IMPACT OF N_2+H_2 MIXTURE PLASMA ON CARBON-CONTAINING FILM

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The short review is done of published data on impact of plasma produced in the N_2+H_2 mixture on carbon and organic films. It is concluded that such plasma can be much more effective in cleaning of the walls of fusion devices from a carbon-based contaminating deposit in comparison with plasmas of discharges in H_2, Ar or He.
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INTRODUCTION

The proper operation of modern fusion devices with magnetic confinement of plasma requires regular use of wall conditioning procedures, the duration of which is much longer in comparison to the duration of working regimes. Thus, any increase of the efficiency of conditioning procedures would significantly enhance the economic use of experimental time.

One possible way to increase the conditioning efficiency was suggested and proved experimentally in [1]. The authors of [1] showed that with the use of low-temperature plasma (T_e ~10 eV) in the mixture of hydrogen with one of heavy rare gases (Ne, Kr, Xe) the partial pressure of molecules containing light impurities (O, C) is noticeably higher than in the plasma of similar discharge produced in pure hydrogen. This fact is a clear indication of an increased release of impurity-containing molecules from the wall surfaces. An attempt to explain the reason of an increased rate of impurities release described in that paper was made in [2], where it was suggested that important role in the process on the surface contaminated with carbon have to play the ions of noble gas hydrides: NeH^+, KrH^+, XeH^+. Such ions are quite stable and can break the bond of carbon atoms of the contaminating film much more effectively in comparison with hydrogen ions. At the same time, they become very unstable being neutralized and split easy to free hydrogen and noble gas atoms. The noble gas atom goes again into the plasma and the hydrogen atom can occupy the free bond, forming a radical that gradually is being transformed into the volatile molecule, which can be pumped.

The authors of [3,4] demonstrated that the existence of noble gas hydrides in the plasma is not necessary; a sufficient condition for activation of chemical erosion of C-based film is the co-existence in plasma of heavy noble gas ions and hydrogen atoms. In such a case, the heavy ions break the C-C bonds, which can be immediately passivated by flux of atomic hydrogen. The important condition for this process to be effective, is probably an access of hydrogen atom flux over the flux of heavy ions. For example, in [3] the saturation for chemical erosion was observed when the ratio of H atom flux to Ar^+ flux exceeded 200. In the opposite case, if the ratio of fluxes is low, the largest fraction of open bonds created by Ar^+ ions recombines with other broken bonds without passivation by H atoms, i.e., without high rate of chemical erosion.

Recently the authors of [5] observed qualitatively similar but quantitatively slightly higher effects if N_2^+ ions instead of Ar^+ ions are used. There are several reasons for the higher efficiency of N_2^+ compared with Ar^+ ions: nitrogen atoms and ions themselves are chemically very active [6]; every N_2^+ ion has two atoms, and the energy transfer from N to C is more effective than for Ar. In addition, in the plasma of N_2+H_2 mixture molecular ions, $N_xH_y^+$, can be formed that behave in many respects similar to the noble gas hydrides. Therefore, such plasma can be much more efficient in cleaning a surface of a carbon-containing film compared with plasma in a noble gas – hydrogen mixture.

The first attempt to influence the vacuum conditions in a fusion device was made in Kharkov [7]. The authors of that paper showed than the conditioning of the torsatron U-3M vacuum vessel by plasma in N_2+H_2 mixture resulted in an essential decrease of the partial pressure of hydrogen and the ultimate base pressure.

In the present paper, based on published materials, we analyze the data when the low temperature plasma produced in the N_2+H_2 mixture is in contact with carbon-based film. The analysis clearly demonstrates that the plasma of such mixture has higher carbon-removal efficiency in comparison to plasma in pure H_2 or N_2.

PECULIARITIES OF N_2+H_2 MIXTURE PLASMA

The primary process in such plasma is electron-induced ionization with creation of N_2^+, H_2^+, and H^+ ions and H atoms. However, in a steady state N_2+H_2 mixture plasma several other ion species were registered [8,9]: N^+, NH_2^+, NH_3^+, NH_4^+, N_2H^+ and H_3^+. Between different N-containing molecular ions, the concentration of N_2H^+ ions in [8] was found to be close to that of N_2^+ ions, when the N_2+H_2 mixture plasma (with $H_2/(N_2+H_2) \approx 30$ %) was maintained by a neutral loop discharge (NLD).

When plasma of similar composition impacts on a C-based film, different C- and NC-containing molecules and ions are produced [10]. This proves the chemical nature of carbon erosion process. As another example, in Ref. [11] the authors state that an important role in erosion of C film by N_2^+ ions is played the CN radical, which can react with hydrogen to form CNH or with another CN radical to form the C_2N_2 molecule.

EROSION OF C AND ORGANIC FILMS BY PLASMA WITH NITROGEN IONS

In Ref. [12] the erosion of carbon films in N_2+H_2 plasmas was investigated as a function of ion energy (in the range 30…200 eV) and mixing ratio. For all energies it was found that the erosion in a mixture of the two gases is higher than that of a plasma produced in hydrogen or nitrogen alone. With variation of the nitrogen fraction in the gas mixture, a maximum of the erosion rate was found for a nitrogen fraction $N_2/(N_2+H_2)$=~24%. The position of this maximum is independent on the ion energy. In Fig. 1 these data are plotted as a function of the ion energy for different nitrogen fractions. The appearance of maximum is an evidence of important role of the chemical processes occurring on C film surface in contact with N_2+H_2 mixture plasma.

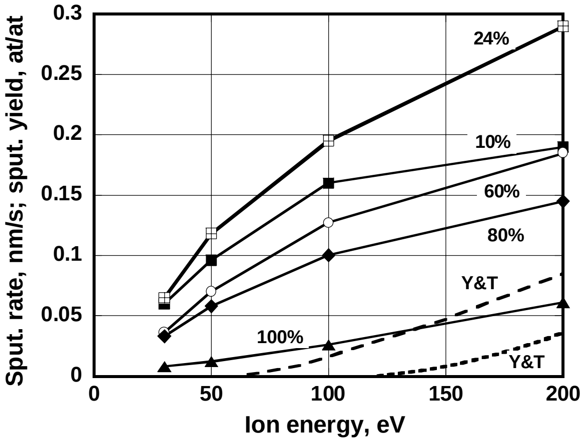

Fig. 1. Data from [12]: results of measurements of sputtering rate of C film under bombardment by ions of plasma produced in mixture N_2+H_2 for different nitrogen fractions (as indicated in the figure). Dashed curve: data from [13] for sputtering of C film by neon; dotted curve - similar data but with taking into account that sputtering effect of N_2^+ ion with E_0 energy is equivalent to sputtering by two N^+ ions with $E_0/2$ energy

For the comparison in this figure, due to a limited published data on sputtering yield by N^+ ions, data are shown from [13] on physical sputtering of carbon by Ne ions (dashed line), and similar data but assuming that carbon is bombarded by twice the flux of Ne ions with half the energy (dotted line). This assumption takes into account the known fact that sputtering effect of N_2^+ ion with E_0 energy is equivalent to sputtering by two N^+ ions with $E_0/2$ energy. In practice, the N_2^+ ion contributes only to a fraction of the total ion flux bombarding the surface in a plasma. Therefore, the real dependence of physical sputtering by ions from a N_2 plasma is assumed to lie somewhere between the dashed and dotted lines.

Qualitatively similar results were obtained in [8] where a quite broad but pronounced maximum in the etch rate of an organic film (FLARE^{TM} type) was found for a $N_2/(N_2+H_2)$ ratio in the range ~30%. From a plasma produced by an inductively coupled discharge (at 13,56 MHz), ions were accelerated to the film by a negative potential of -500 V produced by applying RF power (1.6 MHz) to the film holder. Comparing mass spectra of the ion component and the etch rate measured at different $N_2/(N_2+H_2)$ ratios, it was concluded that the ions NH_3^+, NH_4^+, and N_2H^+ play an important role in film etching. The density of N and H atoms was also measured as a function of $N_2/(N_2+H_2)$ ratio. Only the H atom density, with a maximum at $N_2/(N_2+H_2)$=30%, showed a correlation with the etch rate.

The authors of [9] using a plasma produced in a magnetic neutral loop discharge at 13,56 MHz, measured the etching rate of the same kind film (FLARE^{TM}), as a function of RF bias power (13,56 MHz and/or 2 MHz), and in plasmas with different working gases: Ar, N_2+H_2, and NH_3. Their results, shown in Fig. 2, clearly demonstrate that the efficiency of cleaning the organic film by discharges with nitrogen as a working gas is more than factor 10 higher than the etch rate of an argon plasma, in qualitative agreement with data in [5]. It is interesting to note that good quantitative agreement between etch rates for N_2+H_2 plasma and for NH_3 plasma, seen in Fig. 2, was observed for $N_2/(N_2+H_2)$=0.7, what does very much differ from the N/(N+H) ratio 0.25 in ammonia.

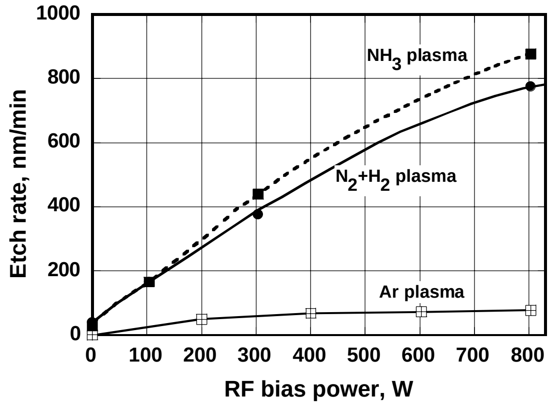

Fig. 2. The etch rate of organic film FLARE^{TM} depending on the bias RF power in different plasma produced in a neutral loop discharge [9]

The authors of [14] demonstrated that plasma of discharge in nitrogen is noticeably more effective in etching of an organic film than plasma of similar discharge in argon or hydrogen. This is in a qualitative agreement with data in [5,9] if one compares the results of C film erosion under bombardment by Ar^+ and N_2^+ ions.

It is noteworthy that some of the films deposited in fusion devices contain high fractions of hydrogen. Therefore, even if the discharge is started with nitrogen as a working gas, under impact of nitrogen ions the hydrogen is elaborated and creates the hydrocarbon molecules that can be pumped out together with nitrogen-containing molecules.

If using a N_2+H_2 plasma for wall conditioning, it is important to have conditions such that nitrogen-containing molecular ions will not be lost by neutralization due to charge exchange processes. For N_2^+ ions such conditions are realized in plasma with relatively low ion energy (below 1 eV [15]) when the cross section for creation of N_2H^+ ions in atom-molecular reactions significantly exceeds the charge-exchange cross section. For ion temperatures higher than 1 eV, the charge exchange process with H_2 molecules leads to restoration of N_2, i.e., to disappearance of N_2^+ ions. For other N-containing ions similar cross sections were not found, however, it is a common rule that the probability of charge-exchange cross sections increases with increasing the relative energy of colliding particles. Fortunately, the plasma of glow discharges is characterized by low ion temperatures, close to the wall temperature, so that charge exchange processes have not to be taken into account.

Finally, from [13] it is known that for the metals which are abundant in stainless steel (Fe, Cr, Ni), the sputtering yields for helium and nitrogen impact differ by a factor of 2.5…3 in the energy range typical for conditioning glow discharge, $E_i \approx 200$ eV. So, at optimal composition of the N_2+H_2 mixture for etching a carbon film, i.e., for $N_2/(N_2+H_2) = 0.24$ [12], the physical sputtering erosion of stainless steel due to bombardment by ions of nitrogen-containing molecules will be less than in the helium glow discharge with similar discharge characteristics (voltage, current). This statement is based on the fact that in the conditions of a glow discharge, when electron temperature, T_e, is below 5 eV, the difference in probabilities of ionization of N_2 and H_2 molecules is rather small [16]. Therefore in the glow discharge plasma the ratio of concentrations of the "primary" N_2^+ and H_2^+ ions should be approximately proportional to the ratio of partial pressures of these gases in the mixture.

CONCLUSIONS

Analyzing the described data, we can make the following conclusive remarks.

1. Plasmas in N_2+H_2 mixtures are very effective in chemical erosion of carbon-containing films even for low ion energies, starting from much below 100 eV. For such low ion energies the erosion rate for the optimal nitrogen fraction ($N_2/(N_2+H_2)\cong 0.24$) [12]) can be ~10 times higher than the erosion rate in a pure nitrogen plasma.

2. Good correlation was observed between the dependence of the etch rate of an organic film, on the one hand, and the mass spectra intensities of the nitrogen-containing molecular ions (NH_2^+, NH_3^+, NH_4^+, N_2H^+), on the other hand, when the film was subject to plasma produced in mixture N_2+H_2 with variable nitrogen fraction, with ions accelerated by RF bias voltage -500 V.

3. The effectiveness of C film erosion can be somewhat higher if the low temperature plasma in N_2+H_2 mixture with an ion temperature below 1 eV is used and ions are accelerated to energies of about hundred eV. This fortunately corresponds to the characteristics of glow discharge plasma used for the conditioning of walls in fusion devices.

4. The physical sputtering of stainless steel walls by N^+ ions of a N_2+H_2 mixture plasma will be below the sputtering rate by plasma with He as a working gas if the glow discharge is provided at optimal composition of the N_2+H_2 mixture found in [12], i.e., with nitrogen fraction $N_2/(N_2+H_2)<0.25$.

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ВОЗДЕЙСТВИЕ ПЛАЗМЫ РАЗРЯДА В СМЕСИ N_2+H_2 НА УГЛЕРОДСОДЕРЖАЩИЕ ПЛЕНКИ

В.С. Войценя, С. Масузаки, О. Моторжима, А. Сагара, В. Якоб

Дается краткий обзор опубликованных данных по воздействию плазмы в смеси N_2+H_2 на углеродные и органические пленки. Делается вывод о том, что использование такой плазмы может быть более эффективно для очистки стенок термоядерных установок от углеродсодержащих осадков, чем использование плазмы разрядов в H_2, Ar или He.

ВПЛИВ ПЛАЗМИ РОЗРЯДУ В СУМІШІ N_2+H_2 НА ПЛІВКИ, ЯКІ МАЮТЬ ВУГЛЕЦЬ В СВОЄМУ СКЛАДІ

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Дається короткий огляд опублікованих даних по впливу плазми в суміші N_2+H_2 на вуглецеві та органічні плівки. Зроблено висновок, що використання такої плазми може бути більш ефективно для очищення стінок термоядерних установок від осадка, який містить у своєму складі вуглець, ніж використання плазми розрядів в H_2, Ar або в He.