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Abstract

Full Text

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EMISSION OF POSITIVE MOLECULAR IONS FROM HEATED SURFACES IN VACUUM

(Presented by Academician B. P. Konstantinov on 14 VI 1961)

To study, in strong electric fields, the surface ionization of atoms with high ionization potentials, the sensitivity of the ion detector in the mass-spectrometric apparatus used earlier (^{1}) was increased to $\sim 10^{-18}$ A/div by introducing a secondary-electron multiplier before the EMU-3 electrometric amplifier.

The mass spectrum of the background of positive thermionic emission from tungsten filaments was first investigated over a wide temperature range T, including low T, in the region in which a rather intense nonstationary emission of positive ions with mass number 101 had previously been found (^{2}). The present communication gives further information on the emission of molecular positive ions from tungsten filaments and from filaments made of other materials.

Figure 1 shows a diagram of the ion source. As usual, in order to obtain strong electric fields, the ion source was made in the form of a cylindrical capacitor with a thin filament H stretched along the axis of the cylinder (^{1}, ^{3}). The diameter of the filaments was from 18 to 50 μ. The power released when such filaments were heated was insufficient to heat the fittings of the source appreciably, which is important in this case. Cylinder $_2$ and the tube of the mass analyzer M-A were grounded; filament H was at a potential of +1300 V, while a potential of different magnitude and sign could be applied to cylinder $_1$. Through slits $_1$, $_2$, and $_3$, part of the ions formed on the filament entered the mass analyzer. To interpret the mass spectra, reference lines could be obtained by surface ionization on the filament of molecules of alkali-halide salts directed from evaporators $_1$ and $_2$. The resolving power of the mass analyzer was ~ 100.

Fig. 1. Diagram of the ion source

Fig. 2. Temperature dependence of the ion current of different masses.

Figure 2: Fig. 2. Temperature dependence of the ion current of different masses.

The apparatus was evacuated by a TsVL-100 oil-vapor pump (working oil D-1-A) and a VN-461 fore-vacuum pump (VM-4 oil). The TsVL-100 pump was connected to the apparatus through a liquid-nitrogen trap. All measurements were carried out at a residual-gas pressure of $(1 \div 2) \times 10^{-7}$ torr and with the trap filled with liquid nitrogen. The temperature of the filaments T, in the range from room temperature to temperatures measured with a pyrometer, was determined from the value of the resistance R, assuming a linear dependence of R on T (^{4}). For filaments that had not undergone preliminary cleaning by heat treatment; in this case a systematic error of $< 5\%$ toward overestimating the temperature could have been allowed, owing to lack of knowledge of the exact value of the monochromatic emissivity coefficient for such surfaces.

With a gradual increase in T of fresh, uncleaned tungsten filaments, starting from $T \simeq 400^{\circ}$ K, a positive-ion emission stable in time over many hours of continuous observation appeared, with mass numbers 59, 85, 96, 101, 102, 202, of which the line with $m = 101$ was the most intense.

Fig. 2. Temperature dependence of the ion current of different masses: 1—for $m = 101$ (102, 94, 96); 2—$m = 59$ (97, 83, 109); 3—$m = 81$ (84); 4—for $m = 73$ (60); 5—for $m = 85$ (86); 6—for CsCl

Heating the filament at $T \simeq 1100^{\circ}$ K led to a subsequent increase in the intensity of all mass lines by two to three orders of magnitude, i.e., activation of the surface occurred. The current density for $m = 101$ then reached $10^{-7} \div 10^{-8}$ A/cm^2. Prolonged exposure of cold activated filaments in the forevacuum and in air did not reduce their emission activity in high vacuum. Ions of practically all masses exhibit the "accumulation" noted in (2): the instantaneous value of the ion current after switching on the filament heating increases as the preliminary time for which the filament has been switched off is increased. However, in a vacuum of $(1 \div 2) \cdot 10^{-7}$ torr the accumulation reaches saturation within times of the order of several minutes, different for different mass lines (for example, 3 min for $m = 101$ and 10 min for $m = 59$).

When a trap with liquid nitrogen is heated and the pressure in the instrument is continuously increased, an increase in the intensity of the principal mass peaks is observed only in a certain interval of trap temperatures, when, apparently, evaporation of some organic substances occurs.

Mechanical cleaning of the surface of fresh filaments with fine emery paper, followed by thorough washing with solvents, leads to a sharp decrease in the ion emission. However, activation at $\sim 1100^{\circ}$ K at a pressure of $\sim 2 \cdot 10^{-7}$ torr restores the emission. Heating the filaments to $T \simeq 1500 \div 1600^{\circ}$ K leads to an irreversible loss of emission not only of the line with $m = 101$ (2), but also of all the other lines. After the surface deactivation that occurs in this case, only the intrinsic emission of atomic ions of alkali metals—impurities in tungsten—is observed. Deactivation of the filaments is always accompanied by an irreversible stepwise change in the radiative properties of the surface, which is manifested in a sharp change, at the deactivation temperature, in the course of the filament resistance as a function of the power expended on heating the filament.

The ion emission of deactivated tungsten filaments can again be restored by oxidation by heating in the forevacuum to dull-red heat. The spectrum of ion emission from tungsten surfaces prepared in this way is much richer than that of activated tungsten filaments, and the intensity of many lines in the spectrum becomes very considerable ($m = 59, 73, 81, 82, 83, 84, 85, 86, 94, 96, 97, 98, 101, 109, 116, 123, 125, 137$). Especially intense are the lines with mass numbers 84, 85, 101 (current density $j \simeq 10^{-7} \div 10^{-8}$ A/cm^2) and 59, 94, 109, and 123 ($j \simeq 10^{-8} \div 10^{-9}$ A/cm^2).

Figure 2 gives typical curves of the temperature dependences of ion currents from an oxidized tungsten filament for a number of mass lines. Some curves in Fig. 2 are similar to analogous ones for currents of surface ionization of atoms: for example, for $m = 81$ and 84, the dependences are the same as

and in the surface ionization of atoms with ionization potentials V_i smaller than the work function of the surface φ. For $m = 85$ and 86, the dependences are similar to those for surface ionization in the case $V_i > \varphi$ (^{3}). However, for most masses the temperature dependences of the ion current have a more complex character, which is probably connected with the presence of several competing processes occurring simultaneously on the surface. It should be noted that the nonstationarity of the emission of ions with mass 101, observed in work (^{2}) when the flash method was used, is only apparent and is associated with the character of the temperature dependence of the ion current of this mass.

In Fig. 2, for comparison, a curve is given for the surface ionization of CsCl molecules on an oxidized tungsten filament. It is seen that the temperature T at which ions of organic molecules and radicals appear differs little from the temperature T at which Cs$^+$ ions appear in the surface ionization of CsCl molecules. The measured ion currents of all mass lines appear in the temperature interval from 400 to 600° K. The intrinsic emission of impurity ions of alkali metals Na$^+$ and K$^+$ from the filaments was observed at significantly higher temperatures, $\sim$ 800°K. All the experimental facts on thermionic emission presented above give grounds for assuming that, on the surface of oxidized tungsten in the temperature interval from $\sim$ 400 to $\sim$ 1500°K, processes of catalytic dissociative ionization of organic molecules of compounds take place; these molecules probably are contained in pump oils or are products of their decomposition. The considerable values of the ionization coefficients found in the experiments indicate relatively small values of the electron affinity energy of the observed positive ions.

Fig. 3. Temperature dependence of the ion current for two values of the

Fig. 3

Figure 3: Fig. 3

electric-field strength: $E_1 = 2.3 \cdot 10^5$ V/cm —solid curves, $E_2 = 2.3 \cdot 10^6$ V/cm —dashed curves. 1 —$m = 101$; 2 —$m = 59$

If the concepts of surface ionization of atoms are applicable to the indicated ion emission, then, depending on the relation between the work function of the surface and the electron affinity of the positive ion, with an increase in the electric-field strength at the surface there will occur either a shift of the temperature thresholds of ionization without a noticeable increase in the ion current, or, conversely, an increase in the ion current without a noticeable shift of the ionization thresholds ([3]).

Figure 3 gives the temperature dependences of the current for masses 59 and 101 for two values of the strength of the electric field accelerating the ions at the surface: $E_1 = 2.3 \cdot 10^5$ V/cm and $E_2 = 2.3 \cdot 10^6$ V/cm. It is seen that, with an increase in the field strength, the temperature threshold of ionization shifts into the region of lower temperatures, while the magnitude of the current practically does not change.

Thermionic emission from nickel, iron, platinum, and gold-plated tungsten filaments was also investigated. A stable emission of ions with mass 101 was observed from nickel and iron, and no emission was found, except for ions of impurity alkali metals, from platinum and gold-plated filaments. For nickel and platinum, analogous results were obtained in work ([2]).

In conclusion we indicate the fields in which the thermionic emission considered above may be of importance:

1. Initiation of the initial conductivity of interelectrode vacuum gaps during vacuum breakdown ([5]). 2. The shot effect of ion emission from grids of electron tubes may serve as a source of noise in tubes.

surfaces (it is known that in tubes with gold-plated grids the noise is reduced). 3. Thermionic emission of charged organic molecules and radicals may be of significance for the mass spectrometry of organic compounds and for the study of physicochemical processes on the surface of solids.

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References

1. E. Ya. Zandberg, *ZhTF*, **30**, 1215 (1960).
2. E. I. Agishev, Yu. I. Belyakov, *ZhTF*, **30**, 223 (1960).
3. E. Ya. Zandberg, N. I. Ionov, *UFN*, **67**, 581 (1959).
4. E. Ya. Zandberg, *ZhTF*, **27**, 2583 (1957).
5. N. I. Ionov, *ZhTF*, **30**, 561 (1960).

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