Plasma Cleaning of Metallic Mirrors from Carbon-Containing Films – New Possibilities for *In Situ* Monitoring of the Efficiency of Wall Conditioning in Fusion Devices

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Abstract: The method proposed for measuring the erosion rate of the carbon film, pre-deposited on the mirror-like surface of the test metallic samples, directly during wall conditioning procedures in a fusion device. The practical realization of the method provided at the DSM-2 stand where deuterium plasma produced in conditions of electron resonance at frequency 2.45 GHz used for cleaning the samples. For controlling C-film thickness the time variation of electrical conductivity of the circuit 'film+plasma+entire scheme' was measured. The final cleaning stage sets according to the saturation section corresponding to the resistance of the entire measuring scheme. To check the state of full purification of samples from a carbon-containing film the reflectance at normal incidence in the wavelength 220-650 nm was measured before C-film deposition, just after C-film deposition, and after finishing the cleaning procedure. In all cases (16 experiments) the approach of total resistance to the 'entire resistance' of the scheme in use was supported by restoration of the reflectance of stainless steel samples to its initial value.

The method can be reversed, i.e. allows one to control *in situ* the appearance of a contaminating layer growing on the surface of a metal sample, preliminary cleaned before being installed in a vacuum vessel.

1. INTRODUCTION

In [1], we have presented the results of postmortem analysis of the samples exposed in the vacuum chamber of the stellarator-type fusion device Uragan-2M (U-2M) during previous experimental campaigns (2015 and 2016). An *ex situ* study showed that all samples became coated with a carbon-containing film, the thickness of which and strength to sputtering depended on sample position. Those results have demonstrated the necessity of finding a way to control the efficiency of wall conditioning *in situ*. One of the obvious ways is to measure the time dependence of the reflectance of a mirror sample precoated with the film, which is more or less similar to the film that covers the walls. Then the rate of mirror reflectance recovery, depending on the time of wall conditioning procedure, would define the efficiency of film removal. In the U-2M device the main component of contaminating film was carbon; thus, before installation into the device, the test mirror sample has to be coated with a C film.

As for U-2M, there is a significant deficiency of cross-sections with counter-ports, where the method based on measuring the time behavior of the reflection property could be used. Here, we propose the method for controlling the rate of carbon film removal from the test sample surface by measuring the film resistance. Only one port is necessary to be used for every test sample directly during wall conditioning procedures.

The practical use of the method was checked at the DSM-2 stand (**D**iagnostic **S**tand for **M**aterial science - 2), and the obtained results are presented and discussed. The process can be reversed, giving possibility to control *in situ* the appearance and growth of the contaminating deposit on the surface of metal "witness-sample" preliminary cleaned before installation in the vacuum vessel.

2. EXPERIMENTAL

The method to provide *in situ* the control of how efficiently the plasma cleans the carbon film, preliminarily deposited on the metal sample (check test piece), is based on measuring the resistance of the film when it is in contact with the plasma during wall conditioning procedure. Due to erosion by plasma

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PACS: 52.40.Hf; 52.55.Hc; 79.20.Rf.

impact, the film thickness $h(t)$ becomes thinner with time, as compared to the value measured at initial contact with the plasma used for wall conditioning. Respectively, the C film resistance will become lower with time. If the physical properties of the film are assumed not to change strongly along its cross-section, then the measured resistance can be treated as the film thickness characteristic. Thus, in principle, it is possible to control the efficiency of C film cleaning during the given wall conditioning procedure.

To check the practical use of the method, experiments were performed at the DSM-2 device [2] with several SS samples coated with a carbon-containing film. The DSM-2 has a simple double-mirror configuration and operates at the electron cyclotron resonance conditions (magnetron frequency 2.35 GHz). With deuterium as the working gas, like in these experiments, plasma density was ~10^{10} cm^{-3} and electron temperature $T_e \approx 5$ eV.

The deposition of amorphous hydrogenated carbon film (hereafter referred to as the C-film) on the samples of initially high optical quality was carried out by using the non-self-sustained discharge excited in the propane-butane mixture under pressure of $4 \cdot 10^{-3}$ Torr [3].
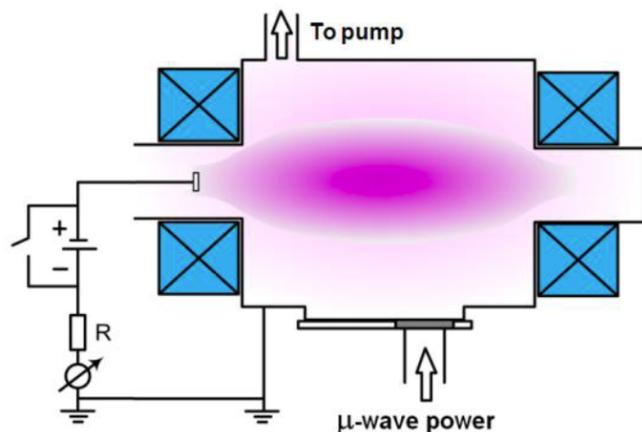
Figure 1: Scheme to measure the time dependence of carbon film resistance at the DSM-2 stand.

The scheme of the experiment at the DSM-2 stand for plasma cleaning is shown in Figure **1**. The stainless steel samples (SS) of size 22x22x3 mm^3 coated with C-film were fixed to the water-cooled copper holder and exposed through an aperture of diameter 8 mm in a sapphire disk ($\varnothing$=22 mm). The center of the aperture was shifted from the disk center; thus the size difference between the sample and the aperture allowed making four exposures for every sample. Each of the 8-mm areas was exposed independently of the others, making it possible to show the same C-film under different conditions, e.g., at different voltages applied to the holder. Before and after the C-film deposition, and after completing the exposures in the DSM-2, the reflection coefficient (RC) of each of 8-mm spots was measured at normal incidence of light within the wavelength range 220-650 nm. When exposing samples to D plasma, the sample holder voltage

was positive or negative within the limits U=5÷28 V. As an example, Figure **2** shows the photo of sample №2 ($h_0 \approx 100$ nm) after four exposures to the D plasma with applying voltages ±14 V and ±28 V. During exposures at fixed voltage, the current I between the sample and the plasma was measured every minute, thus determining the total resistance $R_{tot}(t)=U/I(t)$ in the current circuit as a function of time. For two 8-mm spots, the exposures were carried out with breaks for providing (*ex situ*) additional measurements of reflectance to see the dynamics of its recovery due to the cleaning of the C-film.
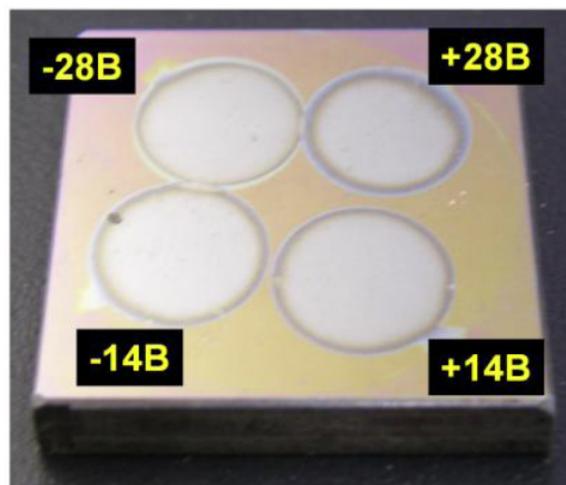
Figure 2: Total view of sample №2 exposed to deuterium plasma with indicated voltages applied to the sample holder.

3. RESULTS

According to the scheme of Figure **1**, $R=R_{tot}$ includes the resistance of C-film R_{film}, the resistance of film-plasma contact $R_{film-plasma}$, and the resistance of the measuring instrument R_{instr}. Figure **3** illustrates the time behavior of R_{tot} for three C film-coated SS samples, starting from the beginning of exposure in deuterium plasma, when the sample holder was supplied with positive potential U=+14 V. On samples №1 ($h_0 \approx 200$ nm) and №2 ($h_0 \approx 100$ nm), two 8-mm areas were exposed at this voltage, and on sample №3 ($h_0 \approx 300$ nm) – one area.

As it follows from Figure **3**, there is quite a difference between the values of the initial resistance and its variation in time for these samples; that points to the difference between their C-film properties.

Note that in spite of the tremendous initial difference of $R_{tot}(0)$ and time behavior, with time all the dependences are approaching the same value, i.e., the resistance of the outer part of the electrical measurement circuit: $R_{instr} \approx 2.6$ kΩ. This fact clearly indicates that the most interesting component of R_{tot}, viz., the carbon film resistance, became close to zero at the final stage of the experiment. Another proof of C-film disappearance is supported by the practically complete recovery of the reflectance, as Figure **4** shows.
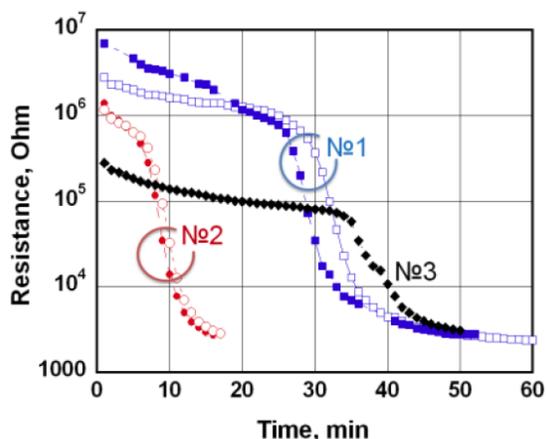
Figure 3: The change of resistance of C-films on three samples versus exposure time in the D plasma at the voltage of +14V.
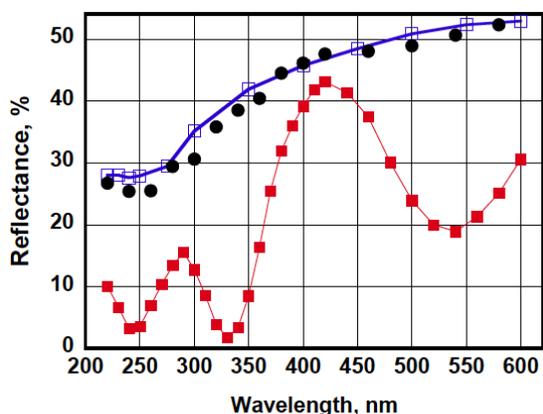

Figure 4: Spectral reflectance of mirror sample №1: □ - initial, ■ - after deposition of C-film, ● - after cleaning in D plasma during 35 min at voltage +7 V.

When measuring the current at voltages (*U*) of the different sign (+ or -), the resistance $R_{tot}(t)$ exhibits qualitatively similar behavior, though shows a quite significant difference in absolute values, as Figure **5** demonstrates. The ratio $R_{tot(-14V)}(t)/R_{tot(+14V)}(t)$ increases with the time of cleaning from ~3.6 after one-minute exposure (early stage of cleaning) to ~13.2 after 50-minute exposure completion of cleaning). This fact is in qualitative agreement with different mobility of ions and electrons in the plasma.

At +28 V voltage, the value to which the measured resistance approached with an increase in the exposure time is highly above the R_{instr} measured at lower applied voltages. At the same time, the optical measurement data showed that after the exposures made at +28 V, sample №3 ($h_0 \approx 300$ nm) was incompletely cleaned at this stage of cleaning procedure, despite the apparent saturation of R_{tot}. It was supposed that the "apparent saturation" was due to the low resistance of the remaining film to electrons of energy 28 eV. The exposure experiments with the two 8-mm areas were continued at voltages of +7 V (one 8-mm area) and +14 V (the other 8-mm area). It is seen in Figure **6** that the measured resistance
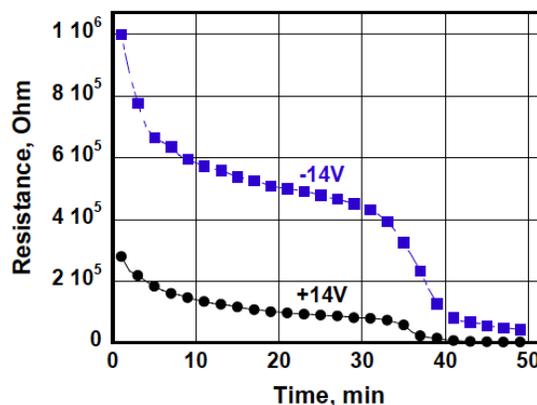
Figure 5: Time behavior of $R_{tot}(t)$ when a voltage of different sign was applied to samples №2: positive (+14 V) and negative (-14 V).

values have significantly jumped within the factors of ~3 (28→14) and ~12 (28→7). With further exposures at the given voltages, the R_{tot} value approached the R_{instr}, which is typical for 8-mm areas of sample №2 exposed at +14 V, and +7 V. The value $R_{instr} \approx 2700$ Ohm was found as an averaged value of those measured when a clear saturation of R_{instr} was observed at voltages +14 V and +7 V. Then the 'inner' resistance, equal to the difference between R_{tot} and R_{instr}, is the characteristic of the plasma-sample contact. These $R_{inn} = R_{tot} - R_{instr}$ values are shown in Figure **7** for three voltages (open symbols), where the saturated levels of R_{instr} for +7 V (shaded triangle) and +14 V (shaded square) are also indicated. The solid line in this figure represents the relation $\sim 1/U^2$.
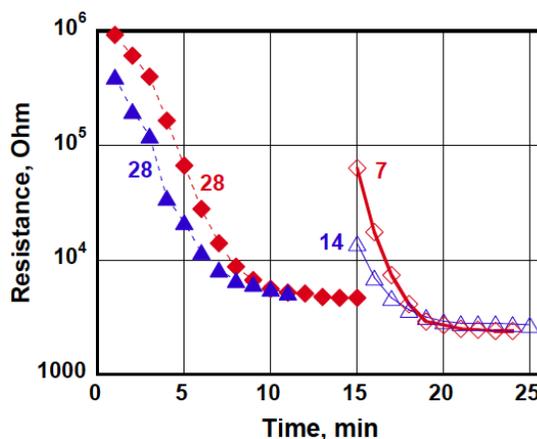

Figure 6: The experiment with varying the voltage supplied to 8 mm areas: 28 V→7 V and 28 V→14 V.

The data of Figures **6** and **7** demonstrates that the summed resistance $R_{film} + R_{film-plasma}$ is strongly dependent on the applied voltage, at least, at the latest stage of the cleaning procedure, as the positive potentials are applied to the samples. However, it is worthy of note that a qualitatively similar correlation was also observed between initial resistance values for sample №2 at +28 V and +14 V, viz., just at the moment of voltage supply, the $R_0(28)_{tot}/R_0(14)_{tot}$ ratio was equal to ≈2.3 (not shown).
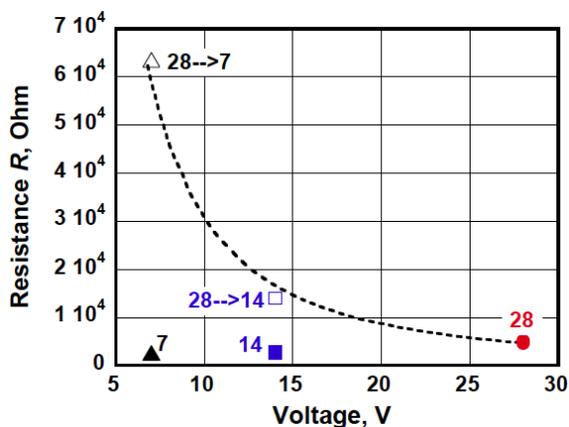
Figure 7: Comparison between 'saturated' resistance values for +7 V (▲), +14 V (■), +28 V (• – two points) and jumps of resistance when passing from +28 V to +7 V (△), and from +28 V to +14 V (□).

Supposing that the C film is homogeneous through its thickness, the time variation of R_{tot} has to be approximately linearly dependent on the etching time. In reality, according to Figures **3** and **5**, regardless of the sign of applied voltage, the time dependence of the resistance has a very complicated time behavior with four clearly seen steps: fast-slow-fast-slow. A fundamentally similar effect of the cleaning process is also characteristic for other values of voltage applied to the sample. The time dependence of film thickness can point to a strong nonuniformity of the cleaning process. At present, we have no explanation for these peculiarities of the cleaning process, except for the last slowing down stage. According to [4], a possible reason for this slowing down is the change in the properties of the lowermost layer of the film, where the C film material can enter into chemical interaction with the SS substrate (Fe, Ni, Cr) to form carbides.

4. DISCUSSION

From the analysis of the initial resistance values measured at a voltage of +14 V (Figure **3**), the specific resistance of the "as prepared film" can be estimated to lie in the range between 10^{10} Ohm·cm and $3.5 \cdot 10^{11}$ Ohm·cm. These values can be compared with the data available in the literature, where a significant number of papers are devoted to investigations of carbon films. Here we refer only to articles [5-8], where the specific resistance of C-films was determined to be in the range $(2.2 \cdot 10^6 - 5 \cdot 10^{13})$ Ohm·cm that significantly overlaps the range of values measured in our experiments. We may state that our C films may be considered as ordinary ones, having the characteristics commonly used in the studies by many groups throughout the world.

The question arises as to the mechanism of C-film cleaning, when positive voltage is applied to the sample. As was mentioned above, the electron temperature in the D plasma of the DSM-2 stand is $T_e \approx 5$ eV [2, 4]. Thus, the mean energy of ions hitting the grounded sample is ~15 eV. With the negative potential of the sample, the positive ions gain additional energy; and precisely this scheme was used for

years in our experiments to simulate the behavior of in-vessel mirrors in the ITER (e.g., [4]). By contrast, the positive potential of the sample slows down ions and accelerates the electrons. In both cases (with + or – voltage applied) the flux of Franck-Condon D atoms remains unchanged. However, the energy of these atoms, ~4.75 eV per pair [9], is insufficient to break the C-C bonds, as this requires ~7.6 eV [10]. Besides, the maximum energy transferred from D atom to C atom makes up ~0.5 of the D atom energy, taking into account the mass of D and C atoms. Therefore, to attain effective chemical erosion of C film by low-temperature H or D plasma (like in the ECR discharge), the plasma must have the component that could break the C-C bonds, which would be then occupied by Franck-Condon D atoms with the step-by-step formation of volatile C-containing molecules [11].

If the sample holder is grounded or under negative potential, the primary role in breaking the C-C bonds belongs to D^+ and D_2^+ ions accelerated by the sheath potential ($\approx 3\ kT_e$). If, however, the sample is under positive potential, the plasma ions are decelerated, and electrons are accelerated. At $U \geq +14$ V, the energy of ions is close to zero, and they cannot break the C-C bonds. Instead, it is the electrons that begin to play the role of C-C bonds breaker.

This statement follows from the data of many experiments concerning the effect of electrons on materials. Over the last decades, a significant number of papers have appeared, devoted to the effects of low-energy electron impact on different organic materials. Some results of the investigations on the reactions in the condensed matter under the impact of low-energy (≤ 50 eV) electrons can be found in the review paper [12]. It was demonstrated that low-energy electrons could modify the material, and liberate its components (atoms or fragments of molecules) in neutral or charge state. The basis for this process is that such electrons exchange their energy with valence electrons of atoms through inelastic scattering [13], thus giving rise to free radicals or ions of the film components. The closest to our results are the data obtained in experiments with hydrocarbon films adsorbed on silicon surface [14]. Chapter 6 of that manuscript describes the results on the interaction of electrons with the epitaxial graphene film deposited on Si(100) substrate. The thresholds for desorption of different kinds of cations were found to lie in the range 20-25 eV. The occurrence of the tail of these energies in the energy distribution of electrons is typical if the plasma is produced under electron cyclotron resonance conditions [15-17]. We can assume that in our situations, along with the main mass of electrons having a temperature of ~5 eV, there is also a tail of energies exceeding the dissociation thresholds of the components of the C-film coating the sample surface.

The carbon film erosion of the sample under positive potential can also be contributed by negative hydrogen ions, which are always present in the hydrogen plasma [17, 18]. The fraction of these ions, n_{H^-}/n_e, can amount up to ~20% [17], depending on the experimental conditions.

But, probably the most critical role belongs to UV emission in the range of Lyman series (H_L) of hydrogen atoms (~10 eV). The impact of this radiation can result in breaking-down of C-C bonds of the carbon-hydrogenated layer, irrespective of the difference in potentials between the plasma and the surface. Radiation in the energy range of 6-10 eV is currently widely used in science and industry, as it follows, for example, from review papers [19, 20].

According to many literature data (e.g., [21, 22]), the efficiency of VUV+UV radiation (including the radiation emitted by hydrogen ECR plasma [22]) in the modification of different kinds of polymer films is very high. The irradiation efficiency in destroying a carbonized layer strongly increases in combination with active particles. In [22], those particles were ozone and atomic oxygen.

As for inner-wall conditioning of fusion devices, this procedure is usually employed in a hydrogen atmosphere, when the Franck-Condon H atoms come to fill the free bonds formed on the carbonized film surface under the impact of UV radiation. In our view, up to now, this process (effect of VUV+UV radiation) has not been adequately considered in connection with the problem of wall conditioning in fusion devices.

In this regard, it seems expedient to present some estimates of the role of various factors when using low-temperature hydrogen (ECR) plasma for conditioning of the vacuum chamber walls from carbon-containing films. Such plasma (e.g., [23]) at a density of H_2 molecules ~$2 \cdot 10^{12}$ mol/cm^3 is characterized by electron temperature ~5 eV, plasma density ~10^{10} ion/cm^3 with a predominance of molecular ions H_2^+ and H_3^+. Taking into account the values of corresponding cross sections [24], the flux of H_L radiation to the walls is about two orders of magnitude below the flux of Franck-Condon (FC) atoms. Thus, without direct contact of such plasma with chamber walls, the rate of wall conditioning will be defined by the flux of H_L radiation that 'liberates' free C-bonds for FC atoms. If, however, the ECR plasma becomes to contact directly with C film on the walls, the rate of free C-bonds 'liberation' increases significantly, resulting in a respective increase of conditioning efficiency.

What is important, in our opinion, the method proposed here for measuring the efficiency of C-film cleaning by plasma, can be reversed, i.e., it can be used to detect the appearance on a sample-witness (and the time evolution) of a contaminating deposit with high enough resistance, i.e., not obviously carbon-based deposit.

The location of the sample-witness, particularly in the U-2M vessel, can be chosen relying on the data obtained with the SS mirrors that were exposed earlier. Namely, according to the results shown in [1], the most suitable are the locations, where the thickest layers were deposited, i.e., between coils 2 and 3 (near the RF antenna) and between the coils 6 and 7.

5. CONCLUSION

The method based on measuring the time behavior of the resistance between plasma and the *carbon film-coated* metal substrate (e.g., SS, as in our experiments) was suggested and tested. The thinning of the C-film is accompanied by a decrease in its resistance, so that the latter becomes a measure of the cleaning efficiency. The state of complete disappearance of the C-film is characterized by the fact that the impedance approaches the external resistance R_{instr} (that is, the resistance of the measuring device, the power source, etc.).

It appears that the method can be reversed, that is, can be used to detect the appearance and thickening of a contaminating layer with a resistance high enough to be measured by the use of an external scheme. In the case of the U-2M device, the best locations of the initially clean witness-sample might be the positions of samples №1 and №3 [1], i.e., where the highest rate of C-film deposition was registered.

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