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Transport and condensation of soft a-C:H film thermal decomposition products

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Abstract

Thermal destruction of soft a-C:H films obtained on a wall of a cylindrical quartz reactor during CH_4 dissociation in inductively coupled RF discharge ($T = 300$ K) has been investigated. The films were sublimated in argon or methane (pressure of 10–100 Pa). A sublimation rate of a-C:H films increased with temperature rise from 450 to 700 K or an increase in a gas-carrier (Ar or CH_4) flow rate in the range of 0.003–0.1 Pa m^3/s. Sublimation products (volatile hydrocarbon molecules) were transported along the tube towards lower temperature regions. Fractional temperature-spatial condensation of hydrocarbons occurred during the transport of sublimation products. A high amount (30–100%) of the sublimated hydrocarbons was involved in condensation depending on the transport conditions (flow rate, sublimation and condensation temperatures).

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1. Introduction

Soft a-C:H films with high content of hydrogen isotopes are usually formed in pumping systems of the majority of operating tokamak machines [1]. The problem of efficient removing of such films should be solved at the stage of the development of the ITER-FEAT reactor [2,3]. Therefore, processes of film sublimation, sublimated products transport and their subsequent condensation in low-temperature zone have been studied.

2. Experimental

Soft a-C:H films were deposited on a wall of a quartz tube (2 cm in diameter, 100 cm in length, deposition zone length of 25 cm) in CH_4 inductively coupled RF discharge at $P = 30$ Pa, $T = 300$ K and methane mass flow rate of 0.012 Pa m^3/s [4,5]. Si-wafers ($10 \times 5 \times 0.3$ mm) were used for C and O film mass thickness measurements by electron probe microanalysis (EPMA) with sensitivity limit of 3×10^{15} at. C, O/cm^2. After 2–4 h of deposition the areal density of films deposited on Si-wafer in the plasma zone reached 120–200 μg/cm^2 or $(6–10) \times 10^{18}$ at. C/cm^2. O/C ratio in films was equal to 0.01–0.03.

Measurement of geometrical thickness of thin films (of the order of 100 nm) by Ellipsometry (El) as well as their areal density by EPMA allowed us to estimate mass density of the deposited films ($\rho \sim 0.9–1.0$ g/cm^3).

Hydrogen content in original films was determined by secondary ion mass spectrometry (SIMS) and residual gas analysis (RGA) simultaneously [6,7]. H/C ratio was typically equal to 1–1.3.

Film structure was examined by the electron diffraction method (primary electron beam energy of 50 keV).

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The results indicated that carbon films were amorphous and poorly ordered. A characteristic distance between carbon atoms was about 0.15 nm. Coordination number N was 2; film density, ρ, determined by the radial distribution function was equal to 0.9–1.3 g/cm^3. Dimension of individual carbon aggregates was about 1 nm according to the half-width of a diffraction halo. The films deformed and charged under an electron beam. According to the complex of the above-mentioned properties and the results of experiments on sublimation discussed below the described deposits could be attributed to soft carbon films (a-C:H) [8,9].

Carbon films had different color depending on their thickness. Thin films ($\sim 10^{17}$ at. C/cm^2) were colorless and transparent. Thick films ($(1\text{–}5) \times 10^{18}$ at. C/cm^2) were of yellowish or brownish color.

A tube section (about 5 cm in length) coated with film was heated from 400 K up to 700 K by an external cylindrical furnace (Fig. 1(a)). The sublimation zone (about 36 cm^2 in area) contained $(2\text{–}4) \times 10^{20}$ at. C. The wall temperature in the center of the heated zone was measured by a thermocouple with an accuracy of 10 K during the experiment. The temperature of a tube downstream from the furnace was measured with a step of 1 cm in special experiments. Gas-carrier (Ar or CH_4, the flow rate 0.003–0.1 Pa m^3/s) passed through the tube. At the sublimation zone outlet the gas-carrier was cooled down to 300 K at the tube length of 15–18 cm. Si-wafers were placed uniformly along the tube. Sublimation products were transported by the gas-carrier to the tube sections held at lower temperatures. Re-deposition of carbon polymer-like films was observed there. In some experiments on sublimation both the soft and hard carbon films were exposed in clean reactor. The hard films were kindly given by Professor W. Jacob (IPP, Garching, Germany).

3. Results

A significant part of the experiments on sublimation of the soft a-C:H films was carried out at the temperature of $T_{\text{subl}} = 620$ K, the gas-carrier pressure at the tube inlet of $P = 30$ Pa, and the mass flow rate of $J = 0.012$ Pa m^3/s (4.8 µmole/s or 2.9×10^{18} Ar or CH_4/s, average flow velocity about $V = 120$ cm/s). Hydrocarbon products of sublimation were transferred by a gas-carrier and as soon as they reached a low-temperature zone at the tube wall, they condensed again as a-C:H films.

A typical carbon deposition rate profiles along the tube for Ar as a gas-carrier are shown in Fig. 2. The deposition rate on the tube wall held at 620–550 K was

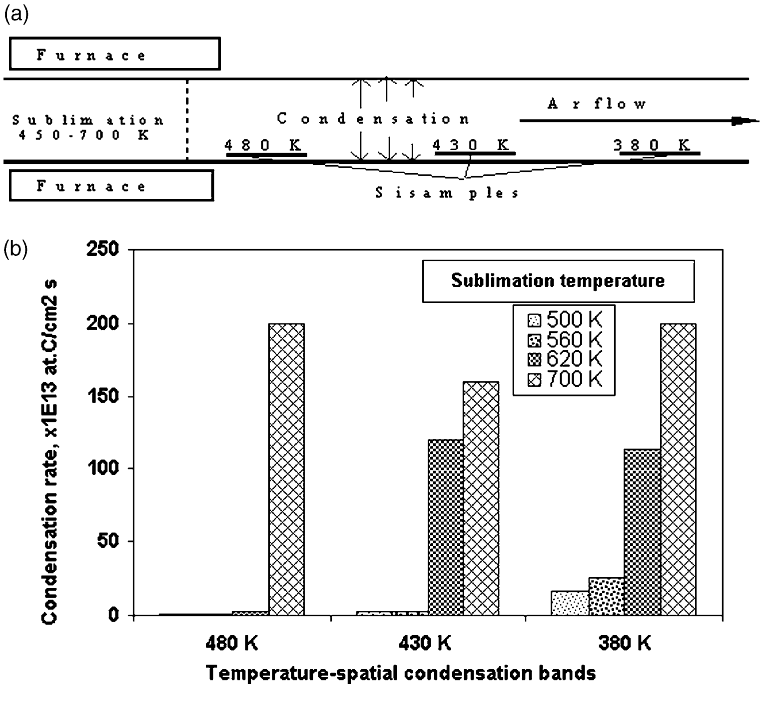

Fig. 1. Scheme of the experiment for investigation of transport and condensation of soft a-C:H film thermal decomposition products (a). Condensation rates of the a-C:H films sublimation products in three selected temperature-spatial bands (480, 430 and 380 K) for four sublimation temperatures ($T_{\text{subl}} = 500$, 560, 620 and 700 K) (b). Argon pressure at the tube inlet 30 Pa; $J = 1.2 \times 10^{-2}$ Pa m^3/s; $V = 120$ cm/s.

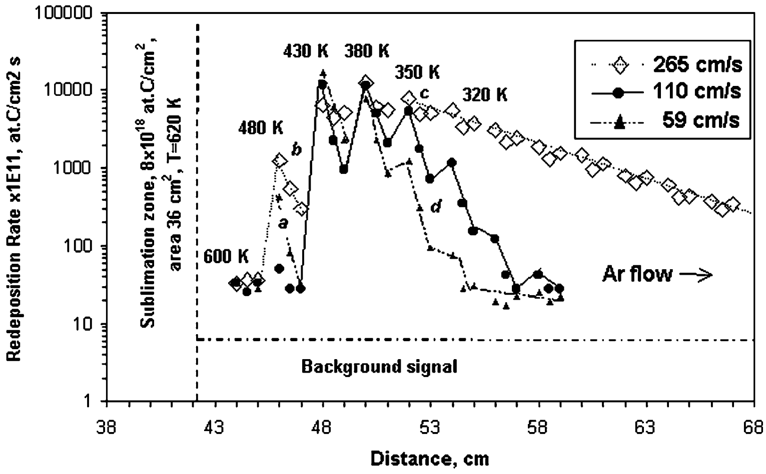

Fig. 2. Sublimation and subsequent condensation of soft a-C:H films in argon flow ($T_{\mathrm{subl}} = 620$ K, exposure time 1 h). Open rhombi refer to the rate distribution for carbon films condensation along the reactor at $P = 98$ Pa and $V = 265$ cm/s. Closed dots are related to that at $P = 34$ Pa and $V = 110$ cm/s. Closed triangles are related to that at $P = 16$ Pa and $V = 59$ cm/s. The average temperature of the every Si-specimen is given as well. The cylindrical furnace coordinates are 34–49 cm. Symbols ***a***, ***b***, ***c*** and ***d*** are referred to the temperature-spatial bands presented on the photo of Fig. 3.

very low during movement of the sublimated species. Mass thickness of carbon films did not exceed 10^{16} at. C/cm^2. It can be stated that deposition of the sublimated carbon products does not occur either on clean Si substrates in the temperature range indicated. However, if Si specimen preliminary coated with soft carbon film was placed in the sublimation zone ($T = 600$–620 K) where the tube wall was the main hydrocarbon source, the film thickness increased but not decreased during the first hour of exposition. Location of the same film and the hard carbon film in the tube part with clean wall ($T = 600$–620 K) results in the almost complete removal of the soft film. At the same time the mass thickness of the hard carbon film reduced slightly. Soft film decomposition started approximately at 450 K.

The profiles of carbon deposition rate along the tube were the same in the experiments with methane or argon as a gas-carrier. These profiles changed slightly during the first three hours of sublimation. However, there was a tendency to gradual reduction of the low-temperature fraction in secondary deposits. Therefore, a quasi-stationary condensation along the tube at fixed temperature gradients could be considered. Saw-tooth changing of carbon condensation rate was observed during the gas transport along the tube in decreasing temperature field. We called this process 'gas mixture fractionation'. As a result of the fractionation the colored bands several mm wide appeared on the tube inner wall. At a constant temperature gradient every colored band corresponded to a certain temperature.

Re-deposition rates decreased or increased when mass flow rate of the gas-carrier decreased or increased respectively (Fig. 2). The same regularity was observed for a number of spatial-temperature carbon condensed bands.

At the increase in the sublimation temperature of initial carbon films from 450 to 700 K the condensation rate of hydrocarbon species increased in all spatial-temperature zones (Fig. 1(b)). Only three selected zones are shown in Fig. 1. Actually, the temperature of the first condensation band nearest to the sublimation zone was 50–70 K lower than the sublimation temperature.

A mass balance indicated that from 30% to 100% of sublimated hydrocarbons re-deposited again in the tube sections held at 480–350 K. Effective hydrocarbon sublimation rate was approximately equal to 10^{15} at. C/cm^{2}s at 620 K and argon flow of 110 cm/s (0.012 Pa m^3/s).

Morphology (optical images) of condensed films had essential distinctions for every band. The initial carbon film deposited in the plasma was uniform in thickness. Formation of rather small islands (1–3 μm in diameter) arranged in partly order fashion on Si substrates was observed during the hydrocarbon re-deposition at 480 K and the argon flow velocity of 59 cm/s (Fig. 3(a)). Large islands (up to 50–100 μm) were generated in the deposition zone at the flow velocity of 120 cm/s. In Fig. 3(b) islands are colored due to interference of light. There is a certain interrelationship in the shape of neighbor islands. This points the certain role of surface migration of adsorbed particles in island formation. In every deposition band the island dimensions decreased downstream. At higher flow velocity and lower temperature ($T_{\mathrm{cond}} = 350$ K) the condensed films were uniform (Fig. 3(c) and (d)). The spot (50 × 50 μm^2) highlighted in Fig.

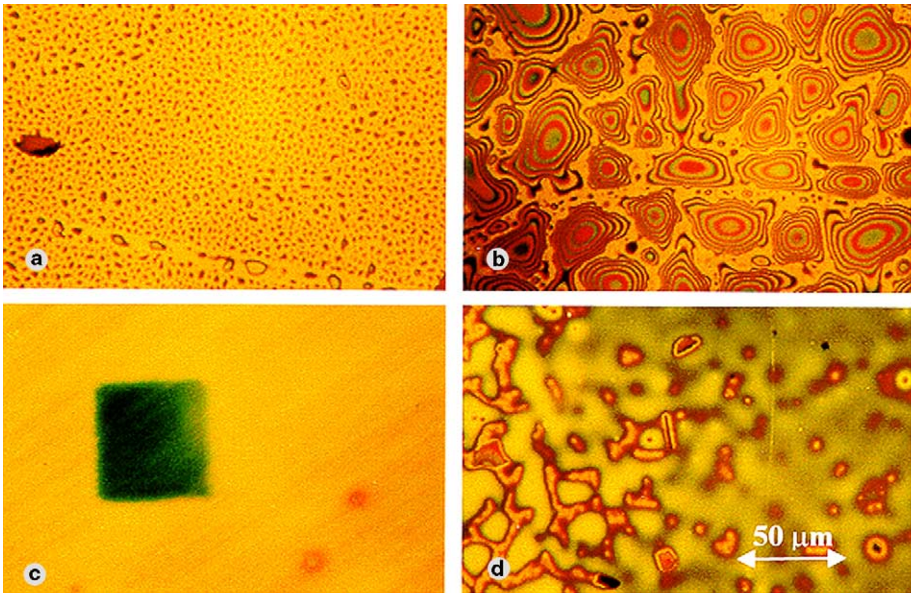

Fig. 3. Optical images of hydrocarbon films re-deposited at 480 K (a, b) and 350 K (c, d). The film thickness in nm for the average density $\rho \approx 1$ g/cm^3 is 25 (a), 400 (b), 400 (c) and 40 (d). Argon flow velocity in cm/s was 59 (a, d), 110 (b) and 265 (c). Maximum island height is about 1.2 μm in Fig. 3(b). Si-wafers were placed in position denoted in Fig. 2.

3(c) is the trace left by electron beam during the film mass thickness measurement by EPMA.

4. Discussion

Carbon films tendency to the low-temperature sublimation and the subsequent re-deposition are two main peculiarities of soft a-C:H films. When the sublimated hydrocarbon species (radicals, molecules) impinge on a soft carbon film surface they can condense once again even at temperature close to the sublimation one. Effective sublimation rate depends upon the sublimated products partial pressure over a-C:H films.

Formation of stationary temperature-spatial condensation bands evidences that hydrocarbon sublimation rate is independent on the a-C:H film mass. In other words the thermal flows of all sublimated fragments in radial direction (both for sublimation and deposition zones) were constant during the 2–3 h sublimation at a constant flow of a gas-carrier.

The condensation rate of sublimated products increases with rise of the gas-carrier flow velocity or of the sublimation temperature. However, the total mass of the condensate increases slightly with a change in the above-mentioned parameters. The resulting condensed mass is up to 30–100% of the initial a-C:H film mass in the sublimation temperature range of 500–700 K.

At volatile molecule formation the dissociation energy for C–C bonds in polymer-like hydrocarbon fragments ($H/C \geqslant 1$) is much less than the atomization energy for carbon clusters in the hard, graphitic or diamond-like films ($H/C < 1$) [10]. Thus, the complete sublimation of soft a-C:H films at $T = 620$ K both in vacuum [8] and chemically inert gas (CH_4 or Ar) indicates that the hydrogen–carbon ratio in the former films is $H/C \geqslant 1$. In contrast with that the hard film mass losses are about 10% only.

Formation of the whole set of sharp bands in a rather narrow temperature range demonstrates an abrupt, almost jump, increase in deposition coefficients (or sticking coefficients) of part of species at reaching a certain surface temperature. Hydrocarbons of molecular mass over 100 can condense in the examined temperature range [10].

Soft a-C:H films are a sort of polymer-like mesa phase, which can produce a wide spectrum of hydrocarbon deposits depending on the sublimation regimes.

5. Conclusions

Soft a-C:H films have the tendency to sublimation in methane and argon ($P = 10$–100 Pa) at temperature over 450 K and to subsequent condensation at temperature of 50–70 K below the sublimation temperature.

Mass fractionation of hydrocarbons occurs during the transport of products of sublimation. High amount (30–100%) of the sublimated hydrocarbons is involved in condensation depending on the transport conditions (flow rate, sublimation and condensation temperatures).

Annealing of a large machine at $T = 500$–700 K for a-C:H films removal may result in hydrocarbon products accumulation in zones held at lower temperatures.

References

[1] M. Mayer, V. Philipps, P. Wienhold, H.G. Esser, J. von Seggern, M. Rubel, J. Nucl. Mater. 290–293 (2001) 381.

[2] G. Federici, J.N. Brooks, D.P. Coster, G. Janeschitz, A. Kukushkin, A. Loarte, H.D. Pacher, J. Stober, C.H. Wu, J. Nucl. Mater. 290–293 (2001) 260.

[3] G. Janeschitz and ITER JCT and HTs, J. Nucl. Mater. 290–293 (2001) 1.

[4] A.E. Gorodetsky, I.I. Arkhipov, R.Kh. Zalavutdinov, A.P. Zakharov, Yu.N. Tolmachev, S.P. Vnukov, V.L. Bukhovets, J. Nucl. Mater. 290–293 (2001) 271.

[5] I.I. Arkhipov, G. Federici, A.E. Gorodetsky, C. Ibbott, D.A. Komarov, A.N. Makhankov, A.V. Markin, I.V. Mazul, R. Tivey, A.P. Zakharov, R.Kh. Zalavutdinov, J. Nucl. Mater. 290–293 (2001) 394.

[6] V.Kh. Alimov, A.E. Gorodetsky, A.P. Zakharov, J. Nucl. Mater. 186 (1991) 27.

[7] V.Kh. Alimov, V.L. Goncharov, M.I. Guseva, B.N. Kolbasov, P.V. Romanov, L.N. Khimchenko, A.G. Domantovsky, VANT, Seria Termonuclear synthesis N. 2, 2000 (in Russian).

[8] K. Maruyama, W. Jacob, J. Roth, J. Nucl. Mater. 264 (1999) 56.

[9] A. von Keudell, C. Hopf, T. Schwarz-Selinger, W. Jacob, Nucl. Fusion 37 (1999) 1451.

[10] J.D. Roberts, M.C. Caserio, Basic Principles of Organic Chemistry. Supplement for Basic Principles of Organic Chemistry, California Institute of Technology W.A. Benjamin, INC, New York, 1964.