Mass spectroscopy of the ion flux produced during inductively coupled plasma nitriding process

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Abstract. Ion fluxes on the surface of sample embedded in inductively coupled plasma have been studied in conditions typical for titanium alloy nitriding: total pressure 0.44 Pa, Ar/N₂ = 70%/30%, and RF power 1500 W. The gas composition was independently monitored by the quadrupole analyser. The ion fluxes were sampled using a specially designed electrostatic extractor and then analysed with a magnetic sector mass-separator. The extractor design allowed us to apply a bias voltage to the plasma facing electrode thus imitating interaction of ions with the surface during the plasma processing. The ion fluxes of Ar⁺, N₂⁺, and N⁺ on the surface were measured. The mass spectroscopy diagnostics unit is suitable for extensive ion content studies in the plasma technology facilities.

1. Introduction

The effectivity of technological plasma processing devices strongly depends on the plasma parameters such as plasma density, electron temperature, plasma potential, and ion composition. The latter is of substantial importance since many of the surface modification processes in plasma depend on mass and energy spectra of ions bombarding the substrate, and on their amounts. For example, the fluxes of atomic nitrogen are essential for plasma nitriding of titanium alloys and steels. This is also important for the plasma ion immersion implantation (PIII) technique, where the N⁺/N₂⁺ ratio affects the energy of incident atoms and hence their penetration depth. It is therefore vital to study the behaviour of ion fractions incident on the material surface during the plasma processing. In our previous paper [1] we have discussed the methods of ion flux analysis for the technological plasma devices. The only reliable way to perform such measurements is to use the charged particles analysis technique, and there are several reports on this topic [1–4].

We have recently described a magnetic sector mass spectrometry unit for analysing fluxes of ions with different masses in the inductively coupled plasma (ICP) reactor used for nitriding [1]. It was shown that the mass resolution of the spectrometer is well-suited to control mass spectra that correspond to ion fluxes incident on the samples embedded in plasma. Such monitoring is a promising diagnostic tool for better characterisation of technological plasmas.

Here, for a given plasma treatment regime, we compare data obtained by optical emission spectroscopy, gas contents diagnostics, and by the ion mass analyses. Absolute ion fluxes produced in the ICP nitriding process were obtained.
2. Experimental

The experiments were carried out in an ICP facility used for surface modification [5] equipped with a mass analysing unit [1]. The ICP discharge was excited by a flat circular antenna Beams&Plasmas RPG-250 cooled by water and protected by a quartz shield. The longitudinal magnetic field was produced by electromagnetic coils. The RF power was supplied by COMET cito 1330 series generator.

The ICP vacuum chamber was evacuated to a base pressure of $1 \times 10^{-4}$ Pa with a turbomolecular pump backed by a dry scroll pump. Argon and nitrogen mixture ($\text{Ar}/\text{N}_2 = 70\%/30\%$) was used as a working gas. The gas components ratio was regulated by mass-flow controllers (MFC).

The gas mixture composition was continuously monitored with a differentially pumped Extorr XT-100 quadrupole residual gas analyser (GA). Low working pressure in the GA was maintained by a regulating valve. The optical emission spectroscopy unit comprising three Avantes AvaSpec ULS2048L channels was used to qualitatively determine the plasma composition.

The mass analysing unit was attached coaxially to the ICP chamber in order to extract and mass-filter the ions from plasma. It consisted of the extractor followed by the magnetic sector mass analyser (MA). The MA configuration and operating parameters were described in detail previously [1]. The extractor, which was immersed into plasma, was a two-electrode electrostatic lens with circular apertures. The entrance aperture and the extracting aperture were 1 mm and 1.5 mm in diameter, respectively. The entrance aperture imitated the surface of a sample subjected to plasma treatment. It was electrically insulated from the rest of the unit and connected to a dedicated electrical vacuum feedthrough. Thus, the bias could be applied to the entrance electrode, and the total current could be measured at various biases. The relative currents of ion species with masses $M_i$ measured in the MA collector circuit were then used to calculate the current densities of ions of each kind, and eventually to obtain the absolute values of ion fluxes.

In a typical regime for titanium alloy nitriding in the ICP reactor, a fixed ratio of Ar and N$_2$ partial pressures was used: $p_{\text{Ar}} = 0.31$ Pa, and $p_{\text{N}_2} = 0.13$ Pa. The forward RF power was 1.5 kW, and the
reflected power did not exceed 2%. The fixed DC bias voltage applied to the entrance aperture of the extractor was \( U_b = -300 \) V.

### 3. Results and discussion

The optical emission spectrum for the discussed discharge regime is shown in figure 2. The most intense lines correspond to \( \text{Ar}^+, \text{Ar}, \text{N}_2, \text{N}_2^+, \text{N}, \text{OH}, \text{H}, \) and \( \text{NH} \). The relative intensities of \( \text{N} \) and \( \text{N}^+ \) emission lines are small compared with those of \( \text{N}_2 \) and \( \text{N}_2^+ \).

![Figure 2](image)

**Figure 2.** Optical emission spectrum of the ICP discharge operated in the Ar–N\(_2\) mixture (RF power 1 kW, total pressure 0.44 Pa).

![Figure 3](image)

**Figure 3.** (a) Mass spectrum of ions extracted from the ICP discharge operated in the Ar–N\(_2\) mixture (RF power 1.5 kW, total pressure 0.44 Pa, \( U_b = -300 \) V). (b) Mass spectrum of gas species registered by the gas analyser under the same conditions.

Figure 3a demonstrates the spectrum of ions, extracted from plasma, obtained using the magnetic mass analyser. Figure 3b demonstrates mass spectrum of gases in the chamber recorded with quadrupole gas analyser (GA), which represents the mass distribution of ions produced inside the GA by its own ionisation source. In the MA spectrum, the signals of Ar\(^+\), N\(^+\), N\(_2\)^+ are the most intense, and the signal of atomic ions N\(^+\) exceeds that of molecular ions N\(_2\)^+. The GA spectrum demonstrates presence of Ar, N, and N\(_2\), as well as NH\(_x\) compounds, the latter with relative intensities considerably higher than those in the MA spectrum. It is generally accepted that the NH\(_x\) species are mainly generated through the surface reactions on the vacuum chamber walls [6]. This might account for high relative content of NH\(_x^+\) generated in GA ionizer. The differences in the N\(^+\)/N\(_2\)^+ ratios as well as in Ar\(^{2+}\) relative intensities are supposedly due to different conditions of dissociation and ionisation in MA
and GA, since MA deals with the ions produced in the plasma reactor, while GA detects ions produced by its ionisation source. The presence of the hydrogen species in the GA spectrum is due to relatively poor pumping efficiency of light gases by the differential pumping system of GA. One should notice that both the MA and GA spectra show significant fraction of atomic nitrogen ions, while the OES lines corresponding to N and N$^+$ are relatively weak. The sensitivity of optical diagnostics is therefore insufficient for reliable determination of atomic nitrogen fraction in our ICP process. 

Under $U_b = -300$ V, the total current measured at the entrance aperture of the extractor was 25 mA. The collecting area was about 20 cm$^2$. Taking into account the relative ion contents measured with MA (see figure 3a), the fluxes of ions arriving to the extractor can be evaluated: $\Gamma_{Ar^+} = 5.7 \times 10^{15}$ cm$^2$s$^{-1}$, $\Gamma_{N^+} = 1.3 \times 10^{15}$ cm$^2$s$^{-1}$, and $\Gamma_{N_2^+} = 9.0 \times 10^{14}$ cm$^2$s$^{-1}$. The discussed diagnostic technique therefore enables to determine fluxes and fluences for ions incident on the substrate during plasma processing of metals.

4. Conclusion
The magnetic sector mass analysing unit [1] was used to determine the absolute fluxes of ions incident on the biased surface immersed to the inductively coupled Ar–N$_2$ plasma. Under fixed ICP nitriding conditions, the absolute ion fluxes of Ar$^+$, N$^+$, and N$_2^+$ ions have been evaluated: $\Gamma_{Ar^+} = 5.7 \times 10^{15}$ cm$^2$s$^{-1}$, $\Gamma_{N^+} = 1.3 \times 10^{15}$ cm$^2$s$^{-1}$, and $\Gamma_{N_2^+} = 9.0 \times 10^{14}$ cm$^2$s$^{-1}$. It was demonstrated that monitoring the gas species contents with a conventional quadrupole gas analyser is insufficient for comprehensive characterisation of the plasma processing procedure. Particularly, the ratio $\Gamma_{N^+}/\Gamma_{N_2^+}$, which is essential for plasma nitriding investigation and implementation, can be yielded only by dedicated mass analyses of the ion fluxes.

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