Codeposit removal by UV laser irradiation

W.M. Shu, T. Tadokoro*, Y. Oya**, Y. Kawakubo and M.F. Nishi

Tritium Engineering Laboratory, Department of Fusion Engineering Research

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-1195, Japan

ABSTRACT

In the development work of an effective method for decontamination of tritium retained in codeposits on plasma facing components of D-T fusion reactors such as ITER, ultra violet (UV) laser irradiation test was carried out using simulated codeposits formed by C_2H_2 or C_2D_2 glow discharge. The UV laser applied was an ArF excimer laser with a wavelength of 193 nm, a pulse energy of 200 mJ and a pulse duration of 25 ns. A removal rate of 13.5 nm/pulse was observed at the laser irradiation with the energy density of 0.05 J/cm^2 for the simulated codeposits whose atomic ratio of hydrogen or deuterium against carbon (H/C or D/C) at the surface was 0.53. Hydrogen isotopes were removed from the codeposits predominantly in the form of gases of hydrogen isotopes by the UV laser irradiation.

I. INTRODUCTION

Tritium safety is one of the most important issues for the development of fusion power. A large fraction of tritium fuel was retained inside the vacuum vessel of both TFTR (Tokamak Fusion Test Reactor) and JET (the Joint European Torus) after deuterium - tritium (D-T) plasma burnings, principally by codeposition with carbon eroded from plasma facing components.[1-3] The amount of tritium retained in future DT machines like ITER (International Thermonuclear Experimental Reactor) will scale-up with the long plasma duration and high duty-cycle operation.[4] From the viewpoint of the safety, tritium inventory in the vacuum vessel should be controlled not to exceed some amount determined properly. Besides tritium inventory control, tritium removal from the vacuum vessel is also required to control plasma fuelling and to reduce the tritium out-gassing during maintenance activities.

Significant progress in tritium removal technologies was made in support of the engineering design activities of the ITER project.[4] Thermo-oxidative erosion at temperatures above 570 K, or oxygen plasma discharges have been found to be effective in laboratory experiments to remove tritium from tritium-containing films.[5-9] These techniques using oxygen, however, have some drawbacks, such as lengthy wall conditioning time to remove oxygen and recover normal plasma operation, and the formation of large quantities

Present address: Power & Indus. Sys. R&D Lab., Hitachi Ltd., Hitachi-shi, Ibaraki 319-1221, Japan
**Present address: Radioisotope Center, The University of Tokyo, Bunkyo-ku, Tokyo 113-0032, Japan*

of tritiated water with four orders greater health hazard than tritium gases (T_2, DT and HT). On the other hand, ultra violet (UV) irradiation method has been developed as an advanced detritiatiom technique.[10-12] Our previous work showed that tritium could be removed effectively from the surface of actual plasma facing components by UV laser irradiation (193 nm, 0.1 J/cm^2).[13] In this study, the application of UV laser irradiation for the removal of codeposits was investigated.

II. EXPERIMENTAL

II. A. Preparation of simulated codeposits

To produce simulated codeposits, a membrane of tungsten or stainless steel as substrate was placed in a pretreatment chamber, which was evacuated to less than 10^{-4} Pa. Then the glow discharge of C_2H_2 or C_2D_2 was carried out to deposit the hydrocarbons on the substrate. The pressure of C_2H_2 or C_2D_2 during the deposition was kept at 67 Pa. The glow discharge voltage was set to be about 1.2 - 1.3 kV and the current was 5 - 20 mA. The simulated codeposits were formed by the deposit of the hydrocarbons, and their thickness was changed by adjusting the time of glow discharge from 3 - 60 minutes.

II.B. UV laser irradiation to simulated codeposits

The sample of simulated codeposits on the substrate was placed in a decontamination chamber, and the chamber was pumped out to less than 10^{-4} Pa. Then, the simulated codeposits was irradiated by a UV laser (an ArF excimer laser), which produces UV laser beam with a wavelength of 193 nm (corresponding photon energy: 6.3 eV), a pulse energy of 200 mJ, a repetition rate of 5 Hz and a beam size of 2.3 cm by 0.7 cm. The laser energy density through a quartz window was 0.05 J/cm^2 on the sample. The released gases during the laser irradiation were analyzed by a quadrupole mass spectrometer.

II.C. Characterization of simulated codeposits by ERD, RBS, SIMS and TDS

After the UV laser irradiation, analyses of ERD (Elastic Recoil Detection) and RBS (Rutherford Back Scattering) were performed to obtain the hydrogen concentration at the surface of the simulated codeposits formed by C_2H_2 glow discharge. The primary 1.7 MeV He^+ ion beams were directed onto the sample at an angle of 80° to the surface normal. The typical ion beam size was 1 mm in diameter. The recoiled hydrogen isotopes were detected by ERD with a silicon surface barrier detector (SSD) at a forward angle of 80° to the surface normal. The fluence of He^+ ions bombarded on the sample during ERD measurements was monitored simultaneously by means of the RBS measurements at the angle of 50° to the surface normal. The concentration of hydrogen retrained in the simulated codeposits was calibrated using the known experimental data of B. Tsuchiya and K. Morita.[14]

The SIMS (Secondary Ion Mass Spectrometry) was also applied to analyze the depth profiles of deuterium and carbon in the simulated codeposits formed by C_2D_2 glow discharge, using the primary ion (Cs^+) of an accelerated energy of 14.5 keV and a beam current of 10^{-7} A. The depth scale for the SIMS profiles was determined from the relation between the sputtering time and the stylus roughness measurement. The ratio of deuterium against carbon (D/C) was corrected with the experimental results (H/C) of RBS and ERD analyses assuming that the isotope effect can be

neglected in the deposition process.

The simulated codeposits formed by C_2D_2 glow discharge was analyzed by thermal desorption (TDS). The signals of quadropole mass spectrometer (QMS) for the mass numbers (m/e) of 4, 20, 28 and 44 were measured as functions of the increasing temperature.

III. RESULTS AND DISCUSSION

III. A. Removal of simulated codeposits

Figure 1 shows simulated codeposits formed by C_2D_2 glow discharge after 300 pulses' UV laser irradiation. As shown in this figure, codeposits of the area irradiated were clearly removed. A removal rate was 13.3 nm/pulse at the laser energy density of 0.05 J/cm^2. The photon energy of the UV laser is 6.3 eV, that is high enough to break the C-H bonds (about 4.5 eV)[15] with one photon absorption. However, the energy is not sufficiently high to cut C=C bond (about 7.2 eV) [15] by one photon absorption. In the previous study using a UV lamp, [11-12] it was reported that only C-H bonds on the surface of the codeposits were decomposed by the UV lamp irradiation. On the contrary, all the codeposits were removed by the UV laser irradiation in the present experiment. This indicates that multiple-photons' absorption may contribute to the codeposit removal during the UV laser irradiation.

Simulated codeposits (4 μm thick) formed by C_2D_2 glow discharge on SS 304 substrate

25 mm

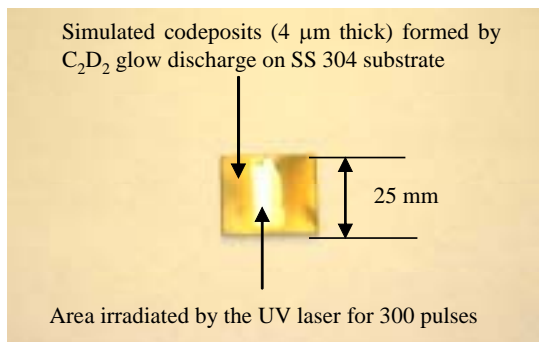Area irradiated by the UV laser for 300 pulses

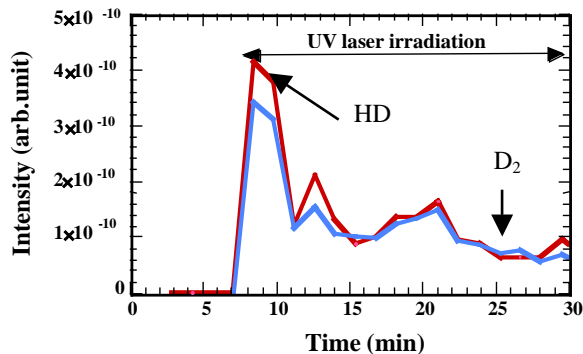Fig. 1.   Simulated codeposits after laser irradiation.

Fig. 2.   Mass spectra monitored at mass number of 3 and 4 before and during UV laser irradiation.

The released gases during the UV laser irradiation were compared with the residual gases in the vacuum chamber before the irradiation. The QMS signals for the mass numbers of 3 and 4 are plotted in Fig. 2 as functions of the time. The partial pressures of HD and D_2 showed a rapid increase immediately after the UV laser irradiation (Fig. 2). In comparison, the partial pressures of HDO and D_2O only showed a slight increase during the UV laser irradiation.[16] This suggests that the UV laser irradiation in vacuum removes hydrogen isotopes from the codeposits predominantly in the form of gases of hydrogen isotopes. This feature of the UV laser irradiation technique is very attractive from the viewpoint of both radiation safety and tritium processing, because the radiation hazard of tritiated water is 4 orders greater than that of tritium gas and tritium recovery process from hydrogen isotope gases is much simpler than that from tritium oxide.

III.B.   Characteristics of simulated codeposits

Figure 3 and 4 depict ERD and RBS spectra of simulated codeposits   formed by C_2H_2 glow discharge, respectively. The ratio of hydrogen against carbon at the top surface was calculated by the correlation of the
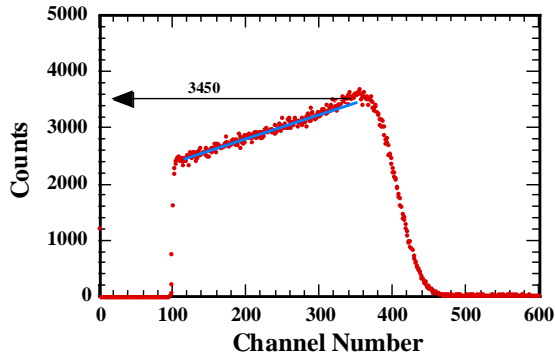
Fig. 3.   ERD spectrum of C-H codeposits.

Fig. 5.   Depth profile of C-D codeposits with
and without UV laser irradiation.

RBS and ERD counts.   A standard sample of H/C ratio of 0.4 gives ERD counts of 555 and RBS counts 99. [14] So, the ratio of hydrogen concentration over carbon (H/C) at the top surface of the codeposits was calculated to be 0.53 from the ERD counts of 3450 and RBS counts of 465 (the difference of 727 and 262).

Using this value, the hydrogen concentration in simulated codeposits was obtained by correcting the SIMS depth profile.   As shown in Fig. 5, the simulated codeposits were removed by 680 nm by 50 pulses' UV laser irradiation (a frequency of 5 Hz and an irradiation time of 10 seconds).   The removal rate of the simulated codeposits was calculated to be 13.6 nm/pulse at the laser energy density of 0.05 J/cm^2.

This value agrees well with the results mentioned above (4 μm/300 pulses). So the averaged removal rate of the simulated codeposits was estimated to be 13.5 nm/pulse at the laser energy density of 0.05 J/cm^2.
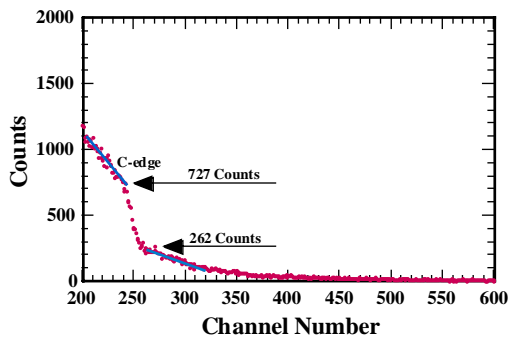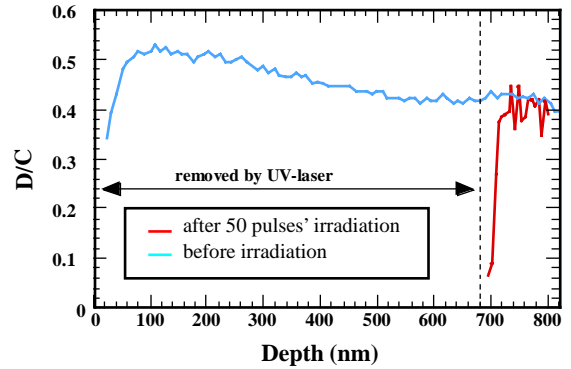
Simulated codeposits formed by C_2D_2 glow discharge were analyzed by TDS, in which the QMS signal traces for the mass numbers of 4, 20, 28 and 44 were determined as shown in Fig. 6. The peaks for mass numbers of 28 and 44 appeared around 500 K, and the most probable candidates for these mass numbers were C_2D_2 and CO at mass number of 28 and C_3D_4 and CO_2 at mass number of 44. Since the total oxygen content in the sample was low, the dominate gases for the mass number of 28 and 44 were considered to be C_2D_2 and C_3D_4, respectively. This assignment was supported by the presence of peaks of the mass number of 20 (CD_4).   In comparison,   the
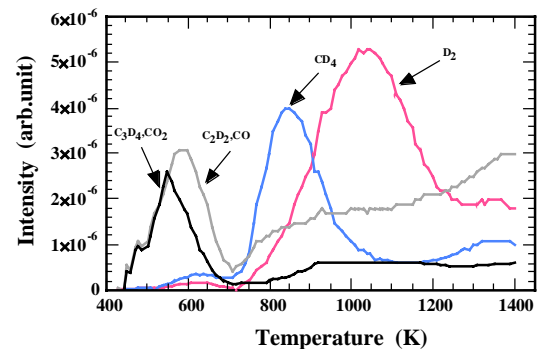

Fig. 6.   Thermal desorption spectra of C-D codeposits
monitored at mass number of 4, 20, 28, 44
at the ramp rate of 50 K/min.

Fig. 4. RBS spectrum of C-H codeposits.

release of D_2 (mass number: 4) occurred at temperatures much higher than those in the forms of deuterium carbides. Release of deuterium molecule occurred from 800 K and it peaked at around 1050 K. This suggests that the breaking of C-D bonds occurred at high temperatures of about 1000 K.

V. CONCLUSION

Simulated codeposits were irradiated with an ultra violet laser at the laser energy density of 0.05 J/cm^2 and the released gases during the irradiation were measured. The characterization of the simulated codeposits were carried out. The following conclusions were deduced:

(1) A removal rate of 13.5 nm/pulse was obtained for the simulated codeposits at the laser energy density of 0.05 J/cm^2.

(2) The partial pressures of HD and D_2 showed a rapid increase immediately after C-D codeposits were irradiated by the UV laser.

(3) The atomic ratio of deuterium against carbon at the surface of the simulated codeposits was determined to be 0.53.

ACKOWLEDGEMENT

REFERENCES

1. D. Mueller, W. Blanchard, J. Collins, et al., "Tritium removal from TFTR," J. Nucl. Mater., **241-243**, 897 (1997).
2. C.H. Skinner, et al., "Modeling of tritium retention in TFTR," J. Nucl. Mater., **266-269**, 940 (1999).
3. P. Andrew, P.D. Brennan, J.P. Coad, et al., "Tritium retention and clean-up in JET," Fusion Eng. Des., **47**, 233 (1999).
4. G. Federici, R.A. Anderl, P. Andrew, et al., "In-vessel tritium retention and removal in ITER," J. Nucl. Mater., **266-269**, 14 (1999).
5. R.A. Causey, W.R. Wampler and D. Walsh, "Comparison of the thermal stability of the codeposited carbon/hydrogen layer to that of the saturated implant layer," J. Nucl. Mater., **176-177**, 987 (1990).
6. W. Wang, W. Jacob and J. Roth, "Oxidation and hydrogen isotope exchange in amorphous, deuterated carbon film," J. Nucl. Mater., **245**, 66 (1997).
7. S. Alberici, H.-K. Hinssen, R. Moormann and C.H. Wu, "Deuterium release rates in a-C:D-layers during oxygen attack," J. Nucl. Mater., **266-269**, 754 (1999).
8. J.W. Davis and A.A. Haasz, "Oxygen removal of codeposited a-C:D layers from tokamak tiles," J. Nucl. Mater., **266-269**, 478 (1999).
9. T. Tadokoro, K. Isobe, S. Ohira, W.M. Shu, M. Nishi, "Depth profile of tritim in plasma exposed CX-2002U," J. Nucl. Mater., **283-287**, 1048 (2000).
10. J.P. Krasznai, R. Mowat, "UV/ozone treatment to decontaminate tritium contaminated surfaces," Fusion Technol., **28**, 1336 (1995).
11. W.M. Shu, S. Ohira, C.A. Gentile, et al., "Tritium decontamination of TFTR carbon tiles employing ultra violet light," J. Nucl. Mater., **290-293**, 482 (2001).
12. Y. Oya, W.M. Shu, S. O'hira, et al., "A study of tritium decontamination of deposits by UV irradiation," J. Nucl. Mater., **290-293**, 469 (2001).
13. W.M. Shu, K. Kawakubo, S. Ohira, et al., "Tritium decontamination of TFTR D-T plasma facing component using an ultra violet laser," Fusion Sci. Technol., (2002) to appear.
14. B. Tsuchiya and K. Morita, "Retention and re-emission of hydrogen in beryllium studied by the ERD technique," J. Nucl. Mater., **233-237**, 898 (1996).
15. J.A. Kerr, "Bond dissociation energies by kinetic methods," Chem. Rev., **66**, 465 (1966).
16. Y. Oya, T.Tadokoro, W.M. Shu, et al., "Tritium decontamination from co-deposited layer on tungsten substrate by ultra violet lamp and laser," J. Nucl. Sci. Technol., **38**, 967 (2001).