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Journal of Nuclear Materials 307–311 (2002) 1502–1506

journal of nuclear materials

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Application of electron stimulated desorption for hydrogen removal from graphite

R. Ishida [a], T. Shibahara [a], T. Tanabe [b,*]

[a] *Department of Nuclear Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

[b] *Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

Abstract

We have applied an electron stimulated desorption (ESD) technique for hydrogen removal from graphite. Hydrogen was charged into graphite by either absorption or ion implantation. The initial ESD yield was about 0.2 atoms/electron, agreeing with the literature values. The desorption rate decreased with succeeding electron irradiation. However, the desorption continued for a long time and more than half of the total H retention was released after 100 s of irradiation. The desorption rate also increased with the incident electron energy, reaching a maximum at around 850 eV and decreased at higher energies. Thus ESD was found to be effective for hydrogen release from graphite.

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1. Introduction

Hydrogen (Tritium) retention in graphite is one of the most important issues not only for hydrogen recycling but also for tritium safety in fusion energy development. To ensure the low recycling regime, various techniques to remove hydrogen from plasma facing materials (PFM) have been developed: baking, discharge cleaning like ECR discharge, He glow discharge, and so on. In-vessel tritium inventory or removal of tritium from the plasma facing component after the main discharge is a key safety issue in a tritium burning machine like ITER [1,2]. In JET, tritium is found in dust and deposited layers even in plasma shadows [3], which is very difficult to remove by above mentioned discharge techniques. Therefore, various techniques such as isotope exchange discharges, air ventilation, oxygen ventilation, photo stimulated desorption, and so on, have also been proposed and applied to remove tritium from in-reactor components [4]. However, none has approved to be more effective than air or moisture ventilation.

The present work is devoted to apply electron stimulated desorption (ESD) for the removal of tritium from graphite. ESD is well known to be effective in desorbing surface adsorbents. However it might not work for absorbed gas in the bulk. Nevertheless we have attempted to apply this technique for hydrogen removal from the bulk regions of graphite. Commercially available graphite is a porous material with the apparent density of only about 3/4 of the theoretical density and have open pores in the bulk connecting to the surface. Thus, incident electrons may be able to penetrate relatively deep into the graphite bulk and excite binding electrons in C–H bonds, resulting in recombination of H_2 and the subsequent migration through the open pores. This motivated us to perform ESD.

2. Experimental

Fig. 1 shows the schematic description of the apparatus used. The system is equipped with an electron source, a sample holder, an ion gun, a vacuum gauge, and a quadruple mass spectrometer (QMS) calibrated by a standard leak and evacuated to ultra-high vacuum.

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[*] Corresponding author. Tel.: +81-52 789 5481/5157; fax: +81-52 789 5177/3791/5158.

E-mail address: tanabe@cirse.nagoyo-u.ac.jp (T. Tanabe).

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PII: S0022-3115(02)01267-9

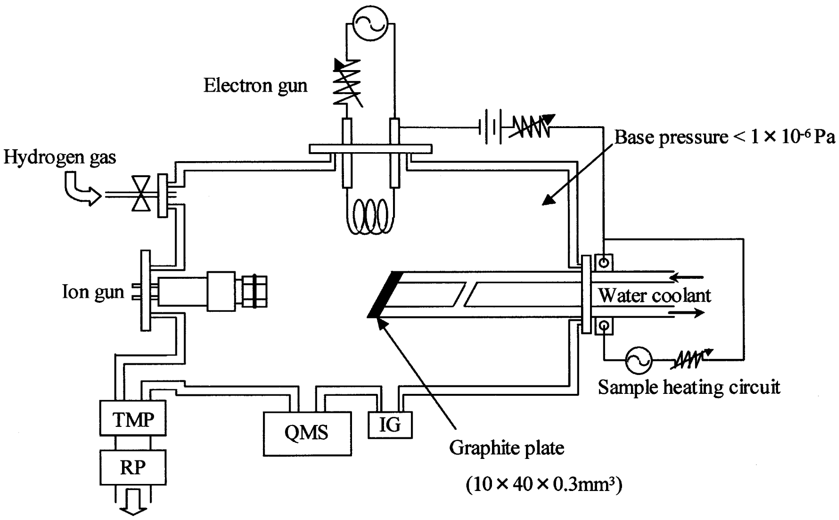

Fig. 1. Apparatus for ESD measurements.

The graphite specimen used here was IG-110U (Toyo-Tanso Co. Ltd.) cut into a strip with a dimension of 40 × 10 × 0.3 mm^3. The sample holder allowed direct current heating of the graphite specimen; the temperature of the graphite plate was controlled between RT and 1300 K.

Two different methods were employed for charging hydrogen/deuterium into the graphite specimen. One was gaseous charging, i.e., the graphite specimen was heated at a temperature ranging 470–870 K in hydrogen (H_2) or deuterium (D_2) atmosphere at 1.0×10^{-2} Pa for 30 min, by which a total of 10^{16} to 10^{17} H_2 or D_2 molecules were absorbed. The other method was ion implantation, i.e., H_2^+ or D_2^+ ions were accelerated to 0.5–1.5 keV and irradiated the graphite specimen with a total dose of 2×10^{20} ions/m^2. The total retained amount of hydrogen/deuterium was determined using the calibrated QMS while outgassing the graphite specimen at 1300 K for several minutes. After the out-gassing process, subsequent charging gave very reproducible results.

For ESD, an electron energy of 400–1200 V was used. Both the electron source and the sample holder were electrically isolated from the vacuum walls to prevent the accelerated electrons injecting the vacuum walls. The electron current density to the target was 0.01–5 mA/cm^2. In order to avoid electron beam heating which could result in thermal desorption, the electron gun was used in a pulsed mode (pulse duration was 1 s and interval was 5 s between pulses. Thus, the resulting temperature increase was kept below 5 K. The H_2/D_2 molecules desorbed by the ESD were monitored by the QMS. After the ESD measurements, the remaining hydrogen in the specimen was also determined by the outgassing at 1300 K.

3. Results

Fig. 2(a)–(d) plotted the ESD yields (the number of desorbed H_2/D_2 molecules per incident electron) against the net electron irradiation time for H_2 gaseous charging, D_2 gaseous charging, H_2^+ ion implantation and D_2^+ ion implantation, respectively. The electron energy was 0.75 keV. The figures show that the initial ESD yields for all cases are fairly large and the ESD yield for one incident electron is around 0.2 atoms/electron, which is in reasonable agreement with the literature for adsorbed gases [5]. Although the yields decrease with the net electron irradiation time, the release of hydrogen continued for a long time and more than half of the total retention was released after 100 s net irradiation.

No significant isotope effect was observed between H_2 gaseous charging and D_2 gaseous charging, nor between H_2^+ ion implantation and D_2^+ ion implantation. Compared to ion implantation, the initial ESD yields of gaseous charging were lower than that of ion implantation, but the yields after about 20 s net irradiation time were higher and continued longer.

The ESD yield also changes with the incident electron energy. The integrated ESD yields for 100 s net electron irradiation normalized to the total retention are compared in Fig. 3(a)–(d), again for the H_2 gaseous charging, D_2 gaseous charging, H_2^+ ion implantation and D_2^+ ion implantation, respectively. For ion implantations, the ESD yields increases with the incident electron energy with a maximum at around 850 eV. Further increase of the electron energy reduces the ESD efficiency. Although the ESD yields of the gaseous charging also show the maximum at around 850 eV, the electron energy dependence is less pronounced.

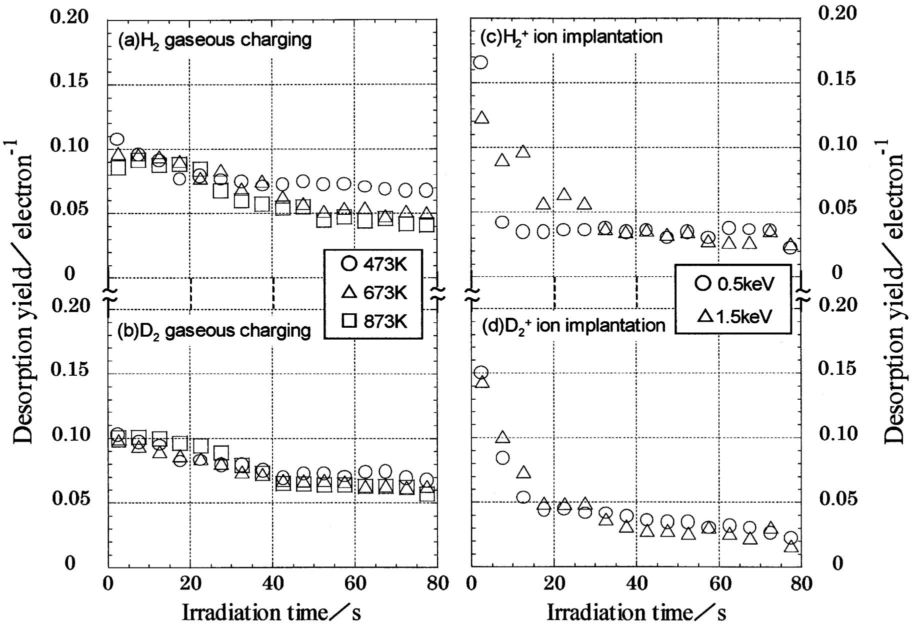

Fig. 2. ESD yields plotted against the electron irradiation time for (a) H_2 gaseous charging, (b) D_2 gaseous charging, (c) H_2^+ ion implantation, and (d) D_2^+ ion implantation. The electron energy is 0.75 keV.

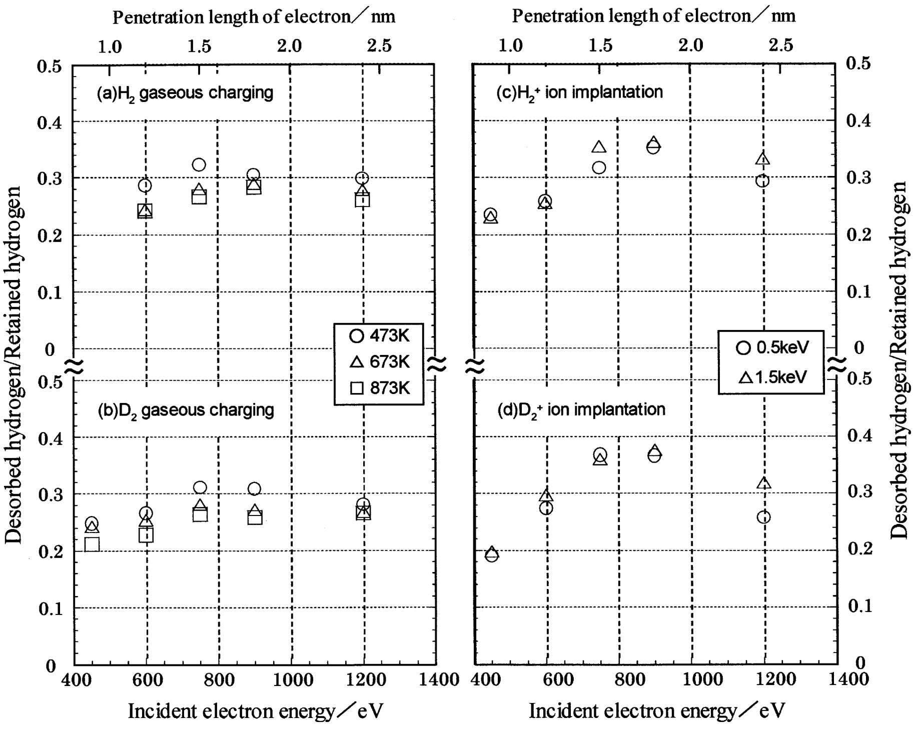

Fig. 3. ESD yields plotted against the incident electron energies for (a) H_2 gaseous charging, (b) D_2 gaseous charging, (c) H_2^+ ion implantation, and (d) D_2^+ ion implantation.

4. Discussions

It is well known that, the electron energy of several tens of eV is sufficient and effective for ESD of surface adsorbed or chemisorbed species [5]. The present results, however, show that 850 eV is the most effective energy. Considering the penetration depth of about 2 nm for 1000 eV electrons, initially released H does not necessarily originate from the implanted depth (about 20 nm for 500 eV H^+) of the graphite specimen but from shallower regions.

Although the depth profiles of gaseous charged hydrogen and ion implanted hydrogen were not measured, we can estimate them as shown in Fig. 4. The implanted profile was calculated using the TRIM code and the profile of the gaseous charging was calculated based on the diffusion model [6] with hydrogen solubility [6,7] and diffusivity [8]. Due to surface trapping, usually the surface concentration for ion implantation is much higher than that predicted by TRIM calculations [9]. The hydrogen depth profiles given in Fig. 4 clearly reflect the observation that (1) the initial yield was higher for ion implantation compared to gaseous charging and (2) the yield then became lower for ion implantation at extended electron irradiation.

To make the continuous hydrogen release possible, either the incident electrons need to penetrate deeper without fully loosing their energy or the H in the deeper regions need to move to the subsurface regions where ESD occurs. The porous nature of graphite could enable deeper electron penetration, and relatively high electron energy at the yield maximum confirms the subsurface desorption by ESD. Nevertheless, the electron penetration depth of around 2 nm is much less than the H depth profiles (see Fig. 4). Therefore the ESD in regions much deeper than the penetration depth are likely not the main cause of the present ESD behavior.

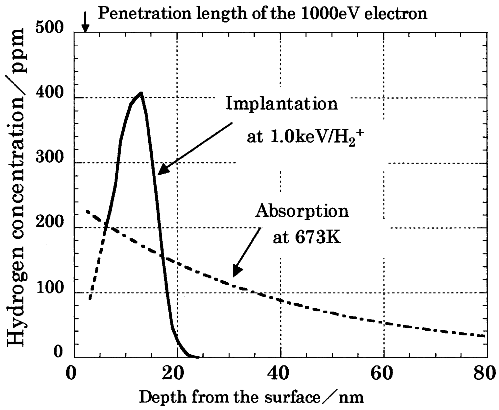

Fig. 4. Calculated depth profiles in graphite for gaseous charged and ion implanted hydrogen. The former is according to TRIM calculation and the latter is based on the solution and diffusion model based on Tanabe and Atsumi [6] with hydrogen solubility [6,7] and diffusivity [8].

Since for the gaseous charged hydrogen, the desorption yield after the extended ESD appears to be a little higher, the migration of hydrogen seems to play a more important role. There are two possibilities. The first possibility is that the hydrogen atom produced by dissociation of a C–H bond from electron excitation may freely migrate through open graphite pores towards the bulk until it is re-trapped or recombined with another trapped hydrogen to produce an H_2 molecule [10]. The other possibility is ordinary diffusion, i.e., atomic hydrogen can diffuse from the deeper regions owing to the hydrogen concentration gradient created by the formation of a depleted zone within the electron penetration range. Since the hydrogen diffusion coefficient in graphite at RT is about 10^{-18} m^2/s [6], we can estimate a diffusion time of 100 s through 100 nm of graphite, which is nearly the same order as the ESD time observed (see Fig. 4). Considering the wide range of discrepancy in reported diffusion coefficients in the literature [6], it is hard to determine which one in the above two mechanisms is the dominant process. The long tails of the ESD time sequences (Fig. 2) seem to suggest that the hydrogen diffusion mechanism is dominant.

Since the binding energy of a single C–C bond (3.60 eV) is a little lower than that of a C–H bond (4.27 eV), free carbon atoms or clusters (radicals) can also be produced. To produce free carbon atoms, however, several bonds must simultaneously be broken, which is more difficult compared to the dissociation of a single C–H bond. In addition, free carbon atoms and clusters can be trapped again by some dangling bonds without producing volatile species [11]. Therefore, according to the desorption model described above, the release of hydrocarbons may be small. To confirm this, we have also measured hydrogen carbon desorption and found that its contribution to the total desorption yield was less than 15%.

5. Conclusions

In the present work, an ESD technique was applied to remove hydrogen from graphite. The initial ESD rate was about 0.2 atoms/electron, agreeing with literature values. Although the desorption rate decreased with continuing electron irradiation, the release of hydrogen continued for a long time. The desorption yields were also found to depend on incident electron energies, with maximum yields occurring around 850 eV incident energy, which is much higher than that for ESD from the top surface. We suggested here that the present ESD process proceed with the following mechanisms: (1) the initial formation of H_2 in subsurface layers by electron excitation accompanying the formation of a hydrogen depleted zone, followed by (2) the immediate release of H_2 through open pores, and finally (3) the diffusion of atomic hydrogen from deeper regions to the depleted zone. Free migration of a detrapped hydrogen atom by electron excitation until its recombination with another trapped hydrogen could be a parallel mechanism. In either mechanism, the production of hydrocarbons must be small as observed.

Thus we have concluded that ESD is effective for hydrogen release from graphite mostly owing to the porous nature of graphite.

Acknowledgements

This work was partly supported by a Grant-in-Aid for scientific research by The Ministry of Education, Culture, Sports, Science and Technology of Japan. We appreciate the critical reading and English revision of the manuscript by Dr A. Chen.

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