Surface diagnostics by ion scattering spectroscopy in gaseous environment

N V Mamedov¹²³, V A Kurnaev², D N Sinelnikov² and D V Kolodko²
¹Federal State Unitary Enterprise «All-Russia Research Institute of Automatics», Sushchevskaya street 22, Moscow, 127055, Russian Federation
²National Research Nuclear University MEPhI, Kashirskoe shosse 31, Moscow, 115409, Russian Federation

E-Mail: m_nikitos@mail.ru

Abstract. Nowadays, it is important to perform in-situ analysis of composition and thickness of ultra-thin (~5-50 Å) surface layers in the course of the surface exposure to plasma or its components. For this aim, a new experimental facility based on the MEPhI Mass Monochromator is being developed, where low and medium energy ion spectroscopy of samples is used just after or during plasma exposure/ion treatment. A differentially pumped energy analyzer is used for recoil ion spectroscopy under grazing incidence conditions in the automated ion mass monochromator. A built-in Penning plasma source is used for plasma/ion treatment of samples. In this paper, the influence of the working gas (during the plasma source operation) on the energy spectra of reflected and recoil ions is studied. It is shown that the peak shape of the energy spectrum of scattered H⁺ ions increases during gas injection, and, at the same time, the signal intensity of the ionized recoils from the sample decreases. Nevertheless, analysis of the surface composition and thickness of the outer layer could be done at pressures ranging up to 10⁻⁴ Torr.

1. Introduction

At present, understanding the dynamics of deposition and sputtering of the materials of the plasma-facing components (PFCs) in fusion devices is essential. In order to improve the plasma parameters, material migration and re/codoposition, which take place under plasma irradiation, are used in addition to boronization and litzation of the PFCs.

Well-known linear plasma simulators (e.g. PISCES, NAGDIS, Pilot-PSI) are used to investigate the plasma-surface interaction. However, the plasma-exposed surfaces are typically analyzed post-mortem with secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES) and Rutherford backscattering spectroscopy (RBS) after being transported to the dedicated analysis chambers [1,2]. While it is possible to use RBS for nondestructive in-situ analysis (as in the DIONISOS setup, for example [3]), it requires the use of expensive accelerators. Additionally, the depth resolution, which is determined by the energy resolution of the detector, can only be adjusted to several tens or hundreds of nanometers, which is insufficient in some cases.

For instance, it was found in modeling the experiments on the linear simulator PR-2 [4] that formation of a thin (~10 nm) oxide layer on the aluminum target strongly increases electron emission.

³ To whom any correspondence should be addressed.
under the plasma impact. This enormously enhanced electron emission can cause different plasma-surface instabilities.

For this reason, it is vital to implement an in-situ analysis method for determination of the composition and thickness of ultra-thin (~5-50 Å) surface layers in the course of the surface treatment by plasma or its components. In this paper, the influence of the working gases (during operation of the plasma source) on the energy spectra of the reflected and recoil ions is studied.

2. Experimental setup
Singly scattered ions or recoil ions form narrow peaks in the energy spectra and provide information about the atomic composition of the outer atomic layer [5]. Moreover, it was shown [6] that the thickness of the thin layers of light elements on the surfaces of heavy substrates can be analyzed with a good depth resolution (~0.3 nm) using scattering of the hydrogen ions with the energies in the keV range.

A schematic of the experimental setup is shown in figure 1. This setup of the modernized ion mass monochromator [7] allows us to separate ions with the mass/charge ratios of up to M/Z = 100 at the maximum accelerating voltage of 40 kV. A heated duoplasmatron ensuring a low level of impurities, with an automated power supply and gas feed is used as the ion source. When operating with helium, the current of He+ ions is two orders of magnitude higher than the total current of all other components. The relative energy spreading in the beam at 5 keV is less than 5×10–3, and its angular divergence is ~0.01 rad.

The diagnostic beam line is differentially pumped with two 70 l/s turbomolecular pumps located immediately after the duoplasmatron and before the aperture into the interaction chamber. The interaction chamber is degassed with a turbomolecular pump with the output of ~103 l/s. This feature makes it possible to use a built-in plasma/ion source based on the Penning-type discharge [8]. It can be positioned in the interaction chamber at variable distance (20-40 mm) from the target surface. This source is capable of working at relatively low pressures (~10–4 Torr) with the maximum current density of 100 μA/cm2 (Ar).

A quarter-spherical remote deflector is used as the energy spectrum analyzer for the ion scattering and recoil ion spectroscopy. The ion current is measured with a secondary electron multiplier. This detector is positioned in the forward direction at the scattering angle of θ = 16°. At the solid angle of scattered particle recording of 1.1×10–3 sr with the half-width of the scattering angle Δθ = ±0.6°, its energy resolution is 0.8%. To keep the secondary emission multiplier below the maximum operating pressure (10–5 Torr) by increased gas puffing into the plasma source, the analyzer is equipped with an additional turbomolecular pump with the 70 l/s pumping speed. The targets, up to 40 mm in diameter, can be replaced without opening the facility by means of a lock system with a self-contained evacuation system. The target is heated with a 120 W incandescent lamp to the temperature of 750°C.

The automated ion beam control makes it possible to perform experiments following predeveloped irradiation programs. Computer control is realized with the Labview and DCON Utility programs using the ADC/DAC manufactured by ICP DAS.

The residual gas composition is controlled by the Extor XT100M quadrupole mass-spectrometer.
In this experimental setup, it was shown that when the target is irradiated with argon ions, registration of the negatively charged recoil ions makes it possible to monitor the dynamics of carbon and oxygen impurity variations on the surfaces of materials with medium and large atomic numbers. Irradiation with hydrogen ions and registration of the positively charged ions allows us to estimate the thickness of the deposited layers by the shift of the maximum of the energy spectrum and the comparison with the spectra simulated with a TRIM-like code.

3. Results and discussion
During the plasma source operation, the pressure in the vacuum chamber can increase up to $10^{-4}$ Torr. Prior to the experiments with the plasma source, the influence of the elevated gas pressure on the energy spectrum of the reflected ions and direct recoil ions was studied. Various gases (H$_2$, Ar, He, Xe) were injected into the vacuum chamber through the mass flow controller of the plasma source. The signal intensity of the H$^+$ ions scattered from the surface (with the initial energy $E_0 \approx$5-10 keV) increased with increasing the vacuum pressure (see figure 2). At higher pressure, a peak corresponding to single-scattering of the primary ion beam on the gas-phase appears. This peak can be used as the additional reference point for calibration of the primary beam energy. For example, the energy spectra
of the H\textsuperscript{+} ions scattered from the Al surface in Ar and Xe gas environments are shown in figures 2 and 3. As can be seen from figure 3, the signal intensity of the scattered ions drops sharply at the pressure of \(\sim 10^{-3}\) Torr. The obtained spectra were normalized to the primary beam current and secondary ion-electron emission was taken into account. The secondary ion-electron emission coefficient was assumed to be the same for the diagnostic ion beam and the fast neutrals resulting from the charge exchange with the gas.

**Figure 2.** Ion scattering energy spectra for the 12 keV H\textsuperscript{+} beam incident on W with the Al layer (4nm) at different Ar pressures. \(I_0\) is the primary ion beam current. The energy spectrum under the low pressure \(P=5\cdot10^{-}7\) Torr is shown in green, the energy spectrum under the high pressure \(P=5\cdot10^{-}4\) Torr in black and the energy spectrum of the H\textsuperscript{+} ion scattered from the gas-phase without W target under the high pressure \(P=5\cdot10^{-4}\) Torr in red.

**Figure 3.** Ion scattering energy spectra for the 12 keV H\textsuperscript{+} beam incident on W with the Al layer (4nm) at different Xe pressures \(I_0\) is the primary ion beam current.)
The change of the positive charge fraction $\eta^+$ during ion beam propagation through the gas-phase was estimated. The ratio of the number of the positively charged particles to the total number of particles when the beam passes through a gas target can be written as:

$$\eta_g^+ = \eta_{eq}^+ + (\eta_0^+ - \eta_{eq}^+) \cdot \exp\left(-\sigma_i^+ + \sigma_s^+\right) \int_0^z ndz$$

(1)

where $\eta_0^+$ is the initial positively charged fraction of the beam reflected from the target, $\eta_{eq}^+ = \sigma_s^+ l(\sigma_i^+ + \sigma_s^+)$ is the equilibrium value of the positive fraction at high pressures (for a “thick” target, $(\sigma_i^+ + \sigma_s^+)nl \gg 1$). $\sigma_i(E)$ is the ionization cross-section of the neutral atom, $\sigma(E)$ the cross section of the electron capture by the positive ion, $z$ is the coordinate along the direction of beam propagation in the gas target and $E$ the kinetic energy of the ion.

In view of the beam attenuation due to scattering, the fraction of the surviving ions that enter the analyzer can be expressed as:

$$\eta^+ = \eta_g^+ \cdot \exp\left(-\sigma_p^+ \int_0^z ndz\right)$$

(2)

where $\sigma_p(E)$ is the transport cross section for the interaction of the incident ion and a neutral particle.

As shown in [9], the cross section for this type of interaction can be expressed as follows:

$$\sigma \approx 2\sqrt{2\pi}a_0^3 \frac{\alpha I_0}{a_0^3 E}$$

(3)

where $a_0 = 0.529 \times 10^{-8}$ cm is the Bohr radius, $I_0 = 13.6$ eV is the ionization potential of hydrogen, $\alpha$ is the polarization efficiency, $E$ is the kinetic energy of the ion. The value of the polarization efficiency, or rather, the coefficient $\alpha/a_0^3$ for basic residual gas molecules and atoms of inert gases can be found in [9].

Taking into account the length of the ion path including the interaction chamber $l_c$, the distance from the input aperture to the energy analyzer $l_a$, the pumping speed of the vacuum chamber and the analyzer, and the size of the analyzer input aperture, the “thickness” of the target gas (argon in this case) can be estimated as

$$\int_0^z ndz = n_c l_c + n_a l_a$$

(4)

where $n_c, n_a$ are the concentrations of particles in the interaction chamber and in the analyzer, respectively.

To estimate the cross sections of the electron capture and loss for hydrogen in argon, one can use the data from [10]. As shown in [11], the fractions of the neutral and charged components in the beam reflected from the target are related through the semi-empirical formula:

$$\eta_0^+ = k \cdot E^\mu$$

(5)

where $k \approx 0.08$, $\mu \approx 0.5$ and $E$ is the ion kinetic energy in keV.

If the dependence (5) is assumed, the positive charged fraction decreases by 2-3%. If we assume the values of the neutral and positively charged components of the beam reflected from the target to be $\eta_0^+ = 5\%$, $\eta_0^0 = 95\%$, which are the values from another example, then the positively charged fraction is estimated to increase by 3-4%. However, as shown in figure 2, the charge fraction is increased by 7-10%. A possible explanation for this result is that a large fraction of the neutral hydrogen atoms are reflected from the surface in the excited state [12], and for such atoms the ionization cross-section is significantly higher than that for the ground-state atoms.

The signal intensity of the negative ions rebound and sputtered from the Ar $^+$-irradiated surface decreases by a factor of ~5 when the pressure in the interaction chamber increases by more than two orders of magnitude (see figure 4), as a result of capture of the electrons by the negative ions in the residual gas. At the same time, the shape of the spectrum does not change. This is in a qualitative
agreement with [13,14]. However, at the elevated pressure, the signal / noise ratio for the recoil ion peaks is greater in the case of negative ion registration than it is for the positive ions.

Figure 4. Signal intensity of negatively charged recoil ions of carbon and oxygen from W during irradiation by Ar + with energy of 7.5 keV, as function of the pressure in the interaction chamber.

4. Conclusions
Possible application of ion scattering spectroscopy at pressures up to several mTorr during plasma irradiation is described. It is found that:

- The increase of the positive fraction recorded by the energy analyzer is attributed to enhanced electron stripping from the reflected neutral atoms (especially from the excited atoms) of hydrogen in argon.
- The increase in intensity and the broadening of the reflection spectrum of light ions in the low-energy range results in a higher sensitivity for the analysis of the sample depth.

Due to neutralization of the singly reflected or recoil ions, a two orders of magnitude increase of the pressure causes reduction of the sensitivity of the elemental analysis by ion scattering by a factor of 3-5, depending on the concentration of the working gas in the interaction chamber.

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