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Deuterium retention in tungsten oxide under low energy D_2^+ plasma exposure

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ABSTRACT

W is a candidate for plasma facing material and oxide layers are highly anticipated on W surface. We have studied deuterium (D) retention in tungsten oxide (WO_3) films and thermal release of deuterium. WO_3 films, prepared by oxidation of W metal sheet, were exposed to D_2 plasma under AC glow discharge at the applied voltage V up to a few kV and DC discharge. D-retention in W has been studied for comparison. The amount of D retained in the WO_3 films and W were analyzed by detecting α particles from the nuclear reaction, D(^{3}He, α)p, using 0.7 MeV $^3He^+$ ions. We find that D-uptake in WO_3 film is much larger than in W. According to thermal desorption, release of D_2 occurs at ∼180 and 450 °C.

1. Introduction

Tungsten is considered to be one of candidates for plasma facing materials in the nuclear fusion project under progress. Oxide layers exist naturally on metal surfaces and will be formed due to O_2 gas introduction for tritium removal [1,2]. Thus, deuterium retention in oxide layers and thermal release of deuterium are important for designing nuclear fusion devices. There are a few investigations for H-retention in WO_3 during H irradiation and the film preparation [3,4]. More investigations would be desired for application to fusion devices.

In this study, WO_3 films of ∼0.5 μm were exposed to D_2 plasma under AC glow discharge at the applied voltage V up to a few kV and DC discharge up to the D energy of 200 eV. The amount of D retained in the films were analyzed by detecting α particles from the nuclear reaction (NRA), D(^{3}He, α)p, using 0.7 MeV $^3He^+$ ions. Dependence of D retention in WO_3 films on V and D_2 gas pressure is described and this is compared with D retention in W and in WO_3 under DC discharge. Thermal release of D_2 is also presented.

2. Experimental procedures

WO_3 films were prepared by oxidation of tungsten metal sheet (99.95% purity) of 0.2 mm in thickness (∼0.5×1 cm^2 in size) in air at 550 °C for 1 h. Crystalline structure of the film is examined by X-ray-diffraction (XRD) and ascribed to orthorhombic or monoclinic structure [4,5]. Rutherford backscattering spectroscopy (RBS) of 1.8 MeV He^+ and 2 MeV H^+ were used to obtain the film thickness and composition. Normal incidence and the scattering angle of 160° are employed for RBS. The film thickness is ∼0.5 μm and the composition is close to stoichiometric (W:O = 1:3) with the accuracy of 10%. D-uptake was performed at room temperature using a similar method [6]. WO_3 films were placed on one of the stainless-steel-disk-electrodes (2 cm in diameter) covered with W sheet (0.1 mm thickness) and exposed to D_2 plasma discharge at the applied voltage V (60 Hz AC) up to a few kV between the electrodes (separation of ∼3 cm) in a glass-tube and the base pressure was ∼0.02 Torr. For exposure of D with well-defined energy, a linear divertor plasma simulator (NAGDIS-II) was employed [7]. Briefly, high-density deuterium plasma is generated by a dc arc discharge using a LaB_6 cathode. The magnetic field strength is 0.25 T. Typical electron density and temperature in the plasma are 1×10^{13} cm^{-3} and 10 eV, respectively. Samples were placed near the plasma edge and D_2^+-ion energy was varied by the bias on the sample. The pressure (presumably D_2) during plasma discharge is ∼10^{-3} Torr. It is assumed that upon D_2^+ ion impact on the sample surface, D_2^+ ions break up into D^+ ions with a half energy of D_2^+ ion energy. The amount of D retained in the films were analyzed by detecting α particles from the nuclear reaction, D(^{3}He, α)p, using 0.7 MeV $^3He^+$ ions. The NRA geometry is the same as RBS and the cross section is taken to be 32.6 mb/sr [8]. In NRA and RBS, the WO_3 film density of 7.2 g cm^{-3} (1.87x10^{22} W cm^{-3}) and W density of 19.3 g cm^{-3} (6.3×10^{22} W cm^{-3}) were employed and the stopping power was taken after [9]. Mass-analysis thermal desorption spectroscopy (TDS) was performed by using a conventional equipment with a temperature-rise rate of 1 k/s [10]. NRA, ^{16}O(d, α)^{14}N was also performed using 1.2 MeV d^+ in order to

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detect O near W surface. The NRA cross section of 5.3 mb/sr at the reaction angle of 160° was employed [11].

3. Results and discussion

Fig. 1 shows XRD patterns before and after D_2 plasma-exposure. No appreciable change was observed in the XRD pattern, i.e., the crystalline structure and quality under the D_2-plasma exposure. This would be anticipated if D's were located within the calculated projected range R_p of 12 nm [7] for D with the maximum energy of 1.06 keV at AC voltage of 1.5 kV (D_2 ions are assumed to be dominant), simply because R_p is much smaller than the film thickness. As described below, however, D's are more likely to be located beyond the projected range. More careful XRD study is required.

A typical NRA spectrum is shown in Fig. 2. The NRA products of α-particles are seen around 1.89 MeV. The spectrum at the energy >1.94 MeV is due to NRA products of protons which partially deposited their energy in the solid-state-detector. The full-width at half-maximum of α-spectrum shown in the inset is 25 keV and comparable with the resolution of the solid-state-detector. Thus, D's are located within the WO_3 film (thickness of 0.5 μm), though no further information about the depth of D in the film

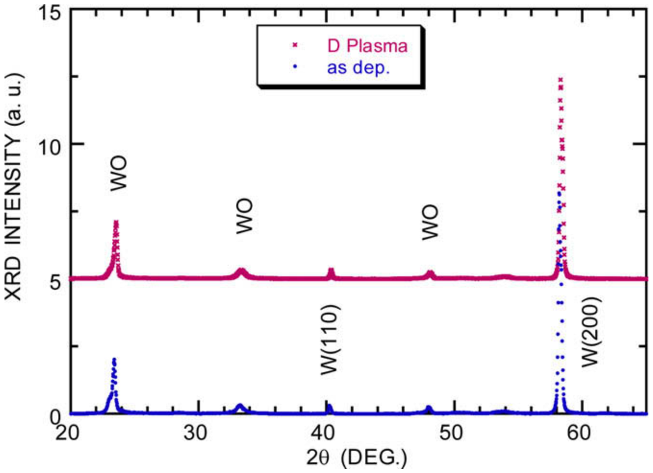

Fig. 1. XRD pattern of as-deposited (lower) and AC-D_2 plasma exposed (upper) WO_3 film. The latter XRD intensity is shifted by five for visible clarity. D_2 plasma exposure condition was 0.5 Torr D_2 at 1.5 kV for 20 min. WO and W denote the diffraction peaks of WO_3 (orthorhombic or monoclinic) and W.

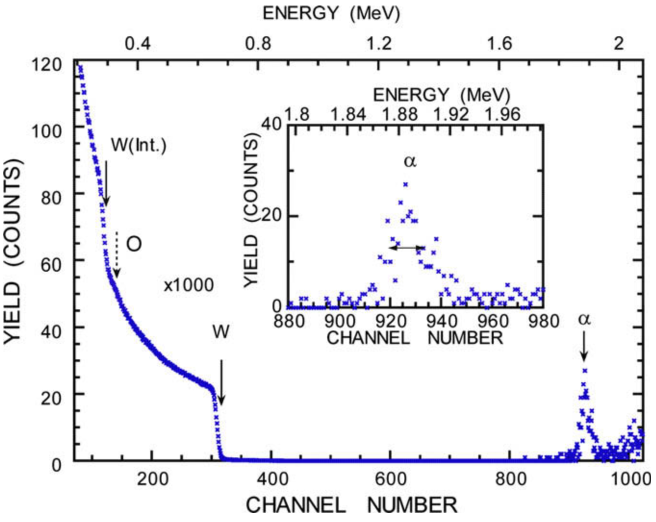

Fig. 2. NRA spectrum of WO_3 film exposed to D_2 plasma (D_2 gas pressure of 0.5 Torr and applied voltage of 1.5 kV for 10 min), obtained by using 0.7 MeV ^{3}He. The incidence was normal to the sample surface and reaction angle of 160°. α spectrum in an expanded scale is illustrated in the inset and horizontal line with arrows indicates the full-width at half-maximum. W and W(int.) indicate the W position located at the surface and WO_3-W interface. O signal is invisible because of very low yield.

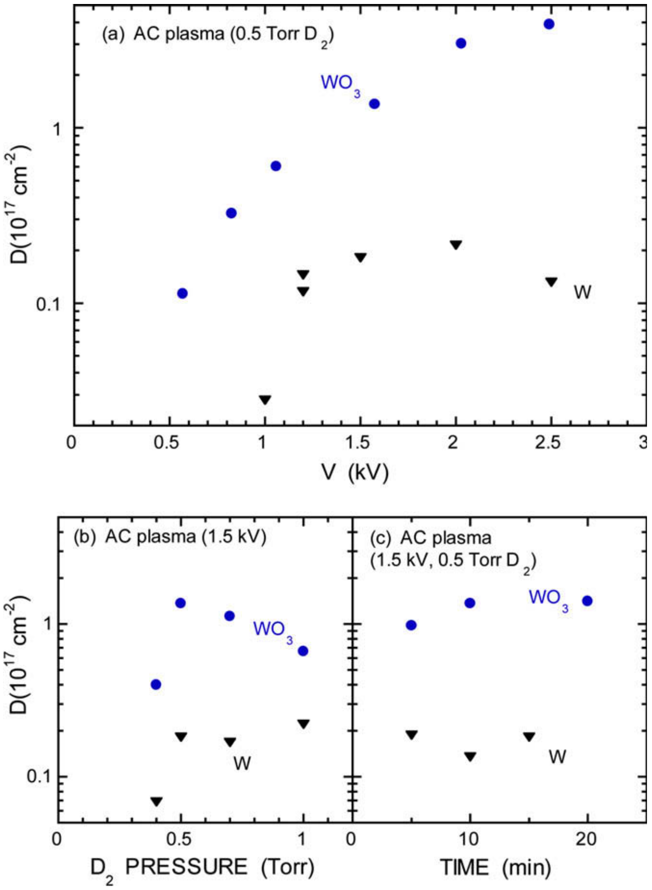

Fig. 3. (a) Applied voltage (V) dependence of D-uptake in WO_3 (●) and W (▼) under AC plasma discharge (0.5 Torr D_2). Discharge time is 10 and 15 min for WO_3 and W. (b) D_2-pressure dependence of D-uptake in WO_3 (●) and W (▼). Applied voltage is 1.5 kV, and discharge time is 10 and 15 min for WO_3 and W. (c) Discharge time dependence of D-uptake in WO_3 (●) and W (▼), under the condition of 0.5 Torr D_2 and 1.5 kV.

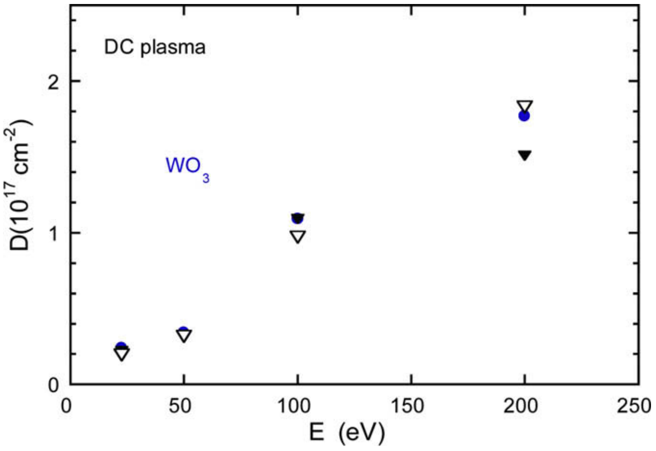

Fig. 4. Dependence of D-uptake in WO_3 on the D ion energy under DC-plasma discharge for ∼10 min.

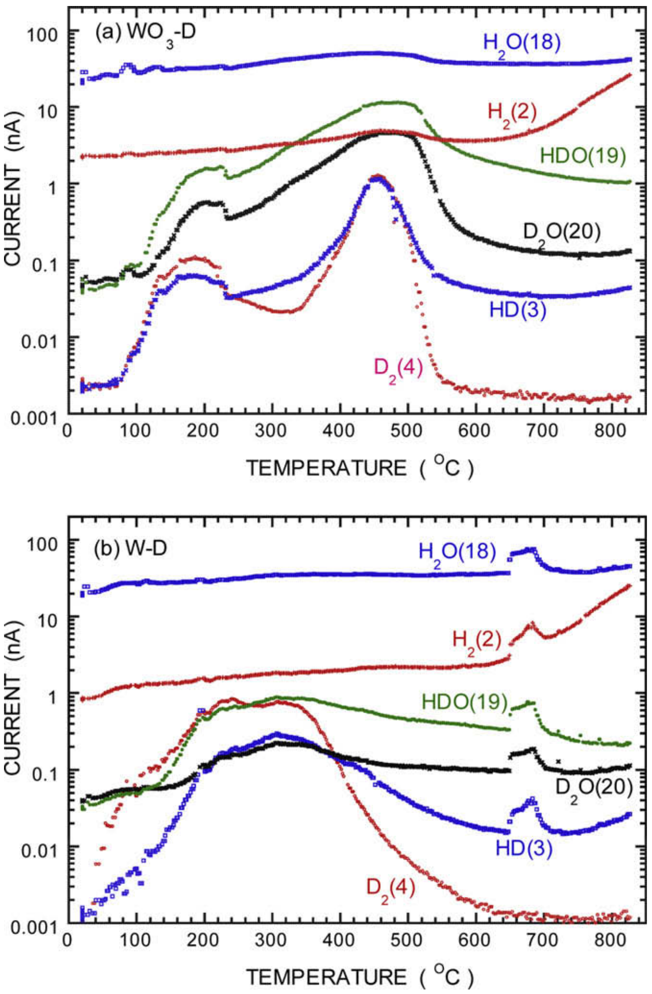

Fig. 5. Thermal desorption from WO_3 film (a) and W (b) exposed to AC plasma discharge. D_2 plasma discharge condition is 0.5 Torr D_2 and the applied voltage of 1.5 kV for 15 min.

could be deduced (depth resolution is poor, ~0.4 μm). Amount of D-uptake is evaluated from the total yield of α-particles and is evaluated as 1.4×10^{17} cm^{-2} for the case of Fig. 2. If these D's are assumed to be uniformly distributed in the projected range of 12 nm mentioned above, x would be ~6 for D_xWO_3. It is speculated that D's are retained in the region much deeper than the projected range. Elastic recoil detection is under consideration to evaluate the depth profile of deuterium. The discharge current was measured to be 1.4 mA (D_2^+) at V = 1.5 kV. This yields the flux of 5.6×10^{15} D cm^{-2} s^{-1} and the fluence of 3.3×10^{18} cm^{-2} for the exposure time of 10 min. Hence, the uptake efficiency = D-uptake divided by the fluence is 4% and is comparable with that for TiO_2 [6].

Applied voltage (V) dependence is shown in Fig. 3(a). D-uptake in WO_3 increases with increasing V, while D-uptake in W saturates at ~1.5 kV. It is noticed that D-uptake in WO_3 is much larger than in W. Here, W surface is uncleaned and oxygen of ~5×10^{15} cm^{-2} (~10 nm of WO_3) was observed by NRA using 1.2 MeV d ions. Thus D-uptake in WO_3 layers on W has a contribution. D_2-pressure dependence is shown in Fig. 3(b). D-uptake takes its maximum at 0.5 Torr for both WO_3 and W. The dependence is very similar for WO_3 and W, implying that WO_3 layers on W has appreciable contribution to D-uptake. According to the discharge time dependence (Fig. 3(c)), D-uptake saturates at ~10 min and less than 5 min for WO_3 and W, respectively. It is also found that D-retention decreases when the sample was kept in desiccator at room temperature. D-retention is reduced to half at 12 and 5 days in WO_3 and W, respectively, and no further reduction is observed for both WO_3 and W. From the results of D-retention for DC-plasma exposure shown in Fig. 4, where D-retention at fluence of 1.6×10^{18} cm^{-2} monotonically increases with D ion energy, the effective energy of D at V = 1.5 kV is estimated to ~100 eV.

TDS is shown in Fig. 5. For D retained WO_3, it is seen that release of D_2 occurs around 180 °C. Interestingly, release of HD, D_2O and HDO occurs around the similar temperature. Observation of HD and HDO release indicates intermixing and reaction between D and H. Release of D_2, HD, D_2O and HDO also takes place at ~ 450 °C. These results suggest that D has two different binding states. Another possibility is evaporation of WO_3 film and this is to be investigated. It is found that H-uptake takes place during cooling after W oxide film deposition [3]. For D retained W, it is seen that release of D_2, HD, D_2O and HDO start to occur at 200 °C and continue at 400 °C or higher temperature. Again, intermixing between H and D is observed.

4. Summary

D-uptake in WO_3 and W has been studied using low voltage AC and DC discharge. We find that D-uptake in WO_3 is much larger than in W. Comparison with DC discharge leads to that the effective energy of D in AC plasma discharge is much lower than the estimated energy from the applied voltage. It is also found that thermal release of D occurs at 180 and 450 °C. The present results imply that D's are distributed deeper beyond the projected range.

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