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Experimental modeling of transport and deposition of hydrocarbon radicals on ITER-FEAT cold trap

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Abstract

The surface loss probability, β, of methyl (CH_3) radicals and atomic (H) hydrogen on a growing film surface was measured at lowered temperatures. The loss of reactive species was investigated by analysis of the deposition profiles along a quartz tube reactor directly coupled with a methane RF discharge (so-called 'stream' technique). The experiments were performed using special external containers with dry ice (~200 K) and liquid nitrogen (77 K). It has been found that $\beta(CH_3)$ on the growing film surfaces increases from 1.6×10^{-4} at 300 K to 6.2×10^{-4} at 200 K. Based on the data analysis, β for H can be deduced. The β(H) values were 3×10^{-4}, 1×10^{-3} and at least 10^{-2} at 300 K, ~200 K and 77 K, respectively. Film deposition from hydrocarbon radicals generated in a magnetron discharge is studied at temperatures from 300 K down to 120 K. Transition from formation of film-like to drop-like deposit is observed with cooling the substrate from 220 to 120 K. The application of the results to the understanding of transport and deposition of neutral reactive species on ITER-FEAT cold trap have been given.

Keywords: High-frequency discharge; Magnetron discharge; Surface loss probability; Deposition; Hydrocarbon radicals; ITER-FEAT

1. Introduction

In future fusion reactors the main flux of the exhaust gas mixture containing ions and atoms of hydrogen isotopes will impinge onto the vertical divertor target manufactured from carbon materials [1–3]. The interaction of the incoming flux with carbon will lead to sputtering and chemical erosion of the target surface. As a result atomic carbon and possibly neutral hydrocarbon molecules and radicals will penetrate the private flux area and be deposited on the cooler surfaces of the semi-transparent liner and another elements of the divertor design, forming amorphous hydrocarbon a-C:H films with a high content of hydrogen (H/C ~ 1). In turn the deposit can be a source of different types of hydrocarbons (including radicals) via chemical erosion by atomic hydrogen [4]. Thermal decomposition and evaporation of the films is another possible mechanism for formation of neutral reactive species [5].

Among hydrocarbon radicals, methyl, which has a very low reactivity, represents the most danger as it can penetrate far into the pumping duct and reach the cryopump. It is known that the deposition of such radicals at 300 K leads to the formation of the hydrocarbon films stable up to 450 K [5]. Unfortunately, there are no data

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on film growth from CH_3 at low temperatures. Today's cryo-pumps work on a two-step regeneration strategy and can be heated up to ambient temperatures only [6,7]. Thus it is possible to contaminate such cryo-pumps by liquid-like high boiling point substances. To protect the ITER-FEAT cryo-pump from the accumulation of the deposits and freeze out all reactive hydrocarbons, a cold trap to be located before the cryo-pump has been developed [8]. The facility will operate at liquid nitrogen temperature with the possibility of regeneration by heating up to 600–650 K. For the design of such a cold trap a knowledge of the main mechanisms of film growth at low temperatures is needed.

Modeling of the transport and deposition of hydrocarbon molecules and radicals on the cold trap and the influence of atomic hydrogen on these processes is the goal of this paper. An inductively coupled RF glow discharge in methane and magnetron sputtering of a graphite target by deuterium were used as a sources of hydrocarbon radicals and atomic hydrogen.

2. Tube reactor experiments

2.1. Experiment

To study the interaction of hydrocarbon radicals and atomic hydrogen with the surface at low temperatures, the so-called 'stream' technique, was used. Generally, this technique includes an experiment in which a stream of neutral reactive species passes through a cylindrical tube reactor and a simple model for the description of the loss of these particles on the inner walls of the reactor [9,10].

The model describes kinetics of reactive species loss on the inner walls of the cylindrical tube for Poiseuille flow. In our case for fast established profile of flow rate the usual transport equation for cylindrical coordinates was used. From the solution of the equation with regard to diffusion along the tube a surface loss probability β which is equal to the sum of sticking and recombination probabilities of various reactive species can be deduced.

In our experiments the reactive species were produced by an inductively coupled RF glow discharge in methane inside a quartz tube reactor. The experimental parameters of the discharge were following: frequency = 13.56 MHz, pressure = 28 Pa, methane gas flow = 6.9 sccm (0.0115 Pa m^3/s), specific power = 0.1 W/cm^3. The plasma area was limited by special metal grid. Behind the grid the ion density drops drastically with a scale length of less than 1 cm along the tube, due to its high sticking coefficient (about 1) on the a-C:H surface [11]. Thus in this area only methane as a gas carrier and neutral products of its decomposition in the discharge such as methyl radicals and atomic hydrogen can pass (see details in [12]).

For the determination of β for hydrocarbon radicals and atomic hydrogen the analysis of a deposition profile of the carbon films on the inner wall surface along the tube reactor was carried out. The carbon films thickness (areal density, more correctly) on silicon wafers placed along the deposition area was measured ex situ using electron probe microanalysis (EPMA). The structure and composition of the deposits were investigated by reflection high energy electron diffraction and gas chromatograph connected with Mass-Spectrometer (GC-MS), respectively.

2.2. Results and discussion

2.2.1. Tube experiments at 300 K

It was obtained that at 300 K the experimental data for the normalized deposition rate as a function of the distance along the tube can be fitted by two exponential decay curves (Fig. 1(a)). These decays may be described by decay lengths $Z_1 = 10.5$ cm and $Z_2 = 29$ cm, respectively. Taking into account that the most probable hydrocarbon precursor in the methane RF discharge is the methyl radical it is reasonable to consider that only this radical makes the basic contribution in deposition [11,13]. Thus these decay lengths can be used for calculation of the surface loss probability β of methyl radicals [9]. This yields $\beta(CH_3)$ values of 5.6×10^{-4} and 1.6×10^{-4} for first and second deposition zones, correspondingly, where first zone is an area just behind the grid up to 30 cm length and second zone is an area from about $x = 30$ cm and further.

Surface loss probability of CH_3 radicals was deduced in [14] and is equal to 2.2×10^{-4}. This value is less than β value obtained in our experiments for the first zone. In [15] it was shown that an additional flux of atomic hydrogen can significantly (from 10^{-4} to 10^{-2}) increase the sticking probability of methyl radicals and hence increase the surface loss probability β of these radicals. This effect corresponds to the growth synergism between H and CH_3. Thus the deposition rate in the first zone may be governed by the additional H atoms flux. To find out the influence of the atomic hydrogen on the enhanced value of β in the first zone the separate experiments were carried out.

In our previous work [12] it was shown that deposition in the first zone of the reactor was absent during heating of the area in the temperature range 380–800 K. Moreover loss of weight owing to surface erosion of well characterized hard hydrocarbon a-C:H films was observed. The experiments were carried out at 650 K in different places of first zone at standard conditions of a methane RF discharge as a source of hydrocarbon radicals and H atoms. Taking into account that the erosion yield by H atoms at 650 K is equal to about 0.02 [16] and knowing the weight loss the H atom flux can be calculated (see Fig. 1(a)). The flux of the atomic hydrogen at the

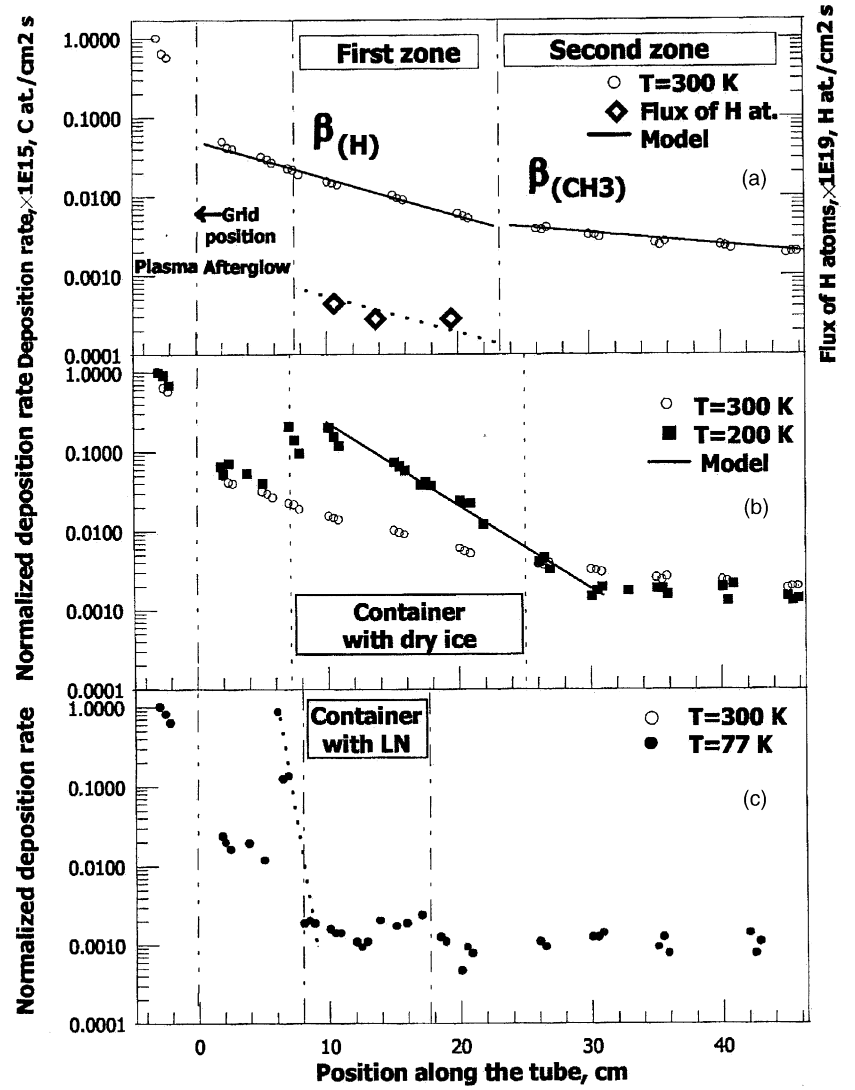

Fig. 1. (a)–(c) Normalized carbon deposition rate as a function of position (x) along the quartz flow reactor for two different temperatures of the cold trap: 200 K (container with dry ice, (b)), and 77 K (container with liquid nitrogen, (c)). In addition, the deposition rate at 300 K as well as flux of H atoms (a) are shown. The solid lines denote the modeling of the deposition profile at 200 and 300 K. The dashed lines only guide for eye.

beginning of the first zone (position $x = 8$ cm behind the grid) is equal to 6.2×10^{15} H at./cm^2 s. The flux of the methyl radicals will be estimated below and is in an interval from 0.3×10^{17} to 1.8×10^{17} mol./cm^2 s for the same position in the tube. Thus the CH_3:H flux ratio is equal to about (5–30):1 (see details in [17]).

According to the synergistic model [18] the growth rate of deposits is proportional to the H flux for comparable or smaller H fluxes with respect to the CH_3 flux. In this view, the decay length Z_l was measured for the surface loss of H atoms and not for the CH_3 radicals. The estimation of β(H) taking into account the diffusion coefficient of hydrogen in methane yields 3×10^{-4}.

It should be noted that β(H), as obtained for our case, is about two orders of magnitude smaller than β(H) obtained from synergistic model of atomic hydrogen loss on the growing surface of a-C:H film (1.4×10^{-2}). At the same time the value is in good agreement with experimentally measured recombination coefficient γ of atomic hydrogen on the 'growth' side of a diamond plate at 300 K (about 4×10^{-4}) [19]. In addition it was observed that H atom recombination activity on the opposite 'smooth' side of the plate is higher than that on the 'growth' side by a factor of 5–10. Thus β(H) depends strongly on the activity on the growing surface. In our case this means that upper layer of growing film in the first zone is close to the diamond surface structure with sp^3 – coordinated surface sites.

In our experiments $\beta(CH_3) = 1.6 \times 10^{-4}$ obtained for the second zone is close to value of 2.2×10^{-4} deduced for CH_3 without atomic hydrogen in [14]. This means that deposition in the second zone occurs without or with a very small contribution of atomic hydrogen.

2.2.2. *Tube experiments at lowered temperatures*

The deposition profiles along the reactor using external containers with dry ice (~200 K) and liquid nitrogen (77 K) are presented in Fig. 1(b) and (c). In the experiments at 200 K the deposition in the first zone was described by a decay length of $Z_1 = 4.4$ cm. It is quite reasonable to suppose that the slope of the decay curve is connected with surface loss probability of atomic hydrogen $\beta(H)$ as well as at 300 K. The model calculations yields $\beta(H) = 1 \times 10^{-3}$. Increasing of $\beta(H)$ value can be caused by changes in the surface structure of the growing film. Indeed, at 200 K very soft films were formed. Moreover, the total amount of deposit along the entire deposition area at 200 K was increased by five times in comparison with that at 300 K. These experimental results can be explained on the basis of a growth film model presented in [20].

According to the model [20], incorporation of CH_3 includes abstraction of surface-bonded hydrogen by direct reaction with incident H or CH_3 which follows direct chemisorption of incoming CH_3 at dangling bonds. The temperature dependence of the net deposition rate is governed by the thermal stability of dangling bonds at the growing film surface. At low temperatures the dangling bond lifetime increases significantly and therefore a greater amount of CH_3 can be chemisorbed. It is necessary to note that additional deposition of methyl radicals can occur only due to decreasing or even complete suppressing of their recombination. With this assumption, CH_3 flux in the tube position of $x = 8$ cm can be estimated to be in the range from 0.35×10^{17} mol./cm^2 s up to 1.8×10^{17} mol./cm^2 s for deposition at 300 and 200 K, respectively.

Cooling of the second zone of the tube reactor down to 200 K was characterized by $Z_2 = 10$ cm and hence $\beta(CH_3) = 6.2 \times 10^{-4}$ (is not shown on the Fig. 1). Total mass of deposit was increased in three times compare to 300 K. In the framework of the growing film model obtained results can be explained as follows.

Without atomic hydrogen, abstraction of surface-bonded hydrogen by methyl is unique opportunity for the creation of dangling bonds which are needed for film growth. At the same time this reaction is a reaction of recombination or loss of methyl radical. Therefore the increasing of the total amount of deposit at low temperatures is possible only owing to more effective utilization of dangling bonds via CH_3 chemisorption. As the efficiency of creating dangling bonds by H atoms is larger than that by CH_3 the total amount of deposit in the last case will be less (according to our data by 3–5 times, respectively). Another explanation, connected with additional input of C_xH_y neutral species into the deposition at low temperatures will be considered later.

The deposition at liquid nitrogen temperature (80 K) just behind the grid (start point $x = 8$ cm) is characterized by only one sharp slope of decay curve ($Z_1 \approx 1$ cm). Unfortunately a formula for β evaluation is fair only for kinetic area of reactive species lost formula and cannot be used in this case [9]. It is clear however that $\beta(H)$ value is not less than 10^{-2}.

Note that the total amount of deposit in both cases (200 and 77 K) was approximately the same. Taking into account that initial fluxes of H atoms and CH_3 were identical and determined by experimental conditions, this means that the thermal stability of dangling bonds both at 200 and 77 K was identical too. At the same time $\beta(H)$ is determined by structure of growing film and therefore can be different. Really, the liquid-like deposit was found out at 77 K. Except a continuous film, the drops of a deposit were found out on the surface of a silicon wafers.

GC-MS analysis shows that the liquid-like deposit consists of a mixture of isomers and homologues of aromatic and unsaturated hydrocarbons with boiling temperatures in the range 400–600 K. Apparently both compounds were formed as a result of surface reactions of methyl radicals at low temperatures. The deposit loses weight on holding in air at 300 K and rapidly decomposes upon heating in vacuum.

At last, behind the area of stable film a deposit which evaporated before reaching room temperature was found. On the basis of visual observations of the deposit behavior during the defrosting of the reactor it can be concluded that the deposit was not water. In our opinion, the nature of the films can be connected with the condensation of C_xH_y stable volatile molecules (for example, C_4H_{10} and so forth) at lowered temperatures. These molecules could be formed via polymerization reactions between ions and radicals in the plasma and than pass through the grid into the deposition area together with other neutral products of methane decomposition in RF discharge. Except CH_3 these neutral species can also contribute into the deposition of stable films (not less than 40% according to [21]). This process can, for example, enhance the total amount of deposit in the second zone at 200 K. Incorporation of C_xH_y neutrals into growing film can be satisfactorily explained as well as for CH_3 radicals in the framework of the mentioned growth film model [20]. It should be noted that this process is only possible if dangling bonds are continuously formed at the film surface by the CH_3/H reactive mixture. Without atomic hydrogen and methyl radicals which can create dangling bonds for stable film formation only the usual condensation of stable volatile C_xH_y species can take place.

3. Magnetron experiment

In this section preliminary experiments are presented in which an attempt is made to answer the question at what temperature the sticking coefficient of the radicals generated in plasma of a magnetron discharge might be increased. A diagram of the experimental setup is shown in Fig. 2. Carbon is eroded from a graphite cathode in form of thermal hydrocarbon molecules (methane and heavier hydrocarbons) and kinetic hydrocarbon radicals [22]. Secondary hydrocarbons are formed due to re-etching of films grown on the discharge chamber walls with D atoms formed in the plasma. The composition of neutrals diffusing through the opening to the main chamber seems to be influenced also by plasma reactions. Deposit formation on the substrate fixed at the cooled holder was checked. Exposure time was 30 min in all the runs. Carbon deposition was evaluated both by substrate weighing and EPMA.

No film deposition was found at 300 K within a detection limit of 10 nm. A typical a-C:D film was deposited on the 220 K substrate. Assuming formation of soft polymer-like film with a density of 1 g/cm^3 the deposit thickness is estimated to be 300 nm. With further cooling the substrate down to 120 K, a drop-like deposit was found. It was found that the same weight gain was measured at 120 K as for 220 K. EPMA measurements show no carbon on the surface in the substrate area between the drops. From TDS measurements it follows that the drop-like deposit exhibits both very soft and hard films behavior: decomposition starts at 400 K whereas significant desorption of HD and D_2 molecules occurs around 1000 K. In addition the drops become black after TDS heating up to 1100 K.

In terms of sticking coefficient of hydrocarbon radicals the results found are explained as follows. A spectrum of radicals is formed in the discharge chamber. They diffuse from the discharge chamber into the vacuum chamber. Here, very reactive radicals like C_2D with close to unity sticking coefficient disappear effectively in collisions with the vacuum chamber walls before impinging on the substrate. The production of low reactive

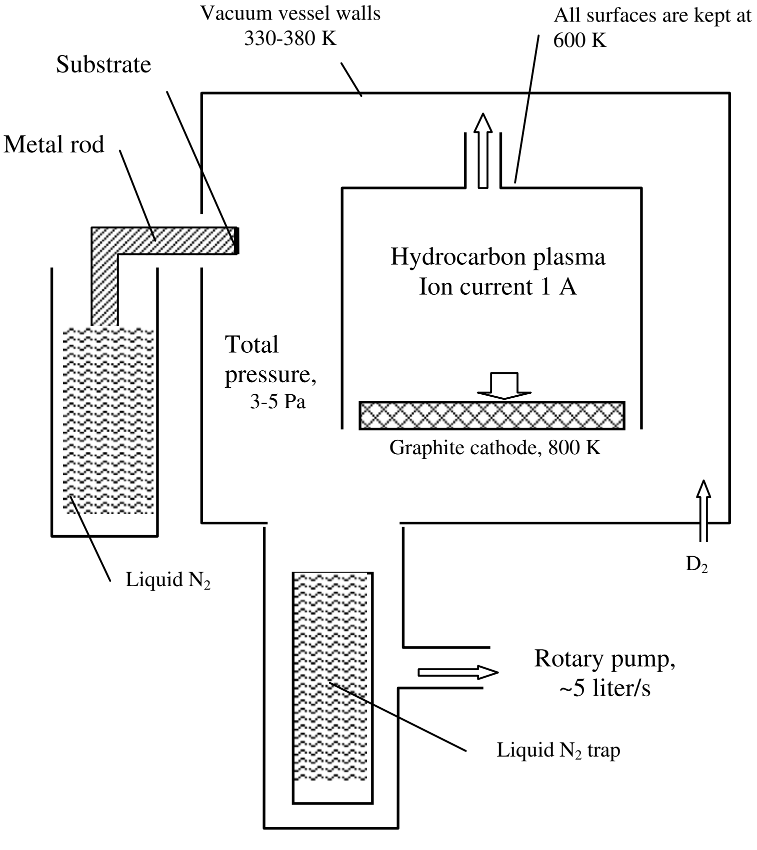

Fig. 2. Experimental setup (magnetron experiment) for simulation of ITER cold trap behavior.

radicals like CD_3 seems to be insufficient to contribute to film growth at all temperatures. The magnetron experiment shows no significant increase in deposit by cooling the substrate below 220 K. Thus other radicals seem to govern the polymerization in the vacuum chamber. The sticking coefficient of these radicals is low at 300 K but increases at least by 30 times at 220 K. Another explanation is connected to the greater thermal stability of radicalic centers created by CD_3 and H atoms at lowered temperatures. In this case CD_3 radicals can be responsible for deposition. Changes in deposit morphology is understood by instability of the deposit due to heavy hydrocarbon condensation and evaporation during warming the substrate up to 300 K.

4. Conclusions

The most important result from tube experiments at low (200–77 K) temperatures is that CH_3 radicals form stable C:H deposits at room temperature both with and without presence of atomic hydrogen. Moreover C_xH_y stable molecules can be incorporated into the deposit via impact of CH_3/H reactive mixture. Therefore in ITER-FEAT case it is very important to know whether H atoms and CH_3 can reach a cold trap. Methyl radicals have a very small reactivity and therefore are able to survive, an average, up to 10^4 wall collisions before loss occurs and necessarily will reach the trap. Surface loss probability of H atoms depends strongly on structure of growing film. If β(H) is about 10^{-4} at 300 K like in our case, then atomic hydrogen will reach the cold trap too. At low temperatures in the presence of CH_3/H reactive mixture a liquid-like C:H deposits which consists from aromatic compounds and poly-alkenes are formed. Usual condensation of stable C_xH_y molecules is probably possible only without additional H and CH_3 fluxes. Such deposits will not be stable and will evaporate at defrosting of the cold trap up to ambient temperatures.

In our opinion it is desirable to place a cold trap design as close as possible to the hot liner for using the advantages of both low temperatures and high flux of atomic hydrogen.

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