Measurement of mass-to-charge beam plasma ion composition during electron beam evaporation of refractory materials in the forevacuum pressure range

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Abstract. We describe here the design of the modernized ion-optical system (IOS) of the standard residual gas analyzer (RGA). IOS electrodes are made of stainless steel. The electrodes are powered outside the vacuum chamber. Reducing the diameter of the entrance aperture to 0.6 mm made it possible to expand the measurement range. These design features of this system makes it possible to measure the mass-to-charge composition of beam plasma ions generated by electron beam evaporation of ceramics and refractory metals in the forevacuum pressure range under a prolonged exposure to high temperature. We present the results of the measured plasma composition during evaporation of aluminum oxide and zirconium ceramics, as well as of titanium.

1. Introduction

The electron beam, formed in the forevacuum pressure range (1-100 Pa) [1], and the plasma that it generates, are universal and effective tools for surface modification of electrically non-conductive materials [2] and for initiation of chemical reactions in plasma. The beam plasma diagnostics mostly employs the probe and optical spectroscopy techniques. Mass spectrometry studies of such plasma are difficult since the ion mean free path under forevacuum conditions is short, not exceeding several millimeters.

To investigate the beam plasma in the indicated pressure range, we have previously developed an inverse time-of-flight spectrometer [3]. However, the resolution of this spectrometer turned out to be insufficient for separation of ionic constituents with close values of masses when evaporating materials of complex composition [4].

Along with time-of-flight spectroscopy, quadrupole mass spectrometers have been also actively developed since the 50s of the last century [5]. Due to the oscillatory nature of the ion trajectories in the fields of this analyzer, the ions can be held up for a long time, thereby ensuring small weight and size, and high resolution [6]. For example, an electrostatic analyzer HIDEN EQP (Hiden Analytical Ltd., England) equipped with a quadrupole mass spectrometer was used to measure the mass-to-charge composition and energy spectra of ions in a magnetron discharge [7] and vacuum arc [8] plasmas.

Replacing the ionizer with the ion-optical system for extracting ions from the plasma in the residual atmosphere analyzer based on the RGA 200 quadrupole mass spectrometer (Stanford Research System) made it possible to carry out measurements of the mass-to-charge composition of stationary vacuum arc plasma [9]. We implemented this approach in the study of plasma generated by an electron beam in the forevacuum pressure range, in an atmosphere of various gases [10], as well as in electron beam evaporation of different metals with a relatively low melting temperature (magnesium, zinc) [11].
However, the design specifics of the RGA ion-optical system that we developed did not allow the mass-to-charge ion spectra of the beam plasma to be studied in the course of prolonged electron beam evaporation of solid targets made of high-temperature ceramic or refractory metals. For such cases, monitoring of the beam plasma ion composition is important for the coating deposition technology. These circumstances prompted our work on the upgrade of the ion-optical system of the beam plasma quadrupole mass-spectrometer based on the residual atmosphere analyzer of the RGA type. The results of this study are presented in the current article.

2. Experimental Setup and Methods

Fig. 1(a) shows the electrode layout diagram of the original version of the RGA-100 residual gas analyzer modernized for measuring the mass-to-charge beam plasma composition [10]. The ion-optical system for extracting ions from the beam plasma and their subsequent analysis includes focusing plate 3, drift tube 4, extracting electrode 5, and insulators 6. Extracting electrode 5 is placed traverse to the electron beam propagation direction at a distance of 3-9 cm from its axis.

Applying a negative potential with respect to the ground to the electrode 5 ensures a directional extraction of the ion flux from the beam plasma to the spectrometer IOS through the 0.7-mm central aperture. With an increase of the aperture diameter, the current signal in the measuring circuit increases, but the pressure range that can be studied shrinks significantly. The operating pressure of forevacuum electron sources is at least several Pascals, while the maximum pressure in the mass-spectrometer in the ion transport and separation regions should not exceed $10^{-2}$ Pa. At higher values of pressure, the analyzed ions experience collisions with neutrals, or recharge, or deflect from trajectory and escape to the IOS walls. The diameter of the ion transport channel (drift tube 4) is 10 mm. Varying the length of the drift tube, one can change the distance between extracting electrode 5 and the electron beam axis. Electrodes 4 and 5 in this manner ensure the formation of the ion flux from plasma and its transport in the high vacuum region to the separation (mass-analyzer quadrupole rods 2) and registration (Faraday cup 1) locations. At the entrance of the quadrupole mass-separator, the ion flux is focused by the 5-mm central aperture in electrode 3 when a negative potential is applied to it. All IOS electrodes are made of duralumin. Electrodes are electrically insulated using capron insulators 6.

As mentioned above, the present IOS was successfully used for studying the mass-to-charge composition of the beam plasma in the electron beam transport region, as well as for electron beam evaporation of metals with a relatively low melting point [11]. Since the mean free path length in forevacuum is short (several mm), it is necessary, when studying the beam plasma under electron beam evaporation, to place the IOS extracting electrode in the direct vicinity of the evaporated target. When evaporating refractory metal or high-temperature ceramic targets, the heat load on the insulation of the IOS assembly elements and connection wires increases due to high temperatures. Overheating the...
insulating materials up to their melting point resulted in the appearance of extraneous spectral peaks, and could lead to a failure of the high-vacuum turbomolecular pump used to evacuate the ion separation and transport regions.

To eliminate these shortcomings, a number of changes were introduced to the design of the ion-optical system (Fig. 1b). Extracting electrode 5 and drift tube 4 (Fig. 1a), as well as the insulator between them, were replaced with cylindrical electrode 5 with a small aperture (0.6 mm) in its entrance end (Fig. 1b). Additionally, electrode 5 was made of more heat-resistant stainless steel. The design of the ion-optical system was changed in such a way that the power supply wires to electrodes 3 and 5 were lead in the area with the least thermal load. These design changes to the IOS made it possible to carry out studies of the beam plasma in the immediate vicinity of the evaporated refractory target.

3. Results of Mass Spectrometry Studies

Fig. 2 shows the mass spectrum of beam plasma ions under the electron beam irradiation on the surface of zirconium ceramics. Air was used as a plasma-generating gas; the chamber pressure was 3 Pa.

![Mass-to-charge spectrum of plasma ions during evaporation of zirconium ceramics.](image)

At low electron beam energy of 3 keV and a current of 100 mA, the ion composition of the beam plasma completely corresponds to the case of electron beam transport in a residual gas medium. The peaks of singly-charge water vapor ions are predominant in the mass-to-charge spectrum. There also present peaks of small amplitude that correspond to ions of nitrogen, oxygen, and their compounds. With an increase in the electron energy, the plasma ion composition does not change until electrons reach the threshold energy at a level of 10 keV. At this electron energy, there is visually observed the formation of a melt pool at the beam’s focus and the spectrum registers only ions of the target material. It should be noted that the predominant ion component in plasma are oxides of stable zirconium isotopes. Zirconium dioxide isotopes are recorded with lower amplitude. There is also registered in the mass spectrum a small amplitude zirconium peak (m=90 a.m.u.). Other stable zirconium isotopes have not been identified due to their weak signals.

A different picture is observed when an electron beam irradiates the surface of alumina ceramics. At low electron beam energy, the mass spectrum also corresponds to the spectrum of gas plasma. However, when the electron energy increases above 5 keV (Figure 3), the spectrum registers ions of admixtures of alumina ceramics: Na, NaO, and Mn. In this case, no visual destruction of the target surface is observed despite the fact that aluminum ions are recorded in the spectra. With a further increase in the electron energy, and hence in the electron beam power, a melting pool is formed with the expectedly
sharp increase in the peaks of aluminum ions and the appearance of weak reflexes of oxides. Admixture ions are not registered in this case.

Figure 3. Mass-to-charge spectrum of plasma ions during evaporation of aluminum oxide ceramics.

Figure 4 shows the mass-to-charge composition of ions generated during electron beam irradiation of the titanium target surface (VT-6 alloy). Up to a beam energy of 6 keV, the ion spectrum is similar to the spectrum of the residual gas atmosphere. With an increase in the electron energy, ions of titanium and of its oxides are recorded in the spectrum. In this case, the signal amplitude of titanium oxide is higher than that of titanium. This fact is explained by the good sorption capacity of titanium, because of which the oxide film formed during the gas sorption from the atmosphere does not have enough time to evaporate.

Figure 4. Mass-to-charge spectrum of plasma ions during evaporation of titanium.
Further increase in the electron energy leads to the prevalence of titanium ions. It should be noted that the spectrum includes traces of all stable isotopes of titanium and its oxides. Also, at high beam energies, the spectrum registers a peak of aluminum ions, which is due to its small concentration in the titanium alloy (5.3 – 6.8%).

4. Conclusion
Modernization of the ion-optical system of quadrupole mass spectrometer based on the residual gas analyzer RGA makes it possible to investigate the mass-to-charge composition of the beam plasma generated by electron beam evaporation of refractory ceramic or metal targets in the forevacuum pressure range. The introduced changes of the electrodes design do not affect the functional capacities of the mass spectrometer. The mass spectra contain traces of ions of the target material and the residual gas atmosphere. Thus, the upgraded ion-optical system of the spectrometer makes it possible to monitor the mass-to-charge composition of the beam plasma during electron beam deposition of metal, ceramic, and cermet coatings.

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