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Work function change of first wall candidate metals due to ion beam irradiation

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Abstract

A new device has been made for examining the work function (WF) change of metallic and ceramic materials due to ion irradiation. The charging effect on the performance of Kelvin probe (KP) was reduced efficiently using appropriate shielding. The oxygen adsorption test on nickel sample showed that the WF changed with the surface coverage monotonically. The surface and near-surface defects might be responsible for the WF increase in the low-energy (500 eV) ion irradiation experiment, as revealed with the TRIM simulation. When damages reached a dynamic equilibrium, the WF tended to saturate. The opposite behavior due to higher-energy (MeV) ion irradiation seemed to be induced mainly by the desorption of gases from the surface, and possible radiation-induced segregation and/or diffusion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ion irradiation; Nickel; Surface effects

1. Introduction

Plasma-wall interactions (PWIs) are among the most important issues towards the practical fusion reactor that may be brought into market in the middle of the coming century. So far, a wide range of metals has been studied as plasma-facing materials (PFMs) as reported in [1–3]. It is widely accepted that the hydrogen isotope recycling, particularly the permeation behavior is strongly affected by the state of the surface, due to the importance of the surface recombination processes [1,3]. It was further speculated that the work function (WF) change, extremely sensitive to the change of surface state, might be used to explain the role of surface impurities that proved to be responsible for the permeation behavior [1].

In view of the successful application of the Kelvin probe (KP) in the research of blanket breeding materials [4], a new device has been constructed for examining the WF change of PFM due to ion irradiation. Hopefully the data can be beneficial in understanding the complicated PWI processes where the current database for fusion applications is still lacking. To our knowledge, little work has been done in the field, especially the work directly concerning the WF change due to ion irradiation. Present paper deals with the construction of the device and the preliminary experiments.

2. Description of the device

The most important component in the new device is a KP whose mechanism is stated in detail in [4]. It measures the contact potential difference (CPD) between sample 'S' and reference 'R' as

$$\mathrm{CPD} = (\Phi_\mathrm{S} - \Phi_\mathrm{R})/e, \tag{1}$$

where Φ and e are the WF in eV, and the elementary charge, respectively. If Φ_R keeps constant, then the change in CPD equals the change in Φ_S multiplied by a factor of $1/e$. In the present case, the probe electrode R was a 2.5-mm-diameter gold grid that was made to oscillate with a piezoelectric transducer.

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The whole system is schematically shown in Fig. 1. The ion beam source consists of a dc-arc discharge section, and a beam extraction and focusing section. The beam flux is measured with a Faraday cup. The probe can be rotated and moved for fine adjustment of the separation between the probe and the sample, which is quite crucial for the reliable performance of the probe [5]. The temperature of the sample surface can be checked occasionally with a rotatable thermocouple. A resistance heater is equipped for heating or annealing the sample. A quadruple mass spectrometer (QMS) is used for gas analysis. A blank port is prepared for an Auger electron spectrometer/low-energy electron diffraction (AES/LEED) analyzer that is intended to be installed in the future. The pumping system consists of a 150 l/s turbo-molecular pump and a 5 l/s rotary pump, and the achievable base pressure is 4×10^{-6} Pa.

Experiments are performed by measuring the CPD and irradiating the sample by turns due to the intrinsic configuration of the probe. To keep the WF of the reference constant, the probe must be protected from the influence of ions and electrons during the irradiation and the heating, as indicated by Hadjadj et al. [6]. In our initial tests, the detrimental influence of the ion beam and the thermal electrons from the heater on the CPD measurements performed on position B was also observed. A series of purposefully designed tests revealed that the secondary electrons generated at position A during the beam irradiation and the thermal electrons from the heater deposited on a small insulating component 1 cm above the probe tip that is used to isolate the tip from the body of the probe. The electron deposition imposed an electrical field between the probe and the sample, thus decreased the CPD reading. The influence lasted for a long time due to slow charge decay (discharge) process on the insulator. The changes in the reading ranged from tens to hundreds of mV, probably depending on the energy of the electrons from different sources, which implied a problem we had to face squarely and to solve because the maximum order of the changes was comparable to that induced by the irradiation.

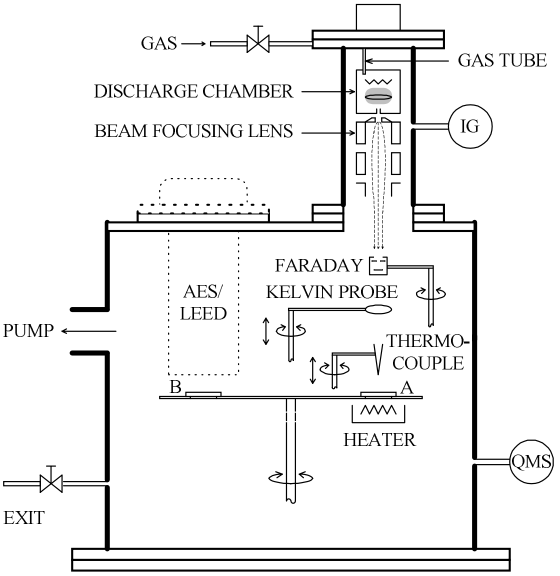

Fig. 1. Schematic figure of the new device.

We have tried to make use of shielding to enclose the beam path, and to confine the secondary electrons, the reflected ions and sputtered atoms within a space over the position A during irradiation, which reduced significantly the charging on the insulating component, and thus decreased drastically the induced changes in CPD to less than 50 mV at any cases in the later experiments. A heater that does not emit electrons is considered to be adopted in the future.

3. Preliminary experiments

Two experiments were performed to demonstrate the correctness of the measurement and to examine the effect of ion irradiation. The first one was oxygen adsorption experiment performed on polycrystalline Ni sample with a purity of 99.95% without using the ion beam from the ion source. The sample on the position A was firstly heated to about 150°C by the heater working at the power of 20 W at which the filament was not hot enough to emit electrons, thus the measurement could avoid the trouble mentioned above. When the WF change saturated, the heater was switched off and the sample cooled down. The adsorption was then carried out at room temperature by introducing oxygen gas into the vacuum chamber step-by-step.

The second experiment was irradiation one performed on the same kind of sample. The parameters were chosen as follows: ion species He^+, ion energy 500 eV, ion flux 2×10^{17} ions/m^2/s and working pressure 1×10^{-2} Pa (He), and the background pressure was 4×10^{-6} Pa after baking-out. The WF changes were found to be hundreds of mV much larger than those induced by the charging effect (<50 mV). Therefore the charging effect could be omitted in the experiment. A parallel experiment was performed for the comparison of different energies, using a He^+ ion beam of 1 MeV, 2×10^{16} ions/m^2/s produced by a van de Graaff accelerator, under the pressure of 1×10^{-4} Pa. The chamber had no capability of baking-out. The irradiation fluences are indicated in Table 1. The experiments were done at room temperature. The samples were cleaned with acetone prior to being loaded into the vacuum chamber.

Table 1
Accumulated fluences ($\times 10^{18}/\mathrm{m}^2$)

	Run						
	1	2	3	4	5	6	7
$\sum F$ (500 eV)	1	5	17	77	257	977	–
$\sum F$ (1 MeV)	0.1	0.3	0.7	1.5	3.5	8.3	20

4. Results and discussion

4.1. Oxygen adsorption experiment

The WF decreased monotonically in the course of the heating process prior to the adsorption, and tended to saturate after 50 min with a total WF drop of about 100 mV. The WF change during the oxygen admittance into the vacuum chamber with the pressures ranging from 1×10^{-5} to 1 Pa is illustrated in Fig. 2. A monotonic increase was observed, but at each point ($>1 \times 10^{-3}$ Pa) where the oxygen pressure was raised, a relatively steep increase was found. The WF decreased slowly after stopping gas admittance, and saturated after several hours.

A model concerning the surface dipole and depolarization on metals yields the WF change [7]:

$$\Delta\Phi = \frac{eN\theta\mu^*}{\varepsilon_0[1 + (9/4\pi)\alpha(N\theta)^{3/2}]}, \tag{2}$$

where N is the number of substrate atoms per m^2, θ the fractional coverage of the adsorbate (at $\theta = 1$ the adsorbate density is N), μ^* the dipole moment of an isolated adsorbate-surface moiety in cm (defined as positive if the negative end is toward vacuum), α the polarizability of the dipole in m^3, and ε_0 is the permittivity of vacuum in SI units; the resulting $\Delta\Phi$ is in eV.

Due to the strong electron affinity of oxygen, when being adsorbed on the surface of Ni sample, the net charge (electron) transfers from Ni surface to oxygen atom, which results in a dipole with its negative end toward vacuum, thus $\mu^* > 0$ and in turn $\Delta\Phi > 0$. Herein we only consider the chemisorption up to one monolayer since the multilayer adsorption appears difficult at room temperature, and even if possible, its contribution should be minute due to no charge transfer between layers. Assuming μ^* is independent of θ, it can be deduced that if $\pi\alpha N^{3/2} < 8/9$, then $\mathrm{d}(\Delta\Phi)/\mathrm{d}\theta > 0$ until $\theta = 1$; if $\pi\alpha N^{3/2} > 8/9$, still $\mathrm{d}(\Delta\Phi)/\mathrm{d}\theta > 0$ for $\theta < \theta_c = [8/(9\pi\alpha N^{3/2}]^{2/3} < 1$. Therefore, in both the cases, $\Delta\Phi$ should increase with θ monotonically.

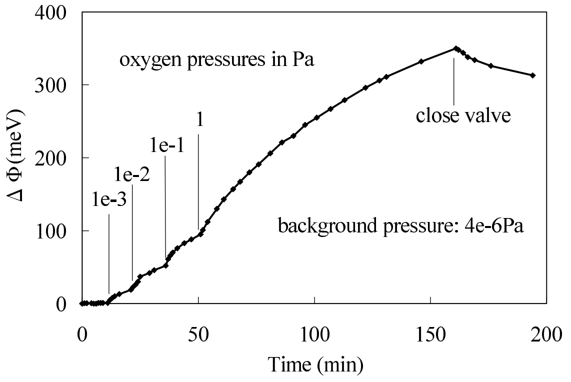

Fig. 2. $\Delta\Phi$ vs time due to oxygen admittance.

Since the sample surface was not cleaned thoroughly via such a method as sputtering plus annealing at high temperature, the surface coverage prior to the heating, θ_0, must be larger than 0, corresponding to $\Delta\Phi_0$. Therefore $\Delta\Phi$ in Fig. 2 was defined as the WF change with respect to $\Delta\Phi_0$. So was it in Figs. 3 and 4, with $\Delta\Phi_0$ being the value prior to the irradiation. The value of $\Delta\Phi_0$ is usually different from case to case, due to different processing histories and conditions in question.

The heating resulted in the desorption of some adsorbed oxygen atoms, thus θ decreased, in turn the WF

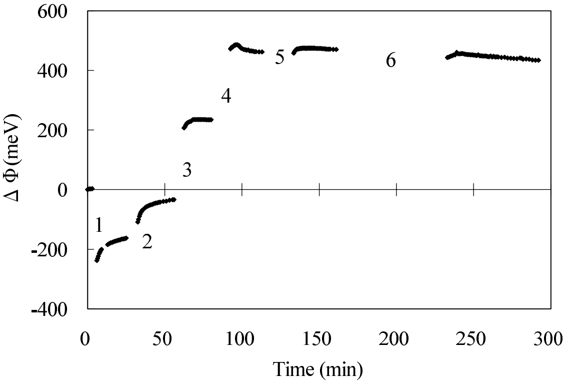

Fig. 3. Time dependence of $\Delta\Phi$ due to low-energy ion irradiation.

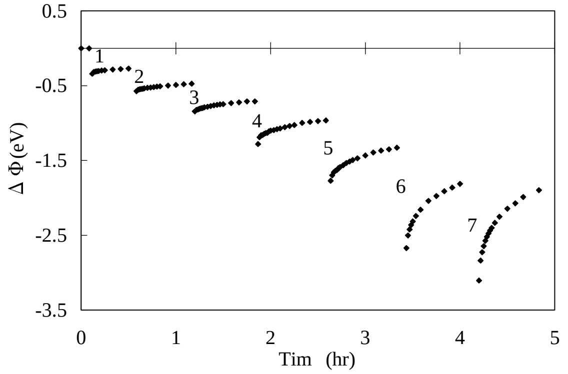

Fig. 4. Time dependence of $\Delta\Phi$ due to high-energy ion irradiation.

decrease occurred. The WF increase in Fig. 2 was obviously induced by the increase of θ due to the admittance of oxygen. The relatively fast increases in the WF immediately after raising the oxygen pressures could be considered as the result of the sudden rise in the striking frequency and thus in the adsorption rate of oxygen molecules on the surface. The slow decrease of the WF after terminating the gas admittance might result from the decrease of the adsorption rate and the transfer of the balance toward desorption. Finally, the new balance was achieved and the WF saturated.

4.2. Irradiation experiment

The initial test with ion beam irradiation gave the result depicted in Fig. 3. The first irradiation decreased the WF by about 250 mV, and the following irradiations increased the WF drastically till the saturation at the accumulated fluence of about 8×10^{19} ions/m^2. The decrease may be the consequence of the desorption and the sputtering of the adsorbed atoms on the sample surface, induced and enhanced by the bombardment of the energetic He$^+$ ions of 500 eV. Thus the WF deceased as θ became small. The following leaps could not be attributed to the desorption simply as it actually favors the decrease of the WF. Herein we assume that with the irradiation to higher fluences, the adsorbed species plays a fading role in the process due to desorbing and/or sputtering away. The defects like surface/near-surface vacancies, adatoms on the surface and interstitials near the surface, together with sputtering effect, determine the surface state that in turn determines the WF of the sample. To observe the influence of the irradiation on the surface and near-surface layer and to distinguish its effect on the WF change from other factors like desorption, computer simulation using the TRIM code (version 98.01 by J.F. Ziegler and J.P. Biersack) with the average surface binding energy of 4.46 eV (the heat of sublimation) and the lattice binding energy of 2 eV was carried out and led to the results in Table 2. The simulation outlined actually the defects' production and distribution though the adatoms generated by the surface capture of the slow sputtered atoms and the thermal expansion of the "spike" near surface [8] could not be estimated by the code. Nevertheless, the simulation indicated clearly that the sample surface was subjected to significant modification due to the irradiation, for instance, after the fourth run (corresponding to the accumulated fluence of 7.7×10^{19} ions/m^2), more than one monolayer of the surface was removed. The saturation of the WF values after the fourth run reflected the dynamic equilibrium of all factors involved in the process.

The irradiation of 1 MeV He$^+$ resulted in continuous decreases of the WF, followed by partial recoveries, as indicated in Fig. 4. The TRIM simulation under the same binding energies led to the results in Table 2. Compared with the low-energy case, the influence of the irradiation-induced defects on the surface state seemed to be negligible, considering the total fluence of 2×10^{19} ions/m^2 in the experiment furthermore. However, the energy transferred to the sample was much larger and more concentrated than that in the low-energy case, taking into account the great differences in the initial energies, and the great differences in the numbers of the backscattered and the sputtering events that carry away a certain fraction of the initial energies. Therefore, thermal desorption might play an active role in the MeV case, which resulted in the decrease of the WF due to the decrease of θ, together with irradiation stimulated desorption. Moreover, the influence of the radiation-induced diffusion and segregation may need to be studied in the future, since they are closely related to the occurrence of bulk impurities on the surface and/or the migration of surface impurities into the bulk, which causes the change in θ, and the change of μ^* in its value and sign. This, together with the desorption effect, might be responsible for the much larger changes (>1 V after fourth run) in the WF in the case, compared to that (100 mV) induced by pure heating to 150°C. The time-dependent recovery after irradiation, probably due to the temperature decreasing, is still an open question for the present.

The experimental results showed that the WF of the sample changed greatly due to the ion irradiations, which gave us a hint that KP might be used as a supplementary method in monitoring the surface changes under future tokamak/reactor conditions. Moreover, the researches on the WF by KP will contribute to the in-

Table 2
Comparisons of TRIM simulations

Energy	500 eV	1 MeV
Ion range	4 nm	1.7 μm
Sputtering yield (atoms/ion)	0.23	0.001
Backscattered ion ratio	0.34	<0.001
Vacancy production rate (numbers/ion)	5.6	385
Vac. production at or near surface (numbers/ion/nm)	>1	0.01
Vac. distribution (80%)	<4 nm	>1 μm

sight into the elementary processes related to the fusion reactor, for whether plasma-facing materials or blanket breeder materials.

5. Summary

A new device, able to examine the WF change due to ion irradiation, has been constructed. The effective reduction of the charging effect on the probe ensured the measurements with an error less than 50 mV. The oxygen adsorption test showed that the WF changed with changing the surface coverage, qualitatively consistent with the theoretical evaluation. The WF increase of the sample in the low-energy (500 eV) ion irradiation experiment might be induced by the production of the surface/near-surface defects, and the sputtering effect, as estimated with TRIM. The opposite behavior under the higher-energy (MeV) ion irradiation seemed to be induced by the desorption of gases from the sample surface.

Acknowledgements

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