Influence of deuterium ion and atomic exposure on dehydrogenation of C:H films

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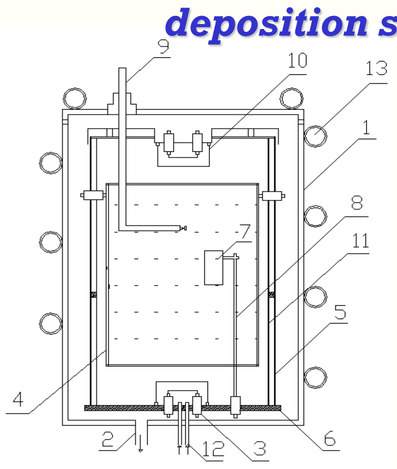
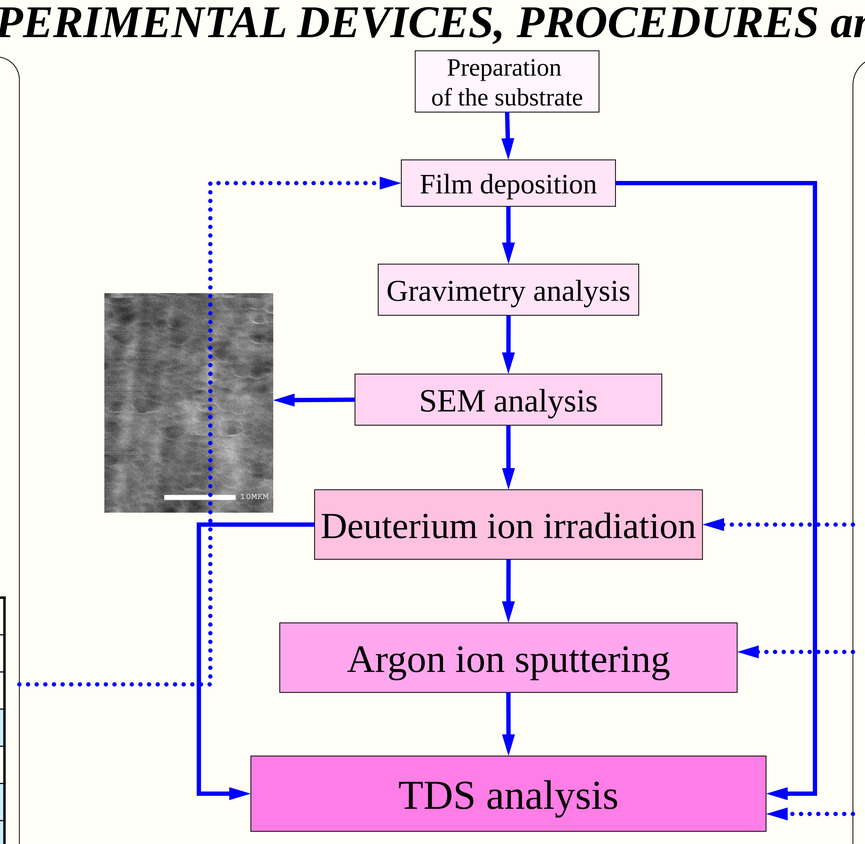
EXPERIMENTAL DEVICES, PROCEDURES and PARAMETERS

Scheme of carbon films deposition system

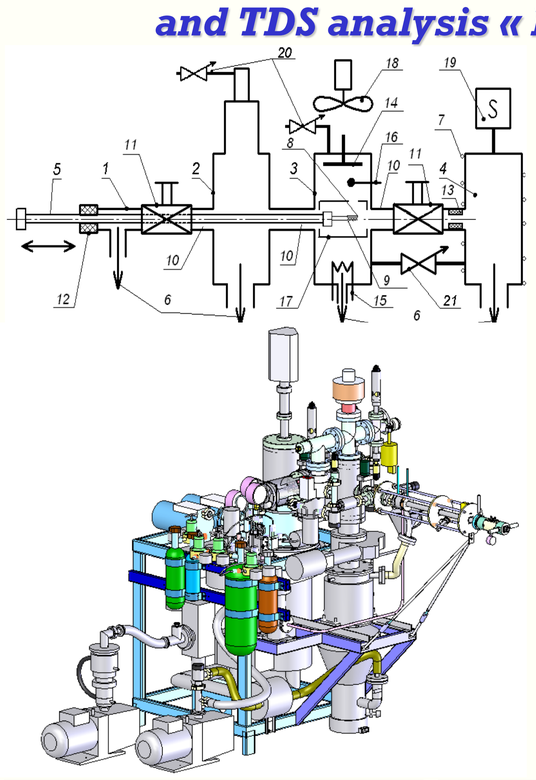


1 - vacuum chamber
2 - to exhaust system
3 - first filament
4 - plasma chamber
5 - second thermal shield
6 - plate
7 - sample unit
8 - support of sample unit
9 - Langmuir probe
10 - second filament
11 - first thermal shield
12 - to puff system
13 - cooling system

Working gas	C_3H_8	55%
	C_4H_{10}	40%
	Ar	5%
Residual gas pressure		1 10^{-3} Pa
Working pressure		0.25 Pa
Parameters of plasma ions irradiation of substrate	Ion energy	400 eV
	Ion current density	4 mA/cm^2
	Mean carbon atoms energy	≈ 100 eV/C
	Mean carbon atoms flux	≈ 1.3·10^{16} C/(cm^2·s)
	Mean hydrogen atoms energy	≈ 10 eV/H
	Mean hydrogen atoms flux	≈ 3.4·10^{16} H/(cm^2·s)
Substrate material		Stainless steel
Substrate dimension		30 40 mm^2
Substrate temperature	annealing	Up to 900 °C
	deposition	400 °C
Rate of film deposition		0.35 nm/sec
Film thickness		2,5 mcm
Film density		≈ 2 g/cm^3
Hydrogen concentration		0.19 ± 0.03



Stand of plasma and ion beam irradiation and TDS analysis « MICMA »

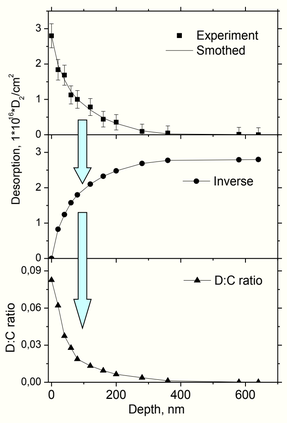


1 - lock chamber
2 - ion gun chamber
3 - plasma chamber
4 - TDS chamber
5 - sample manipulator
6 - pipe branches
7 - water cooling
8 - sample
9 - sample heater
10 - pipe branches
11 - fate valves
12 - feed-through
13 - sealing
14 - anode
15 - filament
16 - probe
17 - shield
18 - cooling fan
19 - gas mass-spectrometer
20 - gas inlet valves
21 - auxiliary pipe-line

Parameters of deuterium ion irradiation	
Residual gas pressure	1 10^{-5} Pa
Working pressure	0.07 Pa
Ion energy	50 and 400 eV/D
Atom flux	1·10^{16} D/(cm^2·s)
Ion fluence	5·10^{19} D/cm^2
Sample temperature	500 K

Parameters of argon ion sputtering	
Residual gas pressure	1 10^{-5} Pa
Working pressure	0.04 Pa
Ion energy	300 eV
Flux	5·10^{15} Ar/(cm^2·s)
Sample temperature	470 K
Sputtering depth	20 – 900 nm

Parameters of the TDS analysis	
Maximal temperature	1500 K
Heating rate	5 K/s
Residual gas pressure in TDS chamber	1·10^{-6} Pa



A method of depth profiles calculation

$$N(x) = \frac{d}{dx}(R_0 - R(x))$$

$$n_D(x) = 10^{-16} \cdot (N_{HD}(x) + 2 \cdot N_{D_2}(x) + \sum_{Y=1}^{4} Y \cdot N_{CH_{4-Y}D_Y}(x))$$

where $R(x)$ – smothed desorption from the sample after sputtring of depth x, $R_0 = R(0)$, $N(x)$ – depth distribution

INTRODUCTION

The aim of the work is to investigate deuterium atoms diffusion in C:H films under deuterium plasma and atomic irradiation and influence of energetic deuterium ions on hydrogen desorption from the surface and bulk of the films.

C:H films with hydrogen concentration 0.19 ± 0.03 were deposited in PCVD reactor. Deposited films were irradiated by deuterium 50 and 400 eV/D ions extracted from plasma. Irradiated C:H films were sputtered by argon ions in the range of 20 nm to 900 nm and then analysed by TDS method. A number of such experiments were carried out. As a result depth profiles of hydrogen isotope distribution in C:H films have been obtained.

Method of hydrogen amount calculation

$$n_H = 10^{-16} \cdot (N_{HD} + 2 \cdot N_{H_2} + \sum_{Y=1}^{3} X \cdot N_{CH_YD_{4-Y}})$$

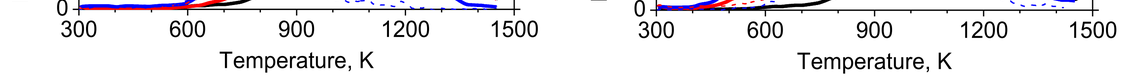
$$\begin{cases} N_{H_2} = k_H \cdot [H]^2 \\ N_{HD} = k_{HD} \cdot [H] \cdot [D] \\ N_{D_2} = k_D \cdot [D]^2 \end{cases} \quad N_{H_2} = N_{HD}^2 / N_{D_2}$$

- ✓ Hydrogen isotopes molecules in C:H films are formed in the bulk of the film [1]
- ✓ Hydrogen recombination should be occurred in place of atoms detrapping, that means equality of k_H, k_{HD} and k_D

N – amount of hydrogen isotopes square brackets mean atomic concentration, k - recombination koefficients

[1] Ch. Wild, P. Koidl. Thermal gas effusion from hydrogenated amorphous carbon films // Appl. Phys. Lett. 1987. V. 51. P. 1506.

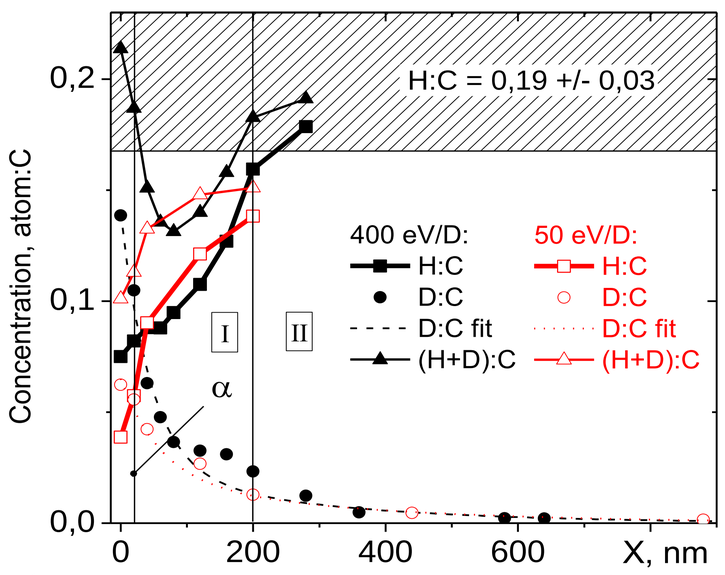
TDS spectra of H_2, HD and D_2 from ion irradiated films



- ✓ TDS spectra of C:H fims irradiated by 50 and 400 eV/D ions are similar
- ✓ HD spectra are similar to H_2 spectra.
- ✓ D_2 mainly desorbs in the range 600 – 1000 K even after sputtering of 120 nm. This indicates that deuterium traps appears in the layers which place much deeper of mean ion deuterium range [2].
- ✓ From depth more than 200 nm (region II) deuterium desorption occurs only in HD.

[2] A.Airapetov, L. Begrambekov, C. Brosset, J.P. Gunn, C. Grisolia, A. Kuzmin, T. Loarer, M. Lipa, P. Monier-Garbet, P. Shigin, E. Tsitrone. Deuterium trapping in carbon fiber composites exposed to D plasma // J. Nucl. Mater. 2009. V. 390–391. P. 589.
[3] A.A. Ayrapetov, L.B. Begrambekov, S.V. Vergazov, A.A. Kuzmin, O.S. Fadina, P.A. Shigin. TDS spectra of hydrogen and their relationship with implantation and retention conditions in graphites. Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques. 2010, in press

Hydrogen isotope distribution in C:H film after deuterium ion and atomic irradiation



$$\begin{cases} \frac{\partial n}{\partial t} = D \cdot \frac{\partial^2 n}{\partial x^2} \\ n(x,t) = n(x - w \cdot t) \\ n_0 = n(x - w \cdot t)\big|_{x=w \cdot t} \end{cases}$$

n – deuterium concentration
n_0 – maximal surface concentration
w – rate of sputtering
t – time of irradiation
D – duffusion coefficient

$$n(x) = n_0 \cdot \exp(-w \cdot x / D)$$

$$n(x) = n_I \cdot \exp(-w \cdot x / D_I) + n_{II} \cdot \exp(-w \cdot x / D_{II})$$

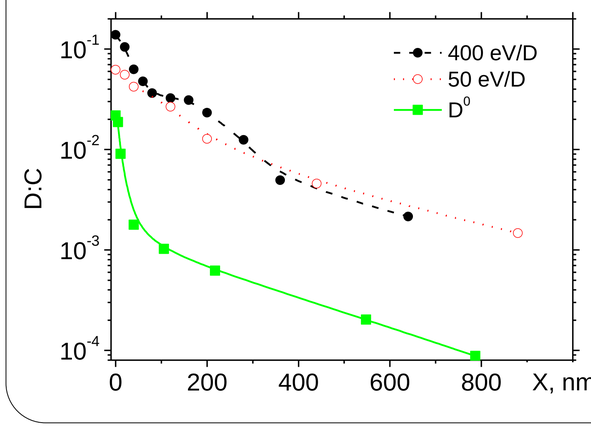
$D_I = 3 \cdot 10^{-14}$ cm^2/c; $D_{II} = 2 \cdot 10^{-13}$ cm^2/c

Maximal D for graphite with T = 500 K: 10^{-15} - 10^{-17} cm^2/c [4]

- ✓ Concentration (H+D):C in region I is significantly less then H:C = 0.19. It means that hydrogen desorption was not only due to isotope exchange.
- ✓ Hydrogen concentration decreased on the depth up to 200 nm that much deeper than mean deuterium ion range with energy 400 eV/D (≈ 10 nm, [5]).
- ✓ Diffusion coefficient of deuterium in the bulk of C:H film higher than its diffusion in graphite about two order of magnitude.
- ✓ Disordering of carbon structure leads to decreasing of the diffusion [6]

[4] H. Atsumi. J. of Nucl. Mater. 2002. V. 307–311. P. 1466
[5]G.G. Ross, G. Granger, M. Gaithier. Depth distribution of 0.4-1.6 keV deuterium ions implanted into polysterene and hydrogenated carbon NIMB 164-165 (2000) 324-336.
[6] V.N. Chernikov, W.R. Wampler, A.P. Zakharov, A.E. Gorodetsky. J. of Nucl. Mater. 1999. V. 264. P. 180.

$D_I = 3 \cdot 10^{-16}$ cm$^2 \cdot$c^{-1}, $D_{II} = 6 \cdot 10^{-15}$ cm$^2 \cdot$c^{-1}



- ✓ Atomic deuterium irradiation led to deuterium trapping mainly in the top surface layers
- ✓ D^0 irradiation did not cause to any noticeable hydrogen desorption from the films.
- ✓ Deuterium desorption occurred in the form of HD
- ✓ Shape of HD spectra are the same to H_2.

CONCLUSIONS. *A new experimental methods of data processing are proposed basing on TDS analysis and sputtering. Depth profiles of hydrogen and deuterium in C:H films were obtained. Diffusion coefficients of deuterium in ion irradiated C:H films were estimated. They equal to ~10^{-13} – 10^{-14} cm^2/s. It was suggested that comparably to graphites high diffusion coefficients of deuterium atoms in C:H layer are due to (i) process of isotope exchange and/or (ii) low amount of dangling carbon bonds in hydrogenated structure.*

Phenomena of hydrogen desorption from deep layers of C:H films under deuterium plasma irradiation was observed. It is attributed to stress growing in the films during particle implantation which leads to creation of the defects that can diffuse into deep layers. These defects provoke hydrogen release from carbon traps due to their potential energy.