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Influence of deuterium implanted in materials surface on Balmer lines emission from backscattering deuterium

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Abstract

We have studied the influence of implanted deuterium (D) on Balmer lines emission from backscattering D atoms under D^+ irradiation of C, Al, Si, Mo and Pd for an incident energy ranging from 5 to 25 keV at a target temperature from RT to 600 K. For clean surface, D_α photon intensity is proportional to the backscattering coefficients calculated by the TRIM code for all incident energies. For 15 and 20 keV injection, the intensity stays constant with increasing fluence in accordance with the simulation that the backscattering coefficient is not influenced by implanted deuterium because the mass of D is much less than that of the targets. Significant D_α photon intensity increase is observed in Si with the injection of 5 keV or less energy D^+. The intensity gradually increases with the fluence until saturation after prolonged irradiation. With increase in the target temperature, the intensity increment is reduced and disappears above 500 K. The decay of the D_α photon intensity accompanied by thermal release of implanted deuterium is also observed. Similar increment of the D_α intensity is observed in C and Pd under 3 keV D^+ injection but not at higher energy. In non-hydride-forming materials as Al and Mo, no increment is observed at all. It is concluded that only dynamically retained deuterium at the top surface layers in the hydride-forming materials given by lower energy incidence modifies the surface electronic structure and consequently enhances the electron capture process of the backscattering deuteron. In this paper, it is clearly shown that in recycling hydrogen from the wall highly energy excited hydrogen particles are produced. The rate of this production is influenced by the surface chemical state. If the amount of such excited hydrogen is significant, it should be taken into account for the energy recycling. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen recycling process at a limiter or divertor plate in fusion devices plays an important role not only in boundary plasma physics but also in engineering aspects. To determine a hydrogen recycling coefficient, the Balmer lines emission of hydrogen (H_α,H_β,H_γ,...) in plasma has been utilized [1–5]. Generally these line emissions are assumed to be caused by the electron excitation of neutral atoms and molecules in boundary plasmas. In a laboratory ion beam experiment, however, it is shown that some of the reflected hydrogen is in excited states and subsequently emits Balmer lines [6,7]. Since the excited atoms are produced through an electron capture at the top surface, the emission must be influenced by the hydrogen implanted in the surface layers. Although the charged fraction and/or ionizing mechanism of backscattering hydrogen atom in the excited states has been extensively studied [8], electronic structure of backscattering hydrogen atoms in the excited states has not been systematically investigated. In addition, as indicated by Tanabe [9], re-emitted hydrogen molecules are not necessarily equilibrated with surface temperature, having large velocity originated from the excess energy released at the recombination. Actually, Pospiescyczk et al. found the exited molecules in

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vibrational and rotational spectra in the vicinity of the limiter surface in TEXTOR [10].

In most of the recycling simulations, however, hydrogen released from the wall has been assumed to be in the ground state. Since the ionization process and further excitation processes of the particles in the excited states are different from those in the ground state, analysis of energy transport or energy exhaust in the boundary plasma should be somewhat modified. If significant amount of hydrogen is released in excited states, it is obvious that the hydrogen release process is influenced by the surface state and hence accumulated hydrogen on the top surface layers should alter the release process or electron population (distribution) among various excited states.

In the present work, we have systematically studied the influence of implanted deuterium accumulated in the top surface layers on the Balmer lines emission from the backscattering atoms under irradiation of D^+ to various target materials. For some of those materials it is known that their electronic states are modified by implanted hydrogen.

2. Experimental

Experiments were carried out in a standard vacuum chamber equipped with an ion source and an optical spectrometer. A differential pumping system allows the pressure in the target chamber to be kept below 10^{-6} Pa during the irradiation. Mass analyzed ions accelerated up to 25 keV were injected to a target through a slit of 5 mm in diameter with an incident angle of 45 degrees with respect to the target normal. The injected ion flux, monitored by a Faraday cup inserted to the beam line in front of the target, was ranging from 1×10^{17} to 1×10^{18} D^+/m^2 s. Graphite (IG-110U), aluminum (Al), silicon (Si), molybdenum (Mo) and palladium (Pd) sheets with purity of 99.9% were used for the target materials. The target was heated by a heater behind it and the temperature was controlled ranging from room temperature (RT) to 600 K. The photons emitted from backscattering particles were focused into an optical spectrometer (Spectra Pro275) whose optical axis was normal to the ion beam and detected with a multichannel analyzer (OMA-III). The Balmer lines of D_α, D_β, and D_γ were simultaneously measured in a wavelength region from 350 to 750 nm, for different target materials, incident ion energy, fluence, flux and target temperatures. The effect of surface oxygen was also examined. The details of the experiment are given elsewhere [6,7,9].

Using the TRIM-92 code, backscattering of implanted deuterium and depth profiles of both implanted ions and displacement damages in the target were calculated and compared to the results.

3. Results

Figs. 1–5 show changes of D_α and D_β intensities with ion fluence under 5 keV D^+ injection to graphite, Al, Si, Mo, and Pd, respectively. For graphite, Al and Mo both D_α and D_β stay constant except the initial decay. Pd shows a slight increase in D_α intensity following the initial decay. All of the initial decays can be well fitted by a exponential function, indicating the sputter cleaning of surface contamination. In addition to the Balmer lines spectra, a broad but very weak emission around 300–600 nm was observed during the initial intensity decay phase which is another evidence of the initially contaminated surface.

Increase of the intensity is significant in Si (Fig. 3) as already demonstrated in the previous work [9]. However, for higher incident energies the intensity increment becomes smaller and above 20 keV no increment was observed even with such a high fluence of $10^{24}/m^2$ (not shown here). With increasing the surface temperature, the intensity increment became smaller and disappear above 500 K. In the second run after annealing at 500 K, the intensity increase was reproduced without the initial decay observed in the first run.

After the D_α intensity was saturated (over the fluence of $5 \times 10^{21}/m^2$ s) at a fixed temperature, we stopped the beam, but monitored the D_α intensity by injecting the beam periodically with very short time duration. As shown in Fig. 6, the D_α intensity thus observed decreased with time. After the intensity returned to the initial value we could reproduce the intensity increase by

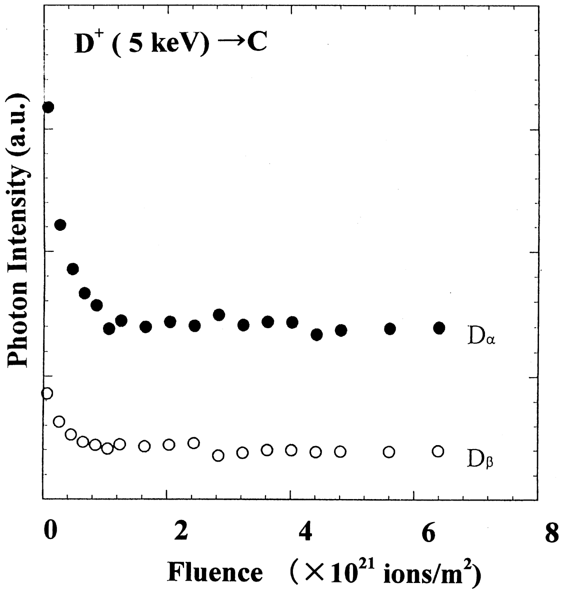

Fig. 1. D_α and D_β intensity changes with fluence of 5 keV D^+ for graphite (IG-110U) target.

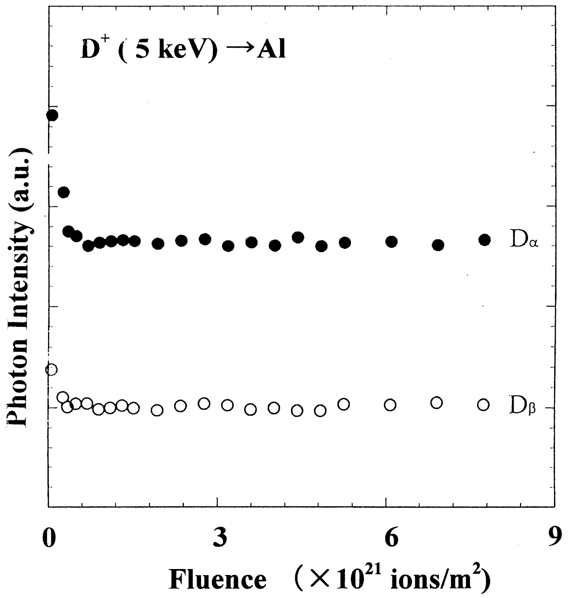

Fig. 2. D_α and D_β intensity changes with fluence of 5 keV D^+ for Al target.

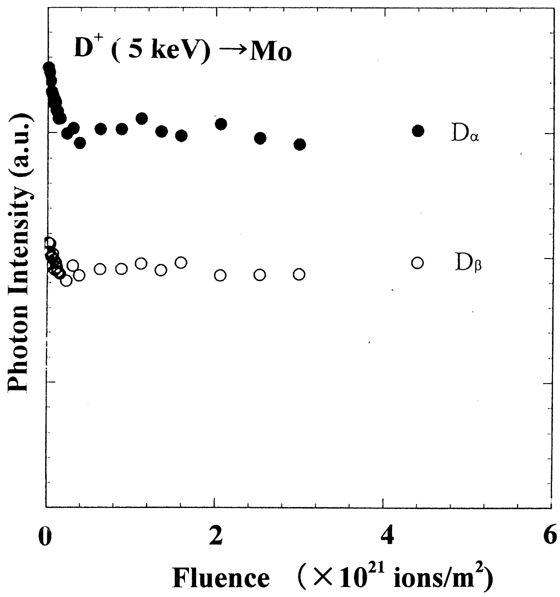

Fig. 4. D_α and D_β intensity changes with fluence of 5 keV D^+ for Mo target.

deuterium injection at the same temperature. The time period needed for returning to the initial intensity became shorter with increasing the target temperature. Considering that the heating at 500 K releases only implanted hydrogen but does not anneal defects in Si [11–13], we can conclude that the intensity increase of the Balmer line emission is hydrogen-related phenomena.

We have also looked for a probable surface impurity effect by introducing oxygen in the target chamber during the measurement, but oxygen did not influence the result except very slight increase of the broad band emission. We believe the surface contaminants, which

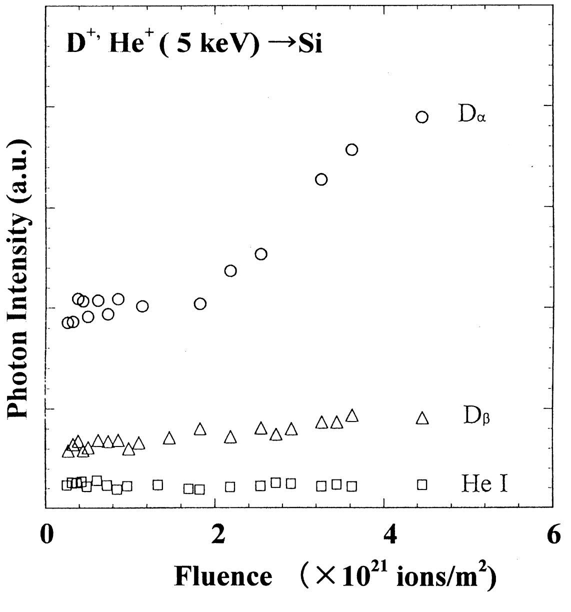

Fig. 3. D_α, D_β and HeI intensity changes for fluence of 5 keV D^+ and He^+ for Si target.

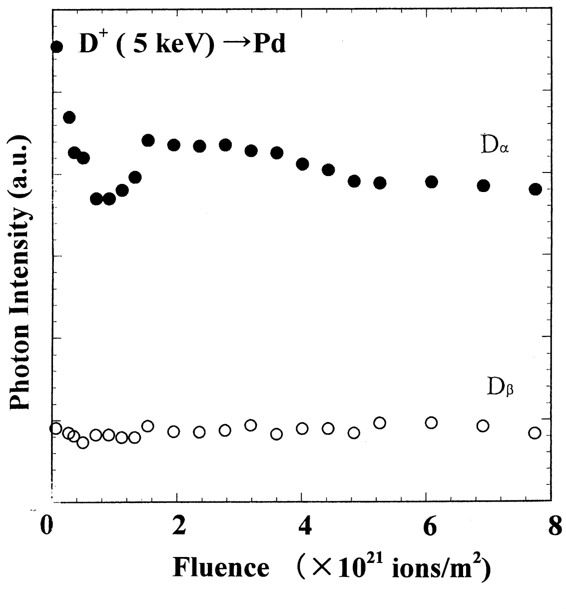

Fig. 5. D_α and D_β intensity changes with fluence of 5 keV D^+ for Pd target.

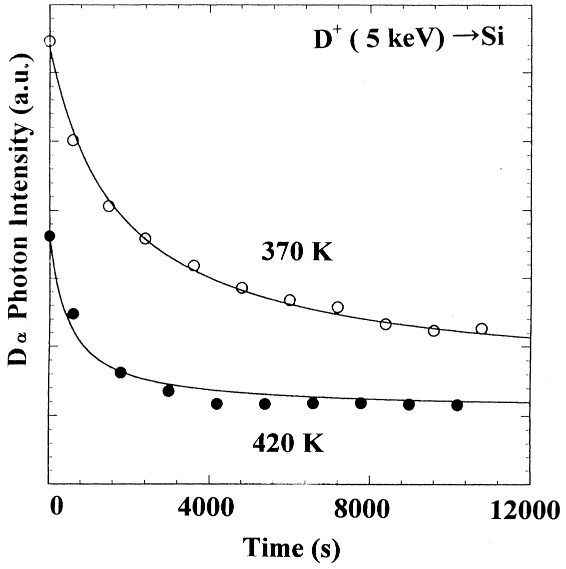

Fig. 6. Time evolution of D_α intensity decay after the termination of ion injection for Si target at 300 and 420 K (D_α intensity was monitored periodically by short duration of ion injection). Lines are only to guide the eye.

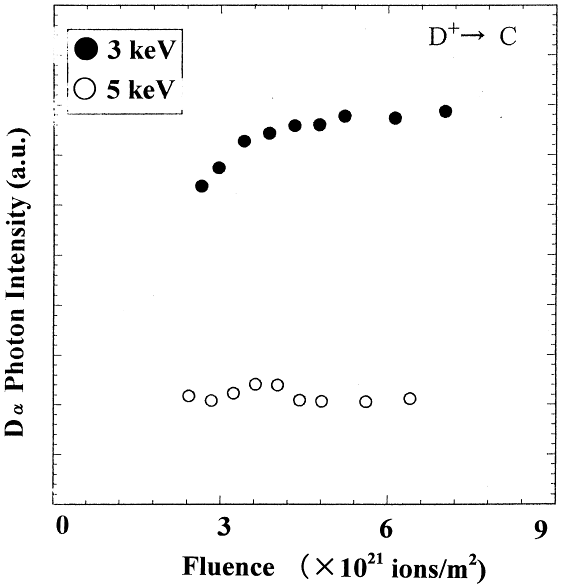

Fig. 7. Comparison of sequential changes of the D_α emission intensity with ion fluence for incident energies of 3 and 5 keV for graphite target (IG-110U).

enhance the emission intensity, are probably some hydrocarbons and/or water molecules as described later.

In the previous work we have attributed the increase of the D_α intensity observed in Si with the fluence to accumulated deuterium in the top surface layers [14]. Therefore, additional experiments were carried out changing the incident energy and the results are given in Fig. 7, Fig. 8, Fig. 9 for C, Si, and Pd, respectively, in which the initial decays were omitted. One can clearly see the D_α intensity increase in C and Pd for 3 keV injection. For Si, on the other hand, the intensity increase was hardly seen for higher energy incidence (Fig. 8). In Al and Mo, non-hydride formers, no intensity change was observed, too (not shown here).

Different from D^+ injection, He^+ injection did not show the intensity increase of HeI line (at 578.8 nm (transition from 3^3D to 2^3P)) emitted from the backscattering He atoms (one example is given in Fig. 3) except the initial exponential decay. We have already indicated that the HeI lines emission is significantly enhanced by surface oxygen [6].

4. Discussion

In the previous work, the intensity increase observed in Si is attributed to the accumulated deuterium in the top surface layers which modify the electronic structure of the surface and consequently change the electron capture process of the backscattering ion. The present results confirm it as following.

Medium energy (1–100 keV) hydrogen implantation in Si is known to result in amorphization or a:Si–H layer formation with the saturation concentration of around

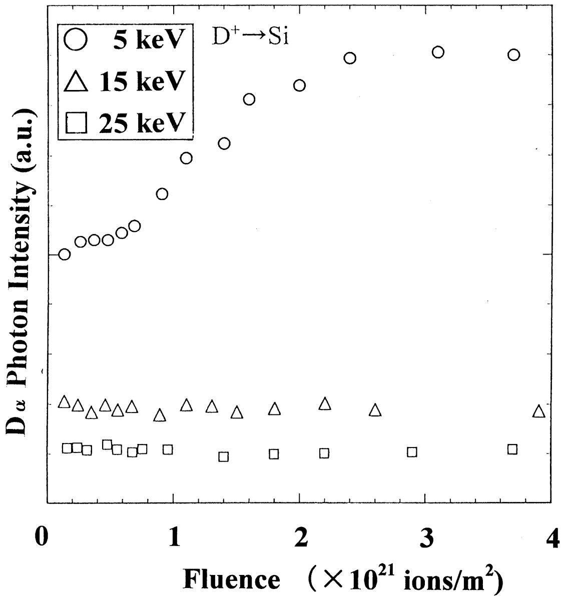

Fig. 8. Comparison of sequential changes of the D_α emission intensity with ion fluence for incident energies of 5, 15, and 25 keV for Si target.

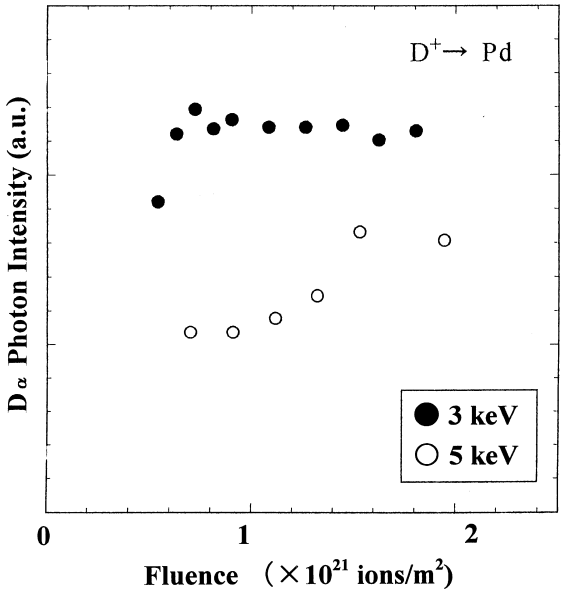

Fig. 9. Comparison of changes of the D_α emission intensity with ion fluence for incident energies of 3 and 5 keV for Pd target.

0.4 in H/Si atom ratio [11,15]. However, the implantation is not necessary to produce the homogeneous damage profiles and implantation depth. But the observed profiles of implanted hydrogen are very similar to the damage profile, because the hydrogen solubility in Si is very small and most of the implanted hydrogen moves to the damaged region assisted by defects [15–17]. As a result a:Si–H layer is produced only in the vicinity of the damaged region. However, higher energy implantation often results in blistering instead of increasing the thickness of the a:Si–H layer to the surface direction [15,18]. Thus hydrogen concentration at the top surface layers is not likely to be 0.4 in the D/Si ratio at higher energies of incident D^+.

According to the TRIM calculation, the accumulation rates of vacancies at the surface within 1 nm for 3 keV deuteron injection is one order of magnitude larger than that for 15 keV injection. Assuming 1 to 1 trapping of hydrogen to vacancy, D/Si atomic ratio at the top surface for 3 keV incidence with the fluence of 4×10^{21} D/m^2 exceeds 0.4 which is the maximum hydrogen concentration of a:H–Si, whereas that for 15 keV incidence remains below 0.1 even over 7×10^{21} D/cm^2 irradiation. These calculations coincide well with the observed intensity increase under 3 keV and 15 keV D^+ injections.

The TRIM calculation also shows that implanted deuterium in the materials has almost no effect on the number of backscattering particles and their energy distributions. The above discussion is also true for graphite as shown in Fig. 7, where 3 keV injection clearly gives an intensity increase. It should be noted that lower energy hydrogen injection is more efficient for hydrocarbon formation in chemical sputtering of carbon [19].

Pd is also a hydride-forming material. But it has a much larger diffusivity of hydrogen than those in C and Si, which enhances hydrogen migration into the bulk, hardly changing electronic structure of the top surface layers.

Since Al and Mo are non-hydride former, their surface electronic structures are not probably modified by the implanted deuterium. In addition hydrogen blistering has often been reported in those materials.

All the above discussions lead us to conclude that the dynamic deuterium retention at the top surface layer would modify the surface electronic structure and consequently influence the electron capture process of the backscattering deuteron. This is also confirmed by the observation that the intensity ratio of D_β/D_α also increases (i.e. higher excited states are favored) with the increase of the emission intensity.

For the small fluence of oxygen on the Balmer emission, we argue in the following way. When hydrogen is bonded to surface atoms, some bonding levels would be produced near the bottom of the valence band of Si and C which could work as an electron source for the electron capture of an empty D 1s level of backscattering D ions. The bonding level with oxygen is much deeper (O 2s and O 2p levels are at around 20 eV below Fermi level) than that of hydrogen (around 10 eV), which would promote the resonance capture of He 1s level in backscattering He ions but not H 1s.

Still one question remains, that is, whether the modification of the electronic structure is substantial or not. If electron capture occurs simply through inelastic collision between surface deuterium atoms and reflected ions, the deuterium ion concentration in the top surface layers is the only matter or importance. In this respect any hydrogen compounds such as hydro-carbons and water molecules as surface contaminants could work to enhance the D_α intensity. Even so hydrogen is bonded to oxygen or carbon atom. Anyhow in no-hydride-forming materials the deuterium concentration in the top surface layers is not high enough to influence the electron capture process of the reflected deuteron.

The interpretation is still speculative and should be quantized. Nevertheless, the present work gives important messages; (1) there is a certain contribution on Balmer emission in the boundary plasma from directly reflected hydrogen atoms at the first wall, and (2) its intensity not only increases with decreasing incident energy (because of the increase of the reflection coefficient) but is also enhanced by the accumulation of hydrogen in the top surface layers in graphite and Si. If such 'higher energy component of hydrogen' is released from the wall instead of the stable ones in the ground state, hydrogen recycling would have a significant effect on energy recycling.

5. Conclusion

In the present work the fluence of implanted deuterium (D) on Balmer lines emission from backscattering D atoms is investigated under D^+ irradiation to graphite, Al, Si, Mo and Pd for an incident energy ranging from 5 to 25 keV at a room temperature ranging from RT to 600 K.

Under 5 keV D^+ injection to Si, the D_α photon intensity gradually increases with the fluence until saturation after prolonged irradiation. The difference between the initial intensity and that after the saturation is reduced with increasing the target temperature and disappears above 600 K. The decay of the D_α photon intensity accompanied by thermal release of implanted deuterium was also observed. Similar increment of the D_α was observed in graphite and Pd under 3 keV D^+ injection but not for higher energy of D^+. In non-hydride-forming materials as Al and Mo, no increment was observed at all. In hydride-forming materials, most of the implanted deuterium is very likely to be trapped at defect sites in the bulk produced by the ion injection, and hydrogen is hardly retained in the top surface layers. Therefore only dynamically retained deuterium at the top surface layers given by lower energy incidence would modify the surface electronic structure and consequently enhance the electron capture process of the backscattering deuteron.

The present interpretation is still speculative and should be quantized. Nevertheless, it is clearly demonstrated that a part of hydrogen recycled from the wall is highly excited. The amount of such excited hydrogen is influenced by the surface chemical state. Because such excited particles take energy from the wall, it is a part of the energy recycling.

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