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Hydrogen trapping in depositing carbon films

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ABSTRACT

The paper presents results of the experiments devoted to investigation of hydrogen trapping in deposited carbon films under various implantation conditions (residual gas, hydrogen atmosphere, accompanying plasma irradiation). Effect of consequent deuterium irradiation on hydrogen trapping is also studied. Influence of such deposition parameters as deposition rate, residual gas pressure, hydrogen pressure, plasma ions energy, substrate material on hydrogen trapping is discussed. A conclusion about trapping mechanism in growing carbon layers is made.

1. Introduction

One of the problems connected with presence of graphite plasma facing components in tokamak vessels is carbon layer redeposition on the first wall surface. The redeposited layers accumulate large quantities of hydrogen isotopes. It hampers operation of modern tokamaks and leads to sufficient problems of tritium trapping in ITER.

Different aspects of hydrogen trapping in carbon layers were investigated in the paper [1–7]. Nevertheless, up to now the influence of deposition conditions on hydrogen trapping efficiency and mechanisms of hydrogen trapping are not studded satisfactory.

The paper presents results of investigation of hydrogen trapping in deposited carbon films in dependence on following experimental parameters: residual gas pressure, hydrogen gas pressure in the deposition chamber, energy of plasma ions irradiating deposited film, substrate material and temperature. A conclusion about trapping mechanism in growing carbon layers is made.

2. Experimental device and methods

Carbon layer deposition was conducted in the experimental device presented in Fig. 1.

Evaporator (1) is formed by to graphite rods connected with their butt-ends. Junction point heats up and carbon atoms evaporate when current is passed through the rods. Evaporated carbon atoms can reach the substrate (2) through a hole in the evaporator casing.

Ion source (3) constitutes of a plasma chamber with an extracting electrode. Hydrogen discharge was started in the plasma chamber, and ions were drawn to the surface of the growing film. Energy of ions impinging the substrate was in the range of 50–1000 eV/at.

Stainless steel and pyrolitic graphite were used as substrate materials. Graphite substrates were annealed at 1500 K before deposition. Stainless steel substrates were annealed at 1200 K and irradiated in argon discharge.

Carbon layers were deposited in residual gas ($P_{\Sigma} \sim 10^{-3}$ Pa, $P_{H20} = 90\%\ P_{\Sigma}$), in hydrogen atmosphere ($P_{H2} \sim 10^{-3}$–1 Pa) and in hydrogen atmosphere ($P_{\Sigma} \sim 8 \times 10^{-1}$ Pa) with accompanying hydrogen plasma irradiation ($j \sim 1.2 \times 10^{19}$–$6 \times 10^{19}$ $m^{-2} \times s^{-1}$). Hydrogen to carbon flux ratio (H_f/C_f) during deposition varied from 10 to 10^5 in different conditions. Hydrogen flux H_f was calculated using gas-kinetic equation formulas taking hydrogen and water partial pressures into account.

Substrate temperature was equal to 300 K in all experiments. Thickness of deposited films varied from 0.5 μm to 1.5 μm.

The device intended to plasma irradiation and thermodesorption investigations [8] was used for consequent irradiation of deposited films by deuterium plasma and for measurement of quantity of trapped hydrogen and peculiarities of its retention in the film. The temperature rump during TDS analysis was equal to 3 K/s. Maximum temperature of sample heating was equal to 1500 K.

3. Results and discussion

3.1. Carbon film deposition in residual gas

In residual gas films were deposited with various deposition time (30–120 min) and various deposition rates (0.05–0.22 nm/s). Residual gas pressure was varied in the range of 1.1×10^{-3}–6.6×10^{-3} Pa.

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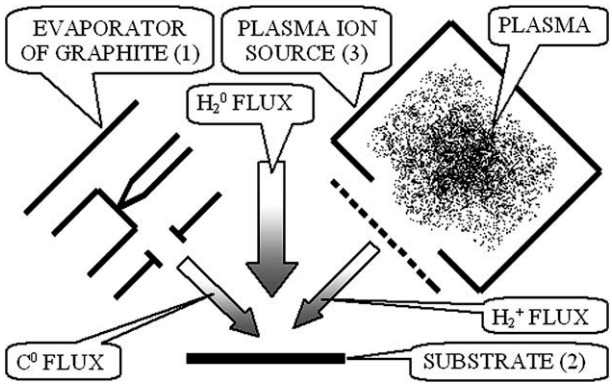

Fig. 1. Scheme of the experimental stand.

The special experimental run was performed for measurement of hydrogen thermodesorption from the substrates prepared for deposition and from the substrates exposed in residual gas, in hydrogen atmosphere and subjected to hydrogen ion irradiation. Last examinations were performed in conditions excluding particle influence on their front surface area. The measurements proved that in all cases hydrogen trapping in the substrate was not higher than some percents of trapping in the carbon films deposited in similar conditions.

Experiments show that hydrogen concentration (H/C) does not change noticeably and remains equal to ~12% for the films deposited in residual gas with deposition parameters varied in the ranges described above. About 10% of trapped hydrogen was released as methane and heavier hydrocarbons. It can be assumed that hydrogen trapped in this case came from the layer of water molecules sorbed on the surface of deposited film. Water molecules concentration in this layer is likely not to depend on the residual gas pressure in these experiments conditions, thus the trapping rate should be constant.

Shapes of thermodesorption spectra of films deposited in residual gas are similar for all deposition conditions, and have one main maximum (Fig. 2) at 1050 K. In the experiments dealing with spectroscopic and thermodesorption from hydrocarbon films [2,7], 1050 K peak was identified with hydrogen trapping in carbon structure with sp^2 carbon atoms hybridisation. Similarity of thermodesorption spectra of the films independently of irradiation conditions allows concluding that hydrogen trapping mechanism was the same for all these films.

Oxygen concentration in films deposited in residual gas (O/C) was in the range (0.03–0.04) and remained constant in whole diapason of experimental parameters as well as it was already mentioned for hydrogen trapping. These values correlate with ratio O/C = 0.02 which was measured on the surface of dense graphite subjected to influence of residual gas containing water vapour [9]. At the same time it is by an order of magnitude smaller than oxygen concentration in graphite implanted by high-energy oxygen ion [10].

Up to 95% of oxygen was desorbed in form of CO and 5% in form of CO_2. Maximum of CO desorption was observed in the 1000–1100 K range, which corresponds to the previously measured results in case of water adsorption [9] and oxygen ion implantation [10].

Estimation shows that totally about 10% of carbon contained in the films was emitted in the forms of hydrocarbons and carbon oxides at the temperatures less than 1200 K. Remaining carbon 'escaped' from the surface in temperature range 1200–1500 K. One can believe that it dissolved in stainless steel substrate.

3.2. Carbon film deposition in hydrogen atmosphere

H/C ratio in hydrogen atmosphere deposited films does not noticeable depend on hydrogen gas pressure and duration of deposition. At the same time one can note that hydrogen desorption as hydrocarbons increases along with pressure growth. 15% of hydrogen desorbs in form of C_XH_Y from the films deposited at 2.4 Pa, whereas it does not exceed 7% when hydrogen pressure during deposition was 0.15 Pa. The increase of hydrocarbons desorption could be the result of presence of high amount of structure defects in the films.

H/C ratio of the films increases with decrease of deposition rate (Fig. 3) and reaches H/C = 0.4 at the deposition rate of 0.07 nm/s. This value of H/C corresponds to the 'saturation concentration' of stopping zone of high-energy ions in graphite [11].

This experimental result can be explained if one assumes that (1) hydrogen is trapped into the film from the constant concentration layer sorbed on the surface and (2) hydrogen could be trapped up to maximum concentration H/C = 0.4.

Under such assumption one can get the following expression for dependence of hydrogen concentration in the film on the deposition time of one carbon layer (t):

$$\mathrm{H/C} = 0.4(1 - \exp(-Awt)) \quad (1)$$

Here: A is hydrogen concentration in the sorbed layer on the surface, w is the probability of an atom being trapped, and $t = 0.3/v$, where v is deposition rate, nm/s.

Eq. (1) fits well experimental data, when $Aw = 0.69\ s^{-1}$ (Fig. 3).

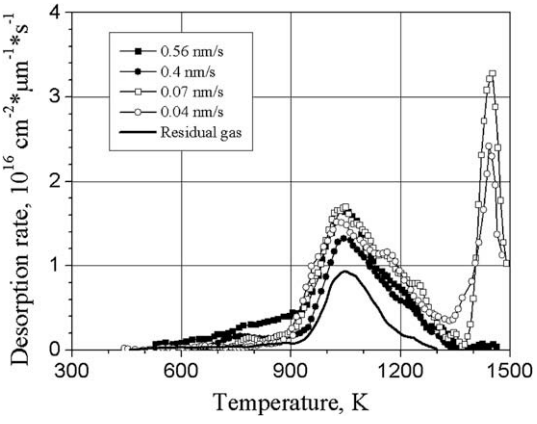

Fig. 2. Spectra of thermal desorption of hydrogen as H_2 form films deposited with different deposition rates.

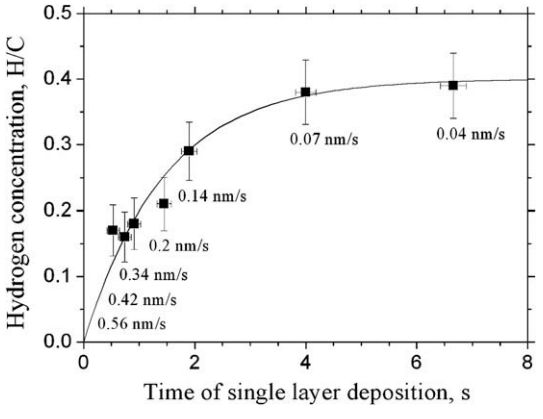

Fig. 3. Dependence of hydrogen concentration in the films on time of single layer deposition (time of single layer deposition inversely proportional to deposition rate).

Increase in pressure does not lead to the change of A and w parameters in conditions of our experiments, thus no changes in trapping occur if rates of deposition are similar, as it was observed in the experiments.

It is interesting to note that ratio H/C does not depend on rate of deposition when hydrogen trapping is provided mainly by water molecules sorbed on the surface (deposition in residual gas). At the same time, the hydrogen concentration in the films deposited in residual gas at deposition rate 0.4 nm/s equals H/C ≈ 0.12. It is much higher than the value, which in accordance with Fig. 3 could be expected for the films deposited in hydrogen atmosphere at the same deposition rate. To explain this fact one can propose that the films contain limited amount of traps available for filling by hydrogen atoms from sorbed water layer. More over the rate of their filling is higher than the rate of their creation.

One can see (Fig. 2) that narrow peak in 1400–1500 K region appears in the TDS spectra of the films deposited with lowest deposition rates. Such peak does not appear in any other cases.

It shows that new high temperature traps and perhaps new structure is formed in the films under low rate deposition. The actual position of this peak seems to be in connection with abovementioned facts of films dissolving in stainless steel substrate during heating up to 1500 K. One can expect that this process is accompanied by sharp release of hydrogen remained in the film, and appearance of the peak reflects this process.

To understand the influence of substrate material on the trapping of hydrogen in carbon films the simultaneous deposition was made on pyrolytic graphite- and stainless steel substrates. Deposition conditions were as follows: hydrogen pressure was equal to 0.15 Pa and rate of deposition was 0.4 nm/s. Hydrogen concentration in the films deposited on pyrolytic graphite substrate appears to be H/C ≈ 0.1, which is twice smaller than concentration in the films deposited on stainless steel. About 30% of hydrogen desorbs in form of hydrocarbons. One can propose that graphite substrate initiate crystallization of depositing graphite film, and thus amount of hydrogen traps decreases.

3.3. Carbon film deposition under assisting plasma irradiation

Low energy 100 eV/H ion irradiation (Fig. 4) does not affect hydrogen concentration in the film, whereas 200 eV/H ion irradiation leads to an increase of the H/C ratio from 0.2 to 0.4.

Under 200 eV/H ion irradiation variation of ion flux densities from 7.5×10^{18}–2.1×10^{19} H × $m^{-2} \times s^{-1}$ and fluencies from 2.7×10^{22}–7.6×10^{22} H × m^{-2} do not change H/C ratio. One can make a conclusion that trapping of low energy ions does not make sufficient contribution in entire trapping. At the same time 200 eV/

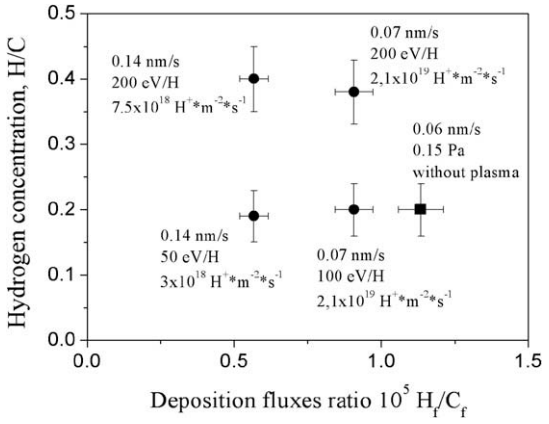

Fig. 4. Hydrogen concentration in the films deposited with accompanying plasma irradiation with different hydrogen ions energy.

Table 1
Hydrogen and deuterium trapping after consequent deuterium ions irradiation (400 eV/D, fluence 5×10^{23} D × m^{-2}, flux 1×10^{20} D × $m^{-2} \times s^{-1}$).

Desorption species	Not irradiated	Irradiated 400 eV/D
$2 \times H_2$, $m^{-2} \times \mu m^{-1}$	1.8×10^{22}	2.2×10^{22}
$4 \times CH_4$, $m^{-2} \times \mu m^{-1}$	2×10^{21}	3.3×10^{20}
HD, $m^{-2} \times \mu m^{-1}$	–	6×10^{20}
$2 \times D_2$, $m^{-2} \times \mu m^{-1}$	–	3.5×10^{21}
(H + D)/C ratio	0.2	0.25

at ions penetrating the films can create new traps in the films due to their kinetic energy.

That is why one can conclude that a retention increase under high-energy ion bombardment can be provided by both by fast ions stopping in the deep layers of the film, and by hydrogen atoms from the layer sorbed on the surface.

Hydrocarbon desorption from plasma assisted deposited films is sufficiently higher than that of the films deposited without plasma treatment. In particular, amount of hydrogen desorbed in form of methane and heavy hydrocarbons increases from 15% in case of hydrogen atmosphere deposition to 22% in case of deposition accompanying by 200 eV/H hydrogen ions irradiation.

3.4. Consequent carbon layer irradiation in deuterium plasma

Consequent ion irradiation sputters the films. Amount of carbon atoms in the remaining part of carbon films was determined through weight loss measurements. Hydrogen and deuterium content in the remaining fragment of the films was measured by their thermodesorption. 100 eV/H ion irradiation leads to a decrease of hydrogen concentration in the films. Contrary to that (H + D)/C ratio of the film irradiated by 400 eV/at increases from 0.2 to 0.25. One can see (Table 1) that deuterium load in total desorption is small. Higher value of (H + D)/C ratio in comparison with H/C ratio of the film before irradiation provides by an increasing of hydrogen concentration in the remaining part of the film.

It can be concluded that high-energy ion bombardment stimulates modification of entire film structure, which results in an increase of equilibrium trap concentration. Some portion of hydrogen atoms release from the ion bombarded layers and is trapped into new generated traps. Thus hydrogen concentration in the deep layers increases. At the same time, low energy ion irradiation leads to creation of new traps only in the near surface layers subjected to sputtering away under consequent ion bombardment. These traps are filled with hydrogen, diffusing from the bulk. Thus the film remaining after ion bombardment contains less hydrogen. So, one can see that ion bombardment affects the whole volume of the film.

The quantity of deuterium desorbed in the form of HD practically equals the quantity of deuterium released as D_2.

In all cases consequent ion bombardment leads to a decrease of hydrogen desorption in form of hydro- and deuterocarbons. This result is opposite to that observed in plasma assisted deposition experiments (see above). It seems that during ion irradiation a transformation of the film structure closes cracks and pores by means of which hydrocarbon molecules can desorb.

4. Conclusion

The paper presents results of investigation of hydrogen trapping in deposited carbon films in dependence on following experimental parameters: residual gas pressure, hydrogen gas pressure in the deposition chamber, energy of plasma ions irradiating deposited film, substrate material. A conclusion about trapping mechanism in growing carbon layers is made.

Experiments show that hydrogen concentration (H/C) in the films deposited in residual gas does not change noticeably and remains equal to ~12% for various deposition rates (0.05–0.22 nm/s) and residual gas pressure (1.1×10^{-3} Pa–6.6×10^{-3} Pa).

Assumption is made that hydrogen trapped in this case came from the layer of water molecules sorbed on the surface of deposited film.

H/C ratio in hydrogen atmosphere deposited films does not noticeable depend on hydrogen gas pressure. H/C ratio of the films increases with decrease of deposition rate and reaches H/C = 0.4 at the deposition rate of 0.4 nm/s.

Experimental results showed that hydrogen is trapped into the film from the constant concentration layer sorbed on the surface, and its concentration in the film does not increase H/C = 0.4.

Low energy 100 eV/H ion irradiation assisting a film deposition does not affect hydrogen concentration in the film, whereas 200 eV/H ion irradiation leads to an increase of the H/C ratio from 0.2 to 0.4.

Consequent irradiation with 100 eV/H ions leads to a decrease of hydrogen concentration in the films. In the film irradiated by 400 eV/at. concentration of both hydrogen isotopes reaches (H + D)/C = 0.25, which is higher than H/C = 0.2 in the film before irradiation. This increase is provided by hydrogen atoms, which release from the ion irradiated surface layers and fill the traps created by high-energy ions in the bulk layers of the film.

So, one can see that ion bombardment affects the whole volume of the film.

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