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Transport of and deposition from hydrocarbon radicals in a flow tube downstream from a CH_4 RF discharge

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Abstract

The stream technique is used for the measurement of the surface loss probability (β) and sticking coefficient (s) of a hydrocarbon radical. A CH_4 RF inductive coupled discharge is used as source of CH_i radicals and H atoms. These species lead to film formation in the downstream region of the tube. The thickness profiles along tube of the deposited carbon films are measured. The areal density and the structure of the carbon deposits on Si wafers, which are mounted inside tube, are studied by EPMA and RHEED. At 300 K the deposition profile of the a-C:H films can be approximated by $\exp(-x/L)$, where x is the position in the tube and L is the transport length. By measuring L, β coefficients can be determined. On the basis of a comparison with literature, one can conclude that methyl radicals contribute predominantly to a-C:H deposition. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon; Fusion reactor; Growth; Redeposition

1. Introduction

One of the main concerns for the ITER design is the formation of tritium codeposits on colder surfaces of the divertor, which are not in direct line-of-sight to the plasma. The low temperature, high particle fluxes of CH_i and H species may lead to the formation of polymer-like hydrogenated carbon films (H/C ≈ 1) in these areas, where ions are absent [1]. To minimize the hydrogen isotope accumulation on the pumping duct areas, the systematic investigation of the radical transport, the loss of hydrocarbon radicals and H atoms on different surfaces are required.

One key input parameter in this problem is the surface loss probability (β) and its components–sticking (s) and recombination (γ) coefficients for certain radical types. These quantities can be measured, at the moment, by time-resolved threshold ionization mass spectrometry [2] and the cavity technique [3]. In the present paper, the application of the stream technique is discussed for the measurement of radical transport lengths and the corresponding coefficients β and s.

2. Stream technique and deposition simulation

The stream technique is based on the flow of a rarefied gas in a cylindrical tube. RF plasma at the tube inlet is the source of the active particles (H atoms and CH_i radicals) capable of producing the carbon deposit and chemically inactive gas molecules downstream. For a laminar flow the molecular concentration of carrier gas is constant (in limits 10%) in radial and longitudinal direction along the tube. The CH_i radical concentration, however, is much less than that of the carrier gas and changes along the tube. By using the kinetic gas theory we can calculate the mean free path of molecules (with known radius) and of radicals, their thermal velocity, the particle concentrations and averaged linear velocity of the downstream flow.

In the gas flow, the CH_i particles may get lost due to gas-phase reactions or due to surface reactions at the

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tube walls. By convention, methyl radicals (CH_3) are the active particles and methane, CH_4, is the carrier gas. Let us suppose that in gas-phase the methyl radicals can be lost due to only one reaction: $2CH_3 + CH_4 \rightarrow C_2H_6 + CH_4$ (r1). For the stationary radical flow and constant temperature along the tube the transport equation for methyl can be written as:

$$\nabla^2 C_i - (k_i/D)(CH_4)C_i^2 - \nabla(C_i \times V/D) = 0, \qquad (1)$$

where k_i is the kinetic rate constant for the trimolecular collision recombination of two particles with a methane molecule, $[CH_4]$ and C_i are the concentrations of methane and methyl, V the laminar flow velocity and D is the diffusion coefficient of methyl.

For reaction (r1) the dimensional analysis shows that the average lifetime t_i of C_i particles in the gas-phase of a reaction volume is given by:

$$t_i = 1/(k_i[CH_4]C_i),$$

where the forward rate constant is given by k_i ($cm^6\ mole^{-2}\ s^{-1}$) $= 9.03 \times 10^{16} \times T^{-1.18} \times \exp(-329/T)$ with T in K [4]. In our case, the average lifetime t_i is equal to 10^5 s for a methyl concentration of $C_i \sim 10^{-3} \times (CH_4) \approx 10^{13}\ cm^{-3}$ ($T = 300$ K). One sees that the average lifetime t_i significantly exceeds the residence time of a gas particle ($\tau_{Res} = X/V = 0.3$ s, X is tube length, see below) in the tube. It means that the second term in Eq. (1) can be omitted.

The main boundary condition for transport equation is the following at any coordinate x [5]:

$$\{D \times (\delta C_i/\delta r)\}_{r=R} = -\{\beta \times v_T \times C_i/4\}_{r=R}, \qquad (2)$$

where v_T is the thermal velocity of the radicals and R is tube radius. After rearrangement, the boundary-value problem can be expressed by the following equations:

$$\delta^2 C_i/\delta^2 x - V/D \times (\delta C_i/\delta x) - (\{\beta \times v_T/2R \times D) \times C_i = 0, \qquad (3)$$

$$C_i = C_0 \text{ at } x = 0 \text{ and } C_i = 0, \text{ at } x = \infty, \ \beta = s + \gamma. \qquad (4)$$

The solution of the problem can be written as:

$$C_i = C_0\ \exp(-x/L), \qquad (5)$$

where L is the so-called transport length:

$$1/L = -V/2D + \surd(V/2D)^2 + \beta \times v_T/2RD. \qquad (6)$$

In the experiment, the carbon film thickness and deposition rate (G, at. C $cm^{-2}\ s^{-1}$) on the reactor surface (along the x-axis) measured. In the frame of boundary-value problem considered for G (taking into account Eq. (5)) we have:

$$G = s/4 \times v_T \times C_0\ \exp(-x/L) = G_0 \times \exp(-x/L). \qquad (7)$$

Measuring the transport length L in the experiment and knowing the values v_T, V and D, it is possible to calculate the β coefficient:

$$\beta = 2R \times D \times (1/L + V/D)/v_T \times L. \qquad (8)$$

It should be noted that for the calculation of the thermal velocity v_T, additional data about the molecular mass of the radicals are necessary.

The stream technique can be used for different types of experiments. If one inserts into the reactor the samples coated with carbon films with a well-known hydrogen erosion yield and change the conditions of deposition to erosion ones, this technique allows to define the flows and recombination coefficients of H atoms.

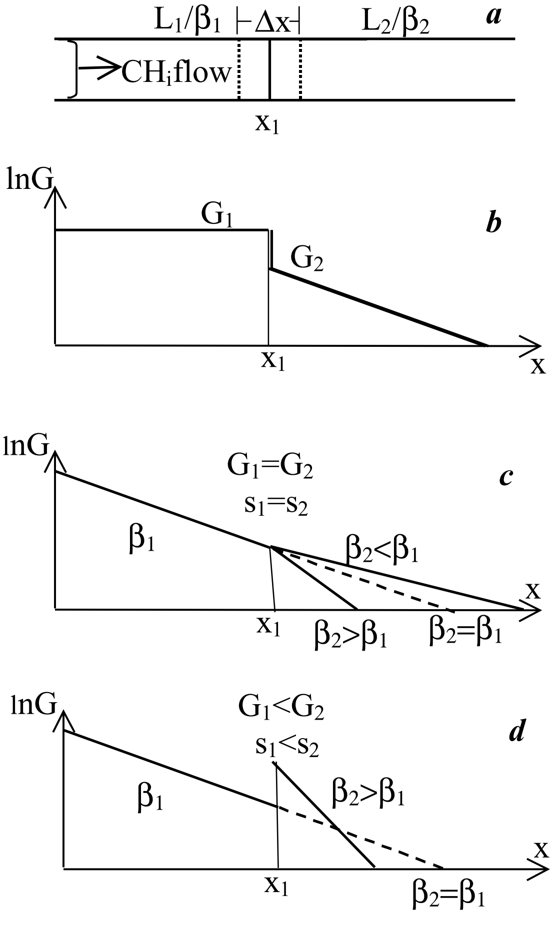

Fig. 1. Downstream scheme (a) and profiles of a-C:H films deposition rates (G) for laminar gas flow with CH_i radicals passing through the boundary (x_1) of two tubes ($R_1 = R_2$) with different transport lengths and thus coefficients $\beta_{1,2} = s_{1,2} + \gamma_{1,2}$; (b) growth rate G_1 =const. along tube 1:$G_1/G_2 = s_1/s_2$; (c) growth rates at position x_1 are equal: $G_1 = G_2$, $s_1 = s_2$, but $\beta_1 > \beta_2$; (d) growth rate G_1 at position x_1 is lower than $G_2 : \beta_2 > \beta_1$.

For the later analysis we consider the case that the β coefficient for radicals changes at a position x_1 from β_1 to β_2 (Fig. 1(a)). The boundary conditions at position x_1 for the concentrations (C_1 and C_2) and flows of radicals at both sides from section x_1 can be written as:

$$C_1 = C_2 \text{ and } C_1 v_{T1} L_1 \beta_1 \approx C_2 v_{T2} L_2 \beta_2, \quad \beta_{1,2} = s_{1,2} + \gamma_{1,2}. \tag{9}$$

The extrapolated values of the deposition rate (G) permits to determine the sticking coefficient (s) ratio in section x_1:

$$G_1/G_2 = s_1/s_2. \tag{10}$$

To calculate the s_1 and s_2 coefficients it is necessary to know the concentration or the flow of radicals in point x_1. These quantities must be measured in separate experiments. The uniform distribution of deposit along the tube (Fig. 1(b)) occurs if the radicals are produced in some region of the tube. If in section x_1 the jump in extrapolated values of growth rate is absent ($G_1 = G_2$, Fig. 1(c)), the changes in β coefficients are caused by changes of the recombination coefficient γ. This can occur if the recombination probability γ depends on the composition of active particles, e.g. H atoms/CH_i radicals ratio. The significant jumps and drops in deposition rates (Fig. 1(d)) could be observed when the certain tube regions have different temperature [6].

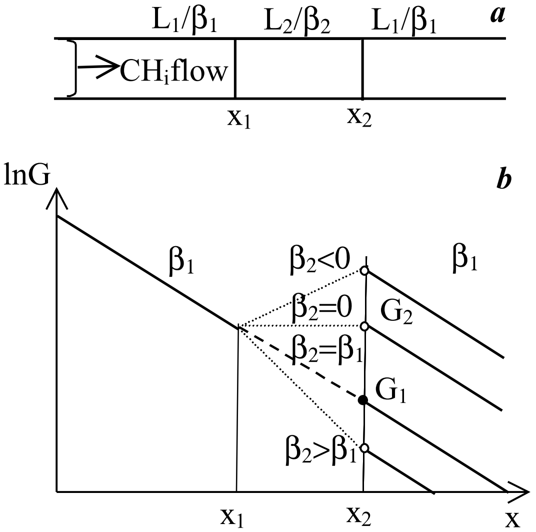

Fig. 2. Downstream scheme (a) and profiles (b) of a-C:H films deposition rates (G) for laminar gas flow with CH_i radicals passing through tube region $\Delta x = x_2 - x_1$ with differing transport length L_2 and thus β_2 coefficient. G_1 is carbon deposition rate in point x_2, if $L_2 = L_1$. G_2 is carbon deposition rate in point x_2, if transport lengths are not equal.

Let us consider the case that the deposition conditions are varied in region (Δx) (e.g. due to temperature changing). The measurement of the carbon deposition profiles on the inlet and outlet reactor sides allows the determination of an averaged transport length (L_2) (and thus also β_2) in chosen region $\Delta x = x_2 - x_1$:

$$\ln G_2/G_1 = (1/L_1 - 1/L_2)(x_2 - x_1). \tag{11}$$

Fig. 2 illustrates some possible cases for a variation of β_2. In experiments [6] with rising the temperature of chosen tube region the β_2 coefficient remained constant ($T = 400$–800 K) or decreased about two times ($T = 1200$ K).

3. Experimental

The quartz tube of $X = 100$ cm length and $R = 1$ cm radius was the main part of the setup (Fig. 3). An RF inductive-coupled discharge (frequency 13.56 MHz, specific power 0.1 W cm^{-3}) in methane flow rate 13.7 sccm $= 6.3 \times 10^{18}$ CH_4 s^{-1} under pressure 30 Pa was used for production of CH_i radicals and H atoms. The plasma region was limited to 30 cm length by a stainless steel grid. Expected pressure difference on the inlet and the outlet tube ends did not exceed 2 Pa. The laminar flow velocity was equal to $V = 280$ cm s^{-1} (corresponds to a resident time $\tau_{Res} \approx 0.3$ s). Mean free path of any gas particle and the thermal velocity of the radicals were equal to $\lambda = 0.018$ cm and $v_T = 6.5 \times 10^4$ cm s^{-1} according to the kinetic theory of an ideal gas (300 K). The CH_3 diffusion coefficient was equal $D \approx 560$ cm^2 s^{-1}. The mean projected distance along x-axis needed for particle to reach the tube surface was equal to ~0.2 cm.

The downstream region of the reactor, behind the grid, could be heated by a cylindrical furnace of 15 cm length. The temperature along the tube was measured by thermocouple with lateral distances of 1 cm and an accuracy of ten degrees in the separate experiments.

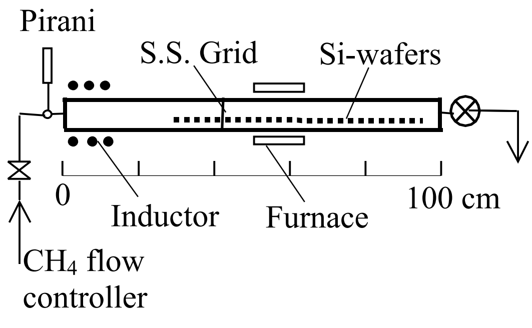

Fig. 3. Schematic of the quartz gas flow reactor with 1 cm radius, coordinate system and measurement apparatus.

The standard Si wafers ($10 \times 6 \times 0.3$ mm) or W samples was placed uniformly along the reactor (60 cm). Film mass thickness on Si-samples were measured by electron probe microanalysis (EPMA) with accuracy 10^{15} at.C cm^{-2}. The carbon film structure was analyzed by reflection high energy electron diffraction (RHEED, energy of electron beam 50 keV).

4. Results and discussion

4.1. Carbon deposition and transport lengths of radicals at 300 K

The growth rates of carbon films in the downstream region can be written in the form $G = G_{0i} \times \exp(-x/L_i)$ with $L_1 = (10.5 \pm 0.7)$ cm, $G_{01} = 4.2 \times 10^{13}$ at.C cm^{-2} s^{-1} ($45 < x < 72$ cm) and $L_2 = (30 \pm 2)$ cm, $G_{02} = 3 \times 10^{12}$ at.C cm^{-2} s^{-1} ($72 < x < 91$ cm) (Fig. 4). The film thickness varies from 6×10^{17} at.C cm^{-2} near the grid down to 1×10^{16} at.C cm^{-2} at a distance (45 ± 3) cm from the grid. According to RHEED analysis the carbon films are dielectric, amorphous, polymer-like materials. We did not detect any other elements (e.g. Si) on special W samples by EPMA.

If the transport lengths L_i are known, it is possible to calculate surface loss probabilities $\beta_1 = 1 \times 10^{-3}$ and $\beta_2 = 3 \times 10^{-4}$ using Eq. (8). Coefficients β_1 and β_2 were calculated for radical molecular mass $M = 15$. Their value decrease by 20% if $M = 30$.

The integration of the deposition profile (Fig. 4) allows the calculation of the average flow of radicals, which is consumed by deposition $2\pi R \times \int G(x)\delta x = (2.8 \pm 0.3) \times 10^{15}$ at.C s^{-1}. Further experiments showed that $2\pi R \times \int G(x)\delta x = (8.4 \pm 1.0) \times 10^{15}$ at.C s^{-1} at 200 K wall temperature [7]. Because practically all hydrocarbons stick at this low substrate temperature we conclude that the total flow of radicals emerging from plasma is $F_0 = (8.4 \pm 1.0) \times 10^{15}$ at.C s^{-1}. Therefore only one third of all radicals is used for deposition at 300 K.

In laminar downstream, the average flow of the radicals is equal to $F_0 = v \times C_0 \times \pi R^2$. Taking into account that $V = 280$ cm s^{-1}, one can get an estimation for the radical concentration near the grid of $C_0 \approx 9 \times 10^{12}$ at.CH$_i$ cm^{-3}.

Eq. (7) allows the calculation of the carbon sticking coefficient s_1 downstream at room temperature on the length $\Delta x_1 = 45/72$ cm: $s_1 = 4G_{01}/v_T C_0 \approx 3 \times 10^{-4}$. On the length $\Delta x_2 = 72/91$ cm the s_2 coefficient is equal to s_1 according to Eq. (10). Thus for position Δx_2 the sticking coefficient s_2 is approximately equal to the surface loss probability β_2.

The carbon deposition rate in the plasma was $G_p = s_p \times v_T \times C_p/4 = (0.6 - 1) \times 10^{15}$ at.C cm^{-2} s^{-1}. Assuming the values of hydrocarbon radical concentration in plasma C_p at the left from the grid is equal to C_0, we made the estimation of the sticking coefficient s_p in the plasma of $s_p \approx 5 \times 10^{-3}$. The calculated values of carbon sticking coefficient and radical concentration in the plasma are close to s_p and C_p values for methyl in the capacity coupled RF glow discharge [2,8].

Eqs. (7) and (9) allow also to estimate the radical flow at outlet tube end. It is equal to 2.4×10^{14} at.CH$_i$s^{-1} or 3% from the inlet flow. The main fraction of all radicals is lost due to deposition and recombination reactions during transport along the 50 cm tube.

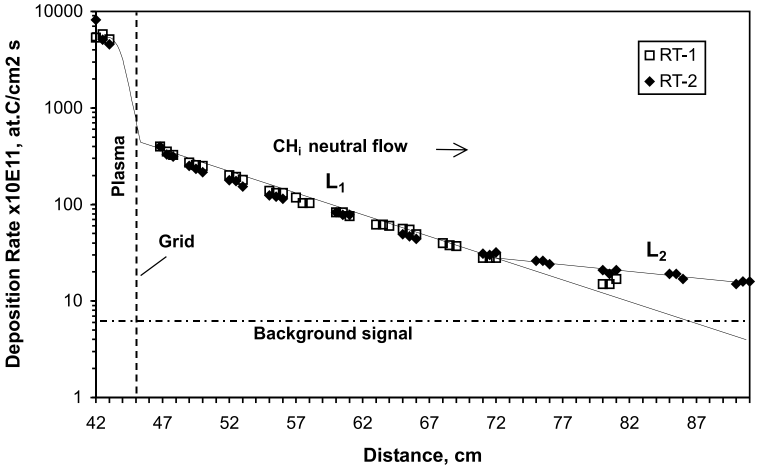

Fig. 4. Deposition rates of carbon films vs position x along the tube. Carbon was deposited on the Si wafers at 300 K. Exposure time was 4 h. Methane flow along tube axis 6×10^{18} CH$_4$ s^{-1}, methyl flow $\sim 8.4 \times 10^{15}$ CH$_3$ s^{-1}. Grid coordinate was 45 cm. Open squares and filled rhombi are results of two separate experiments.

The exponential drop of carbon deposition rate along the tube according to $\beta = 10^{-3}$ [2] leads to the conclusion that mainly methyl radicals are present in the CH_i flow emanating from the plasma.

4.2. Determination of the atomic hydrogen flow emerging from plasma

When the middle reactor part in the region $\Delta x = 15$ cm was heated up to $T = 380$–800 K the growth rate G of carbon films decreased by 1.5–2 orders of magnitude compared to G at 300 K [6], although the transport length and thus the radical concentration profile in the gas phase along the tube axis remains unchanged. The very small growth rates ($T = 380$–800 K) might be explained by hydrogen re-erosion of the films. To verify this hypothesis and to estimate the H atom content in the gas flow we exposed the a-C:H coated sample to the radical flow for 1.5 h at $T = 650$ K (position of Si substrate 60–61 cm) and measured the decrease of the areal density of the carbon film. The H atom content in the CH_i radical flow was estimated under assumption that the erosion coefficient of the chosen carbon film at the indicated temperature is well known. The experimental data and the assessment of the H atom concentration in the radical flow are given below.

Film thickness, initial/final, at.C cm^{-2}	$2.3 \times 10^{18}/1.8 \times 10^{18}$
Carbon erosion rate, at.C cm^{-2} s^{-1}	0.93×10^{14}
Assumed erosion coefficient, at.C/at.H	0.02 [9]
H flux, at.H/cm^2 s^{-1}	4.6×10^{15}
H atom thermal velocity, cm s^{-1}	3.6×10^5
H concentration, at.H cm^{-3}	6×10^{10}
CH_3 concentration, CH_3 cm^{-3}	2×10^{12}
CH_3 flux, CH_3 cm^{-2} s^{-1}	3.2×10^{16}

According to Fig. 4 the deposition rate of a-C:H films at $T = 300$ K ($G = 1 \times 10^{13}$ at.C cm^{-2} s^{-1} at coordinate $x = 60.5$ cm) is one order of magnitude less than the measured carbon erosion rates. This illustrates that a small H atom fraction (1–10% from those of CH_i radicals) can influence significantly on the a-C:H film deposition at elevated temperature.

5. Conclusions

1. The downstream technique allows to investigate the CH_i radical transport and deposition at different experimental conditions. If the type of radical and the inlet flow are known, this technique gives the opportunity to determine the surface loss probability and the sticking coefficient s of main hydrocarbon radicals forming a-C:H films.
2. At RT the deposition process of hydrocarbon radicals emerging from CH_4 RF plasma is characterized by two transport lengths $L_1 = 10.5 \pm 0.7$ cm and $L_2 = 30 \pm 2$ cm. Assuming that the main radical providing the deposition of a-C:H films is methyl, the coefficients $\beta_1 = 1 \times 10^{-3}$ and $\beta_2 = 3 \times 10^{-4}$ have been determined.
3. Some special experiments on carbon deposition at 200 K and carbon film erosion (650 K) permitted to make the qualitative estimates of the concentrations for hydrocarbon radicals (2×10^{12} CH_i cm^{-3}) and atomic hydrogen (6×10^{10} at.H cm^{-3}) in the neutral gas flow in the downstream region.

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