PECULIARITIES OF INTERACTION OF LOW-ENERGY PROTONS WITH TUNGSTEN SURFACE

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The results of investigations of the interaction of protons with energy of 250…260 eV with the surface of tungsten foil are presented. Sputtering of tungsten occurs at a rate of ~ 0.5 μm/h at a temperature of 300°C and an ion current density of 1.5 mA/cm^2. The surface of tungsten significantly changes after the irradiation process. The substantial surface cleaning occurs from oxides due to surface sputtering, and also because of their reduction in hydrogen plasma. The hydrogen content increases near the surface of the tungsten sample after irradiation with protons. The hydrogen content decreases in depth in tungsten.

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INTRODUCTION

The aim of this work is a comprehensive research of the results of the hydrogen ions interaction with the constructural materials used in nuclear reactors and in the future fusion devices. In comparison with traditional power plants, materials in nuclear and especially in thermonuclear plants operate in much more difficult conditions [1, 2]. When neutrons and protons irradiate the first wall of a thermonuclear reactor, their transformation into hydrogen atoms takes place. As a result of interaction with the material of investigation sample, the protons are converted to atomic hydrogen, which leads to gas sputtering and the appearance of hydrogen brittleness of materials. At elevated temperatures (up to 150°C), high (~ 800°C), and especially ultrahigh temperatures (more than 800°C), there is an increased diffusion of hydrogen atoms into the depth of the material. This reduces corrosion resistance. At present, many reviews have been published on the effect of proton irradiation of the reactor wall, especially the first wall of a thermonuclear reactor (TNR), where deuterium and tritium will be used. According to some calculations [3], the hydrogen concentration that occurs in the first wall of the reactor can become critical for the material, with respect to its resistance to hydrogen brittleness [4].

The constructural materials for the first wall of fusion reactor change all the time. In the 1980s titanium, niobium and tantalum carbides were used as the first wall [2], nowadays, for example, ITER ELMs use Ti-Zn-Ni (Ti 41.5, Zn 41.5, Ni 17) alloys [5], beryllium lining [7]. For mirrors and diverters are used tungsten coatings and tungsten [6].

The tungsten (W) is considered as the promising material of elements in contact with the plasma in future fusion reactors such as ITER [9] and DEMO [10], due to its physical properties such as low coefficient of physical sputtering and high melting point. In addition, W is considered as a promising material for the internal mirrors of optical diagnostics of plasma and construction material for the diverter in ITER [11].

The numerous studies in Ukraine and abroad are carried out by scientists and materials scientists who are engaged in the construction of tokamaks, stellarators, and also investigate possible terms for prolonging the operation of functioning reactors.

But until now, a complex investigation of the effects of the interaction of hydrogen ions and its isotopes with various materials by using the methods of secondary ion mass spectrometry (SIMS), X-ray luminescence analysis; scanning electron microscopy; optical microscopy; X-ray diffraction analysis, has not been carried out. The SIMS method makes it possible to determine the isotopic composition of various materials (metals and alloys) before and after irradiation, as well as by layer-by-layer removal of surface films in order to determine the depth of penetration and hydrogen concentrations in the materials under study, depending on the interaction time, proton energy, dose, and sample temperature.

1. EXPERIMENTAL SETUP

The researches were conducted on the modernized experimental source of hydrogen (protons) that was described in [8]. The planar plasma chemical reactor (PCR) was used to produce hydrogen ions. It consisted of two electrodes of various sizes, one of which was active (with an electrode diameter of 150 mm) and the HF potential was applied to it. The second electrode, 110 mm in diameter, is grounded, but it serves as a substrate holder.

The heater made of molybdenum wire have been manufactured and calibrated for heating substrate holder up to 1000°C [8]. But not all processed materials were kept at such high temperature. Therefore, researches were first carried out to the temperature of 400°C. The heater was screened by with three screens which made of molybdenum foil to reduce the heating of additional floating electrodes and the grounded pats of the plasma ion source. The ion source housing and power inputs of the heater were cooled with water. The scheme of the upgraded experimental setup is shown in Fig. 1.

The floating duralumin electrodes were mounted on ceramic insulators. The floating electrodes have a significant capacitance, so the RF discharge began to burn on them. This led to the appearance of a plus potential on the substrate holder. In this regard, positively charged hydrogen ions were not attracted to the substrate holder. The deposition of atomized neutral atoms

of the upper electrode on the surface of the samples was the result of this. Therefore, floating electrodes were completely isolated by fluoroplastic plates placed on top of the electrodes from the possibility of burning an RF discharge on them. The part of the substrate holder was covered with high-temperature ceramics from corundum to reduce its area. But it was not enough to obtain a negative self-bias voltage 250…300 eV. Therefore, it is necessary to produce an additional regulated source with a voltage of 1 kV and a current of up to 1 A. The power source was connected to a hydrogen ion generator through special filters. The negative pole is connected to the substrate holder, and positive to the active electrode.

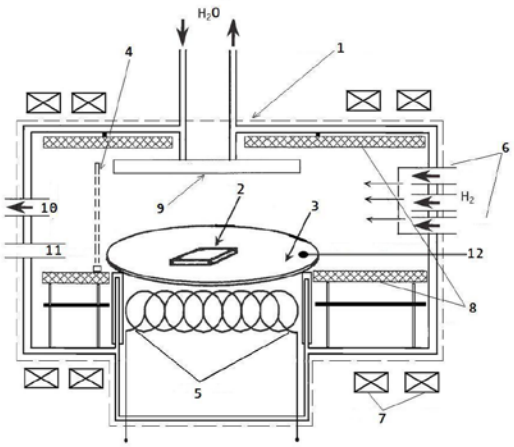

Fig. 1. The scheme of the experimental setup: 1 – chamber; 2 – substrate; 3 – substrate holder (grounded electrode); 4 – plasma quencher; 5 – heater; 6 – gas inlet system; 7 – magnetic coils; 8 isolated floating electrodes; 9 – active electrode; 10 – pumping system; 11 – vacuummeter; 12 – thermocouple

The RF discharge modes were chosen so that there were no breakdowns between the active electrode and the substrate holder to avoid radiation damage Proton irradiation was carried out at currents of RF discharges in hydrogen of 5.5 A, the negative bias voltage (without breakdown) 250…260 V. Exposure was 11.0 hours, the temperature of heating 150…400°C. Working pressure in the PCR of 0.13 Torr at an intensity of magnetic field 300 E. Average proton energy was 250…260 eV.

2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1. RESEARCH OF THE SURFACE CHEMICAL COMPOSITION OF THE IRRADIATED SAMPLES

The chemical composition of the surface of the samples was investigated by the method of secondary ion mass spectrometry (SIMS) after their treatment with hydrogen ions. The investigations of treated and untreated samples were carried out in the range from 1 to 250 atomic mass units (amu), as well as individual masses in the depth of penetration into the samples during their sputtering with an argon ion beam up to 1200 s. The sputtering of the samples was carried out by argon ions with energy of 500 eV with a primary ion current of 4 mA.

SIMS is based on measuring the ratio *m/z* of the ions emitted by the surface and measuring the currents formed by them under the action of a primary ion beam (where *m* is the ion mass and *z* is its electric charge). SIMS is one of the most powerful and informative methods for analyzing the surface of solids. It allows determining the elemental and molecular composition of the samples, conduct isotope and analysis of impurities in depth, and the likes. The main advantages of the method are the high elemental sensitivity, which in modern instruments reaches 10^{12}…10^{14} cm^{-3} (Fig. 2), large dynamic range and depth resolution.

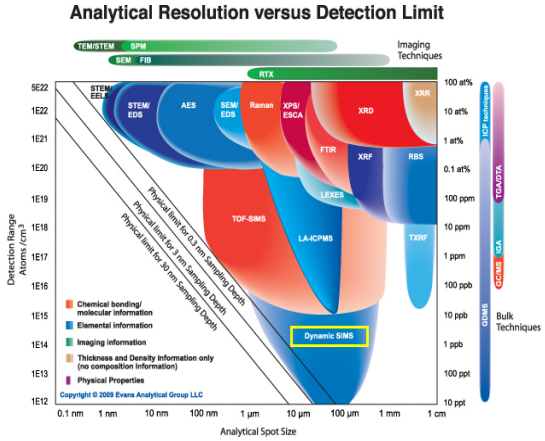

Fig. 2. The boundaries of the detection of atoms in various techniques

The schematic diagram of the method is shown in Fig. 3. The knocked secondary ions are collected by a system of electrostatic lenses and focused into a narrow beam with the same energy and are separated in the mass separator, the ratio of the ion mass m to its electric charge q. The separated secondary ion currents carry information about the type of atoms and the type of molecules on the surface of the samples, and the magnitude of the currents – about their concentration. SIMS is divided into static and dynamic depending on the density of the primary current.

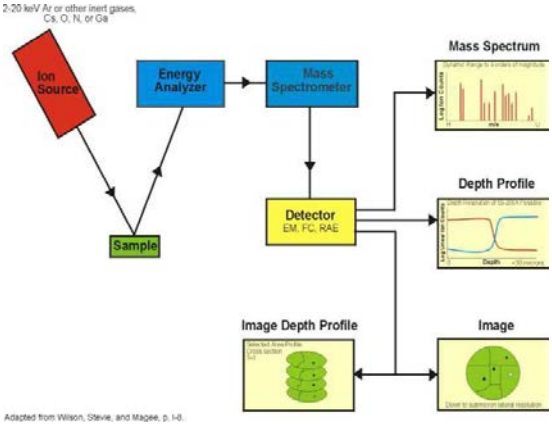

Fig. 3. The schematic diagram of the mass spectrometer operation

In a static SIMS, the ion current density is less than 10^{13} at/cm^3, which allows an elemental and molecular analysis of surface and adsorbed layers. The interaction of ions with the sample surface is considered as a static event at such current densities. In this case, the probability of formation of the secondary ion will be affected by the energy distribution over the surface of the mono-

layer. The number of ion-surface interaction events increases with increasing primary current density to 10^{17} at/cm^3, and the sputtering regime changes from static to dynamic. This means that it is impossible to consider the interaction of the ion as a static event, and the need to consider the interaction of the whole flow of ions with the surface, i.e. the dynamics of the system. In this case, the energy distribution over the surface loses its meaning, since such a large flow gives each atom the surface energy sufficient to break all the molecular bonds. The conducting molecular analysis becomes impossible.

Most of the samples were foils from various pure metals and metal alloys. Part of the sample was closed by mask during processing in the plasma. Mass spectrometric analysis of both (treated and untreated) parts was carried out. The holders were placed in the lock chamber of the device, which was pumped to a vacuum level no worse than 7.5×10^{-7} Torr.

The registration of the SIMS spectra occurred under the following conditions: ion type Ar^+; primary ion energy of 500 eV; the primary ion current 4 mA; type of spraying HFM; the frequency of sputtering of 50 kHz; duty cycle voltage 0.6; the area of analysis 5 mm; the chamber pressure of 7.5×10^{-7} Torr; the gas pressure in the cell plasma of 2.3×10^{-3} Torr; plasma power of 220 W.

2.2. INFLUENCE OF HYDROGEN PLASMA TREATMENT ON SURFACE OF TUNGSTEN SAMPLES

The effects of irradiation of low-energy hydrogen and helium ions on the W surface were investigated in [14]. One of the factors that affect the surface properties of W is swelling (blistering), which occurs when the implanted gas concentration is high. Blistering appears on the surface of W when irradiated with ions of hydrogen plasma, even with energies much less than the threshold of the displacement of W atoms [15, 16].

In Fig. 4, it can be seen that after treatment of the W samples in the hydrogen plasma during 11 hours at a temperature T = 300°C and an ion energy E = 260 eV, an increase of hydrogen ion H^+ occurs approximately 5 times. Molecular hydrogen ion H_2^+ on mass spectra is practically not observed (only about 0.02%).

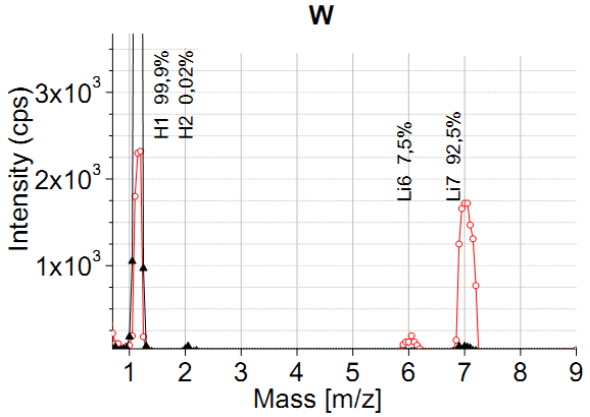

Fig. 4. Increase of hydrogen ion H^+ in mass spectra of secondary ion emission in W samples after treatment in hydrogen plasma

The hydrogen concentration an increase not only at the surface but also in the depth of the sample occurred, after treatment of the W samples in a hydrogen plasma for 11 hours at temperature T = 300°C and ion energy E = 260 eV (Fig. 5). The increase in hydrogen concentration over the depth of sample W is approximately 14%. It can be assumed that the penetration of hydrogen into the deeper layers of W occurs due to diffusion, including radiation-induced diffusion. It should be noted that in the near-surface layer of tungsten, peak intensity greater than twice the intensity of the hydrogen ion in the deeper layers is observed. But it falls very quickly.

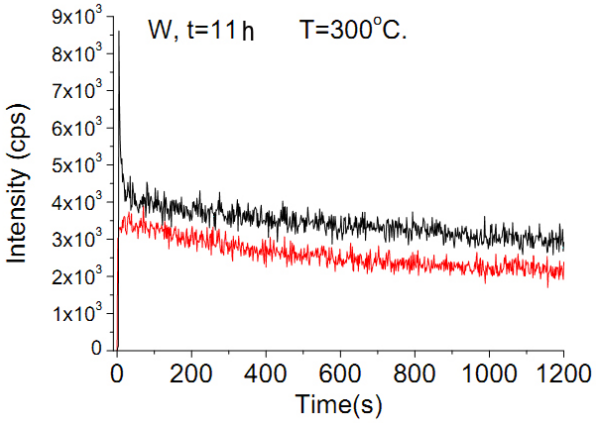

Fig. 5. The changes in secondary emission of hydrogen ions H^+ in W sample in the process of etching with 500 eV argon ions (Upper curve – after treatment, lower curve- before treatment). W, t=11 hours, T = 300°C

Fig. 6 shows the changes in the mass spectra of secondary ion emission in the mass range m/z = 175…220 in W samples after proton treatment. Before treatment in a hydrogen plasma, the peak values of the isotopes of the oxides WO^+ and WO_2^+ with respect to the isotope peaks of pure W^+ are not the same as after the treatment. If the magnitude of the W^+ peak is taken as unity, then before the treatment in the hydrogen plasma, the proportion of the oxides ions WO^+ and WO_2^+ with respect to tungsten ion W^+ is equal to 0.86 and 0.06, respectively.

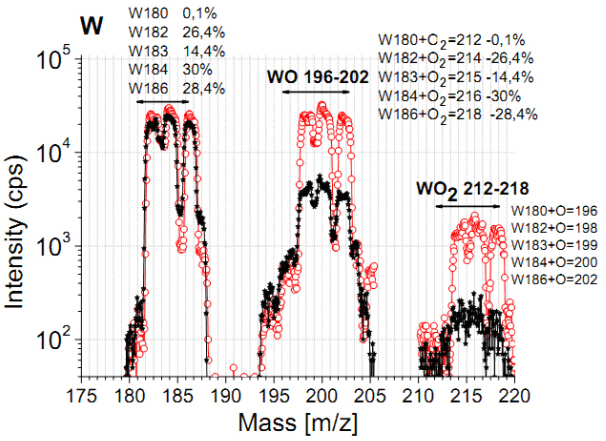

Fig. 6. Changes in the mass spectra of secondary ion emission in the mass range m/z = 175…220 in samples W after proton treatment (circles - sample before processing, triangles – sample after treatment)

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After treatment in plasma, the ratio of the intensities of the WO^+ isotope peaks to the W^+ isotopes in the mass spectrum is 0.2 and the intensities of the WO_2^+ isotope peaks to the W^+ isotopes are equal to ≈ 0.009. The peak of WO^+ decreased by 4.3 times, and the peak of WO_2^+ in 6.7 times.

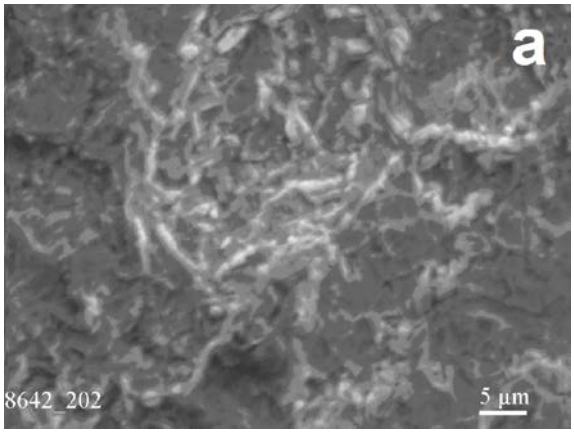
Thus, one can speak of a decrease in oxides in the tungsten sample after treatment. The cleaning of the surface of tungsten occurs under the influence of two processes. The first is the sputtering of the oxidized tungsten foil. During the processing (11 hours) of tungsten foil, a thickness reduction of ~ 5…6 μm (~ 0.5 μm/h) occurs. The second is the possible reduction of oxides in hydrogen plasma. To justify this assumption, we present the results of a number of papers. Thus, in work [15] arguments are discussed regarding the activity of hydrogen plasma during the reduction of metal oxides and semiconductors. It is known that the plasma changes hydrogen molecules to atomic, ionic, vibrationally - activated and other excited particles. Hydrogen in the atomic, ionic and excited states can restore almost every metal oxide even at lower temperatures. In Ref. [16], the reduction temperature of MoO_3, WO_3, Fe_2O_3 oxides, when using atomic hydrogen as compared with molecular hydrogen, decreased from 610 to 43°C, from 535 to 25°C, from 310 to 40°C, respectively.

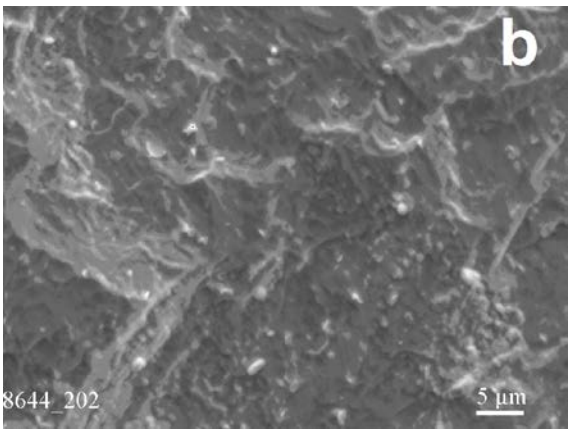
2.3. INVESTIGATION OF SURFACE CHANGES AFTER IRRADIATION BY METHOD OF RASTER ELECTRONIC MICROSCOPY

The investigation was made of surface changes after proton irradiation of tungsten samples using scanning electron microscopy. The significant surfaces of changes were observed after proton irradiation at the temperature of 300°C.

In Fig. 7 electron images the surface of tungsten before (see Fig. 7,a) and after processing (see Fig. 7,b) are given. Significant decreases in the surface irregularities after surface treatment by protons and the appearance of a finer structure on the surface of the metal are observed. The blistering of the tungsten surface was not detected in these investigations.

The separate cavities are observed in the photographs of the end face of a tungsten sample (see Fig. 7,c). They can appear with a relatively deep penetration of hydrogen in the depth.





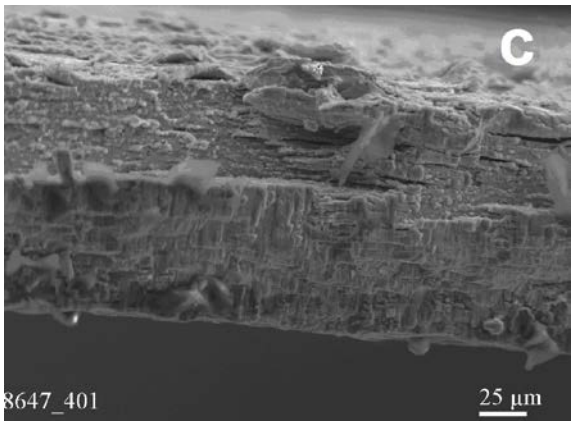


Fig. 7. The structure of the surface of the tungsten foil before treatment (a) and after treatment with protons (b, c) (main HF discharge current 5.5 A, proton energy 250 eV, exposure 11 hours, heating temperature 300°C, operating pressure $1.2 \cdot 10^{-1}$ Torr)

CONCLUSIONS

There is an accumulation of hydrogen not only on the surface, but also (in a lesser degree) in the depth of the tungsten sample. Molecular hydrogen is observed at the level of noise.

The investigation of the surface of irradiated and irradiated samples showed significant differences. After treatment in hydrogen plasma, a decrease in the amount of oxides on the surface of tungsten samples is observed. The substantial surface cleaning occurs from oxides due to surface sputtering, and also because of their reduction in hydrogen plasma.

REFERENCES

1. I.M. Nekluydov, G.D. Tolstolutskay. Helium and hydrogen in structural materials // *Problem of Atomic Science and Technology. Series "Physics of Radiation Damage and Radiation Material Science"*. 2003, № 3, p. 3-14.
2. L.B. Begrambakov, M.Yu. Gerchikov, M.I. Guseva, et al. Investigation of the interaction of thermonuclear-energy ions with the surface of carbon-confining structural materials for thermonuclear reactors // *IAE im. I.V. Kurchatov*, 1984, v. 56, iss. 1, p. 29-31.
3. V.M. Sharapov, A.E. Gorodetsky, A.P. Zakharov, A.I. Pavlov. Hydrogen balance in the INTOR reactor // *Atomic Energy*. 1984, v. 56, iss. 1, p. 29-31.

4. V.M. Sharapov. Hydrogen permeability of the first wall of a thermonuclear reactor // *Atomic energy*. 1986, v. 60, № 6, p. 391-397.
5. V.O. Mahlay, I.E. Garkusha, et al. Effect of irradiation by hydrogen plasma on the structure and phase composition of Ti-Zn-Ni alloys containing quasicrystalline foil // *Scientific Council on Plasma Physics and Plasma Electronics*. Kyiv, 2015, p. 53.
6. V.O. Mahlay, I.E. Garkusha, N.N. Aksenov, et al. Combined exposure to tungsten by stationary and transient hydrogen thermal loads // *Scientific Council on Plasma Physics and Plasma Electronics*. Kyiv, 2015, p. 23.
7. A.A. Gervash. Multilayered first wall with beryllium lining for the international thermonuclear tokamak reactor // *St. Petersburg*. Thesis 118.
8. V.A. Petryakov, O.A. Fedorovich, B.P. Polozov, et al. Influence of the high-frequency discharge parameters and heater design on the substrate temperature in the plasma-chemical reactor "Almaz" for the synthesis of carbon diamond-like films // *TKEA-2014*, № 5-6, p. 39-45.
9. G. Federici, P. Andrew, P.P. Barabaschi, et al. Key ITER plasma edge and plasma/material interaction issues // *J. Nucl. Mater*. 2003. v. 313-316, p. 11-22.
10. K. Tobita, S. Nishio, M. Enoeda, et al. Design Study of Fusion DEMO Plant at JAERI // *Fusion Eng. Des*. 2006, v. 81, p. 1151-1158.
11. A. Litnovsky, V.S. Voitsenya, A. Costley, et al. First mirrors for diagnostic systems of ITER // *Nucl. Fusion*. 2007, v, 47, p. 833.
12. T. Sugie, S. Kasai, M. Taniguchi, et al. Irradiation test of Mo and W mirrors for ITER by low energy deuterium ions // *J. Nucl. Mater*. 2004, v. 329-333, p. 1481-1485.
13. W.M. Shu et al. Microstructure dependence of deuterium retention and blistering in thr near-surface region of tungsten exposed to high flux D2 plasmas of 38 eV at 316 K // *Physica Scripta*. 2007, v. 128, p. 86-99.
14. D. Nishijima et al. Hidrogen blister formation on cold-wotked tangsten with layered structure // *Japan J. Appl. Phys.* 2005, v. 44, № 1A, p. 389-382.
15. K.C. Sabat, P. Rajput, R.K. Paramguru, et al. Reduction of Oxide Minerals by Hydrogen Plasma: An Overview // *Plasma Chemistry and Plasma Processing.* 2014, v. 34, iss. 1, p. 1-23.
16. A.A. Bergh // *Bell Syst. Tech. J*. 1965, v. 44 (2), p. 261-271.

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ОСОБЕННОСТИ ВЗАИМОДЕЙСТВИЯ НИЗКОЭНЕРГЕТИЧНЫХ ПРОТОНОВ С ПОВЕРХНОСТЬЮ ВОЛЬФРАМА

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Приведены результаты исследований взаимодействия протонов с энергией 250…260 эВ с поверхностью вольфрамовой фольги. Происходит распыление вольфрама со скоростью ~ 0,5 мкм/ч при температуре 300°С и плотности ионного тока ~ 1,5 мА/см^2. Поверхность вольфрама значительно изменяется после процесса облучения. Происходит существенная очистка поверхности от оксидов из-за распыления поверхности, а также из-за их восстановления в водородной плазме. После облучения вольфрама протонами существенно увеличивается содержание водорода вблизи поверхности образца. Содержание водорода в вольфраме плавно уменьшается по глубине.

ОСОБЛИВОСТІ ВЗАЄМОДІЇ НИЗЬКОЕНЕРГЕТИЧНИХ ПРОТОНІВ З ПОВЕРХНЕЮ ВОЛЬФРАМУ

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Наведено результати досліджень взаємодії протонів з енергією 250…260 еВ з поверхнею вольфрамової фольги. Відбувається розпорошення вольфраму зі швидкістю ~ 0,5 мкм/год при температурі 300°С і щільності іонного струму ~ 1,5 мА/см^2. Поверхня вольфраму значно змінюється після процесу опромінення. Відбувається істотне очищення поверхні від оксидів через розпорошення поверхні, а також із-за їх відновлення у водневій плазмі. Після опромінення вольфраму протонами істотно збільшується вміст водню поблизу поверхні зразка. Вміст водню у вольфрамі повільно зменшується по глибині.