma Interactions with Molybdenum: Formation of Volatile Molybdenum Oxides

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The oxidation of molybdenum by oxygen plasma was studied. The oxygen plasma was discharged by helicon wave at the frequency of 18.1 MHz and at the power of 200W. The weight change of molybdenum in oxygen plasma was measured at 400 °C and at oxygen pressure of 5 Pa. The specimen was found to be oxidized and to lose its weight drastically with the oxygen plasma, while the weight change of the specimen in the oxidation without plasma was not observed under the same conditions. The energetic species of oxygen atoms generated by rf plasma is regarded to accelerate the oxidation of molybdenum and the oxidation leads to the formation of volatile molybdenum trioxide at the surface.

**Keywords:** molybdenum, oxidation, oxygen plasma, oxygen

Molybdenum based alloys are used for high temperature applications such as resistive furnaces and spacecraft applications and fusion devices because of their high melting point, high-temperature strength and good thermal conductivity. In oxidizing atmosphere, however, it is widely known that molybdenum begins to sublime forming a molybdenum trioxide above 500 °C and the oxide volatilization is important at 600 °C. Although the oxidation behavior of molybdenum has been studied [1, 2], the behavior of molybdenum with oxygen plasma under low oxygen pressure has not been well reported. It is important to investigate the oxidation characteristics of molybdenum which is exposed to the plasma environments from the viewpoint of the contamination to the plasma, and the structural toughness. In this study, the influence of the rf oxygen plasma on molybdenum was examined and discussed in comparison with thermal oxidation.

The experimental apparatus with rf plasma is schematically shown in Fig.1. The apparatus consists of the rf discharge chamber, the reaction chamber with sample holder, the gas-feeding and evacuation system, and the data acquisition system. The rf power of 200 W with 18.1 MHz is launched to oxygen plasma

in a pulsed manner ( rf duty ratio: 50 sec. on/ 10 sec. off) through the helicon antenna. The magnetic field was supplied by three magnetic coils. The specimen was set on the sample holder equipped with a heater and a thermocouple; the molybdenum specimen was kept at 400 °C, at which temperature the sublimation of molybdenum oxide is neglected. Oxygen was fed into the chamber through the leak valve, and is evacuated from the chamber by the diffusion pumps combined with rotary pump. The pressure in the chamber was measured by an ion gauge and a capacitance manometer, and the oxygen pressure was maintained at the most appropriate pressure of 5 Pa for generating the stable oxygen plasma during the experiment time. The base pressure of the reaction chamber was below  $1 \times 10^{-3}$  Pa.

The molybdenum specimen was pre-conditioned by means of mechanical polishing with SiC paper, P800 through P1200 grit, and with 1 μm diamond paste. The sample was degreased with acetone in an ultra sonic cleaner and stored in a vacuum desiccator until testing. The weight change was measured by weighing the sample before and after the oxidation test. The thermal oxidation was also conducted under the same conditions of oxygen pressure and temperature, in order to compare with the plasma oxidation.

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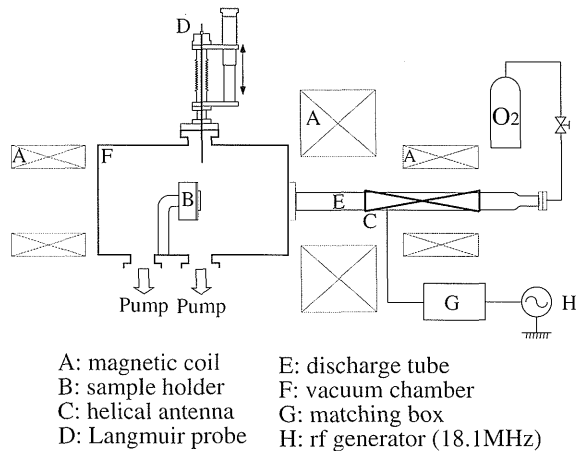


Fig. 1 Schematic diagram of the experimental chamber.

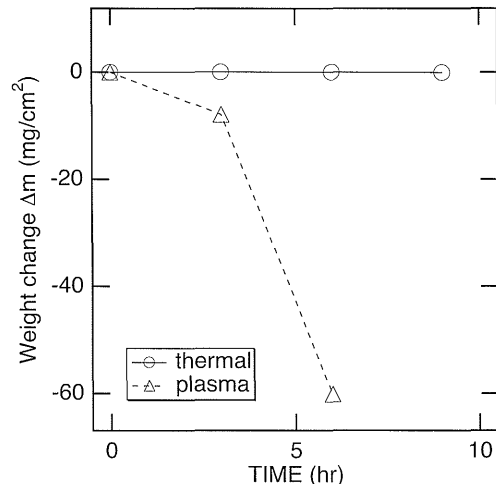
Plasma was diagnosed, using a Langmuir probe. The probe rod was positioned at the sample holder. The electron temperature, plasma density, and plasma potential were 4 eV,  $2 \times 10^{16} \text{ m}^{-3}$  and 20 V, respectively, at the oxygen pressure of 5 Pa. The weight change of molybdenum specimen are plotted as a function of time in Fig. 2. After thermal oxidation, the weight change of molybdenum was confirmed to be negligibly small. Adherent oxide was considered to be formed on the molybdenum surface at the experimental temperature of 400°C and at 5 Pa in the similar process to the one in an atmospheric condition [3].

On the other hand, the large weight changes were seen in the plasma oxidation process. Molybdenum metal is oxidized, forming three layers [4]: the outermost  $\text{MoO}_3$ , the innermost  $\text{MoO}_2$  to the metal and the intermediate layer between  $\text{MoO}_2$  and  $\text{MoO}_3$ , which can be expressed by  $\text{Mo}_x\text{O}_{3x-1}$  ( $\text{Mo}_4\text{O}_{11}$ ,  $\text{Mo}_8\text{O}_{23}$ ,  $\text{Mo}_9\text{O}_{26}$ ).  $\text{MoO}_3$  is distinctly volatile; the melting point is 795°C and the sublimation temperature is 1155°C.  $\text{MoO}_2$ - $\text{MoO}_3$  eutectic is 778°C. At higher temperatures, the evaporation rate of molybdenum oxide increases because of the presence of the liquid phase.

The volatilization rate of  $\text{MoO}_3$ , however, is very small below about 600°C. The  $\text{MoO}_2$  layer grows to a stable thickness at low temperatures. The oxidation of molybdenum occurs by the diffusion of oxygen ions through the oxide to the metal-metal oxide interface [5–7]. The thickness of the oxide layer is considered to be controlled by the rate of diffusion of oxygen ions through the suboxide, and the path length

for diffusion of oxide ions will be constant. The results indicate that the oxygen plasma increases the supply of oxygen ions to  $\text{Mo}$ - $\text{MoO}_2$  interface, and consequently the growth of molybdenum oxide promotes the formation of  $\text{Mo(VI)}$  oxides,  $\text{MoO}_3$ , which is volatile and sublimates.

To promote the oxidation, strong oxidizing materials are necessary. In oxygen plasmas, oxygen molecules are dissociated and oxygen atoms are generated. The dissociation energy of oxygen is 5.16 eV. Furthermore, oxygen atoms are ionized in the plasma. The energetic species of oxygen in the plasma is considered to work as the oxidizing reagent for molybdenum from metal to  $\text{MoO}_3$ . The present results indicate a caution for the use of molybdenum as the heat resistant material in the plasma processing where oxygen is contained.

Fig. 2 Oxidation of molybdenum at 400 °C and 5 Pa O<sub>2</sub>.

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