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Physical processes in the Pirani type low vacuum sensor

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Auger electron spectroscopy and thermoresistive methods are used to study the physical processes leading to gas cooling of heated molybdenum filaments in a wide temperature range of 350−1300 K and pressures of $760-10^{-3}$ Torr, corresponding to the operating range of a Pirani-type vacuum sensor. Nitrogen was used as the gas. It is shown that nitrogen atoms chemisorbed on the surface do not contribute to gas cooling, which occurs only due to physisorbed N_2 molecules. In the intermediate vacuum region of $10^{-3}-1$ Torr, the heater is cooled due to the equilibrium between the flux of incident and thermally desorbed molecules, which is well described by the Hertz–Knudsen formula and first-order desorption with an activation energy of ~ 0.55 eV. On the contrary, at high pressures close to atmospheric, this cooling occurs due to the thermal desorption of gas molecules from an almost filled monolayer, which reduces its relative efficiency by many orders of magnitude.

Keywords: vacuum, adsorption, Pirani sensor, molybdenum, thermal desorption, nitrogen.

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Introduction

Measurement of low vacuum using a sensor proposed in 1903 by Marcelio Pirani [1] is a common technology widely used worldwide [2–4]. The sensor operation is based on the dependence of the resistance of the metal filament heated in vacuum on the pressure in the vacuum system. Despite the rather simple design, the physical processes occurring in the sensor are very uncommon and are still not fully understood, despite the large number of publications related mainly to the engineering side of the issue [5–8]. These processes description, even in international standards [2], respected textbooks [9], encyclopedias [10] and textbooks of leading engineering and physics universities [11] is full of errors and default shapes.

In fact, the thermal conductivity of gas does not depend on pressure, and the lower the gas pressure is, the more accurate this statement is [9]. Marcelio Pirani was the first to show that the sensor operation is determined precisely by the processes at the boundary between the surface of the metal filament and the gas, namely, the heat flux transferred from the filament to the gas depends on pressure; thus, the temperature of the filament also depends on the gas pressure under conditions of constancy of the power dissipated in it. This dependence has a monotonic, but strongly nonlinear character [2], the nature of which, according to modern concepts, does not follow from the ab initio of molecular kinetic theory or adsorption theory, and is described by introducing of an empirical parameter called „molecules accommodation coefficient“ [2,9].

The purpose of this work is to consider the processes occurring in the Pirani sensor from the point of view of modern concepts of surface science and the development of a physical picture of the ongoing processes.

1. Procedure and methods of experiment

The physical processes in the Pirani type sensor were studied using molybdenum as the heater material and nitrogen as the gaseous medium.

The experiments were carried out in two vacuum setups.

The first one is a UHV Auger spectrometer with a prism energy analyzer, described earlier in [12].

The experiments were carried out under ultrahigh vacuum conditions ($P \leq 1 \cdot 10^{-10}$ Torr) in a high resolution Auger spectrometer ($\Delta E/E \leq 0.1\%$) with a prism energy analyzer. Directly heated textured molybdenum ribbons $1 \times 0.02 \times 40$ mm, uniform in work function ($e\varphi = 4.45$ eV) were used as samples. The ribbons were cleaned by heating with alternating current to $T = 2200$ K in oxygen atmosphere ($P(O_2) \sim 10^{-5}$ Torr) and in ultrahigh vacuum. After cleaning, only Auger peaks of molybdenum were observed. During cleaning, the ribbons were textured, and a (100) face came to the surface. The ribbons temperature was measured: above 900 K — with an optical micropyrometer, and below 900 K — using extrapolation of the temperature dependence on the filament current of the ribbons. The temperature heterogeneity along the sample was less than 10 K over length of 40 mm.

The Auger signal of nitrogen with energy of 379 eV was used for measurements, the measurements were carried out in the peak-to-peak mode. At the same time, the Auger signal of molybdenum was measured at energy of 221 eV. The shape of the Auger signals of the adsorbate and substrate corresponded to the standards [13].

As the second experimental setup we used a vacuum laboratory bench based on an oil-free spiral fore vacuum pump, in which the experimental sample of low-vacuum Pirani-type sensor manufactured by „Technan LLC“ with a heater in the form of Mo-filament with a diameter of $150\,\mu$m was installed. The vacuum was measured by two vacuum gauges: VIT-2 with PMT4 sensor, which allows to measure pressure in the range of $0.1-10^{-3}$ Torr, and TYRACONT VSC43MV baratron, which allows absolute pressure measurement in the range of 760–0.1 Torr. The sensor was powered from a stabilized laboratory unit B5-47 with direct current. The bench had a needle leak, which allowed smoothly change of the nitrogen pressure in the chamber, and a port for a gas cylinder connection.

The temperature of molybdenum filaments for the entire range of pressures and temperatures was determined using the well-known formula $R_t = R_0(1 + \alpha t)$, where $\alpha = 4.7 \cdot 10^{-3}{}^\circ\mathrm{C}^{-1}$ [14]. In the region of pyrometric temperatures in high vacuum a micropyrometer was additionally used, and good agreement was obtained with the temperature determined by the above method. To accurately determine the resistance of the molybdenum filament a four-wire system was used, when the filament supply was „decoupled“ and the voltage drop across it was measured.

2. Results and discussion

To carry out the experiments, nitrogen with a purity of 10^{-6} was injected into the Auger spectrometer to a pressure of $3 \cdot 10^{-5}$ Torr at the substrate temperature of 300 K, and the intensities of the Auger signals of nitrogen and molybdenum were measured. No peaks other than those of nitrogen and molybdenum were observed. When the system was kept under these conditions for 100 s, which approximately corresponds to an adsorption dose of about 3000 L (in Langmuirs), saturation was achieved on the surface: the Auger signals of nitrogen and molybdenum remained constant, and did not change during further holding in nitrogen. After that, nitrogen was pumped out, and the dependence of both Auger signals on temperature was measured.

The measurement results are shown in Fig. 1. It can be seen that adsorbed nitrogen is present on the surface at room temperature. Even a very slight heating up to ~ 400 K leads to the removal of a part of nitrogen from the surface: the intensity of the Auger signal of nitrogen drops by almost two times, while the Auger signal of molybdenum increases by ~ 1.2 times, indicating that part of the nitrogen leaves the surface, apparently due to thermal desorption. After that, a thermally stable coating remains on the surface: the Auger signals of the adsorbate and the substrate practically do not change up to 1000 K, after which they begin to decrease. At $T = 1400$ K the Auger signal of nitrogen is lost in the noise, and the value of the Auger signal of molybdenum reaches the „plateau“ corresponding to the clean surface of molybdenum. This indicates that the surface is practically free of adsorbed nitrogen.

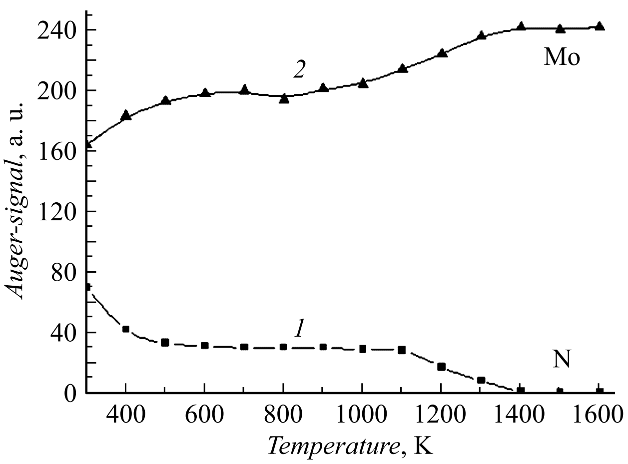

Figure 1. Change in Auger signals of nitrogen (*1*) and molybdenum (*2*) during heating of molybdenum ribbon in ultra-high vacuum after nitrogen adsorption at room temperature at $P = 1 \cdot 10^{-5}$ Torr for 100 s.

Apparently, in accordance with the materials presented in [15], we can assume that at higher temperatures region a layer of chemisorbed atomic nitrogen is formed on the surface, which does not participate in the adsorption-desorption equilibrium at low T. On the contrary, in the temperature range 300–400 K, weakly bound nitrogen is found on the surface, which is easily removed from the surface.

Fig. 2, *a* shows the dependence of the molybdenum filament resistance on the filament current under vacuum $(10^{-3}-10^{-8})$ Torr (curve *1*) and at nitrogen atmospheric pressure in the chamber (curve *2*). It can be seen that the curves differ greatly — nitrogen noticeably cools the filament, the resistance and the temperature decrease. Using the dependence $R_t = R_0(1 + \alpha t)$, one can determine the filament temperature. For example, at $I = 2.2$ A nitrogen at atmospheric pressure (760 Torr) reduces the filament temperature by more than 700°C.

It is convenient to represent Fig. 2, *a* as a dependence of R_1/R_2 on the filament current, where R_1 — filament resistance in vacuum, and R_2 — in nitrogen atmosphere (Fig. 2, *b*). It can be seen that the curve has a maximum at $I = 1.2$ A, corresponding to $R_1/R_2 = 2.5$. For $I > 1.2$ A, the ratio R_1/R_2 decreases and, in principle, theoretically tends to 1 when the filament temperature (radiated power) is so high that the effect of nitrogen cooling sharply decreases. Obviously, the filament resistance and temperature will depend significantly on the nitrogen pressure in the chamber.

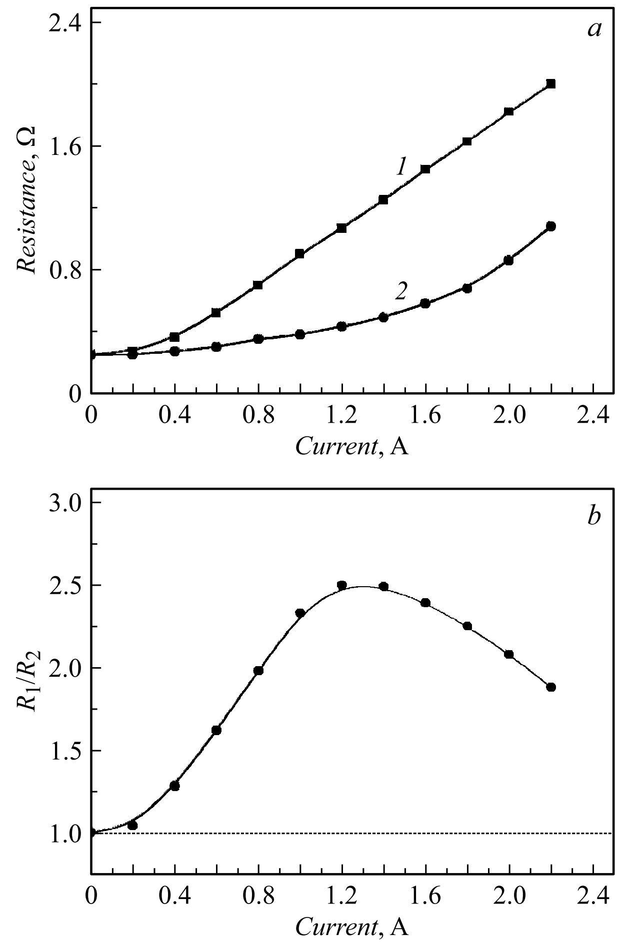

Figure 2. *a* — change in resistance of molybdenum filament with diameter of 150 μm and length of 84 mm as function of the current through the filament. Chamber pressure (Torr): *1* — 10^{-3}; *2* — 760 (atmosphere); *b* — dependence of R_1/R_2 on the current through filament with diameter of 150 μm and length of 84 mm; R_1 — filament resistance at pressure 10^{-3} Torr; R_2 — filament resistance at atmospheric pressure 760 Torr.

Fig. 3 shows the change in the filament temperature as function of the nitrogen pressure in the chamber at filament current $I = 0.8$ A. Experience shown that at $P < 10^{-3}$ Torr the temperature is constant, and in the region $P = 10^{-3}$–760 Torr it decreases from 470 to 90°C.

Let us analyze the results of the experiments presented in Fig. 3. It is known that N_2 molecules can be in two ground states: at medium temperatures the adsorption of N_2 is dissociative — the molecules fragment, the atoms occupy centers with a strong bond with a binding energy ~ 3 eV on molybdenum and 3–4 eV on other metals (Re, W, Fe) [16]. The concentration N of such centers is close to the concentration of surface metal atoms; for example, for the face (100)Mo $N \approx 10^{15}\,\mathrm{cm}^{-2}$, and the probable location of the atom — „pits" between four metal atoms, as this was also observed for other gases, for example, oxygen on the face (100)W [16,17]. At low temperatures and even more at high pressures $P \approx 10$–760 Torr, all strongly bound sites should be occupied by nitrogen atoms, and now the adsorption of molecular nitrogen will have a physisorption nature. Indeed, for molybdenum and other metals the binding energy of nitrogen N_2 with the surface is ~ 0.5 eV [16], and the concentration of such weakly bound sites is apparently also close to $N \approx 10^{15}\,\mathrm{cm}^{-2}$.

Let us discuss the physical picture of the processes on the surface of a molybdenum filament in contact with gas (N_2). It is known that the density of the gas flow to the surface ν is determined by the expression [9]:

$$\nu = P(2m\pi kT)^{-1/2}, \tag{1}$$

where m — mass of gas molecule, k — Boltzmann constant, P — gas pressure.

For example, for gas pressure $P = 10^{-3}$ Torr and $T = 300$ K $\nu = 2.2 \cdot 10^{17}\,\mathrm{cm}^{-2}s^{-1}$. Then for the filament temperature $T = 743$ K and $P = 10^{-3}$ Torr (Fig. 2) under equilibrium conditions, the surface concentration of nitrogen atoms located on strongly bound sites will be equal to [16]:

$$N = \nu\tau = \nu\tau_0 \exp(E_1/kT). \tag{2}$$

If we set $\tau_0 = 10^{-13}$ s and $E_1 = 3$ eV, then the nitrogen concentration on the surface is $N \gg 10^{15}\,\mathrm{cm}^{-2}$, i.e. all strongly bound sites are reliably occupied by nitrogen, and further decrease in temperature with nitrogen pressure increasing in the chamber will be determined by molecular adsorption on weakly bound centers only. It is easy to calculate that a noticeable desorption of nitrogen from strongly bound sites will be observed at temperatures above 1100 K, when the lifetime of the nitrogen atom in the chemisorbed state will be less than 1 s (Fig. 1).

It is also seen from Fig. 3 that at pressure $P \geq 1$ Torr the temperature of the filament stops to change and reaches 90°C, despite significant pressure increasing up to atmospheric $P = 760$ Torr. It is reasonable to assume that under these conditions, the maximum concentration of N_2

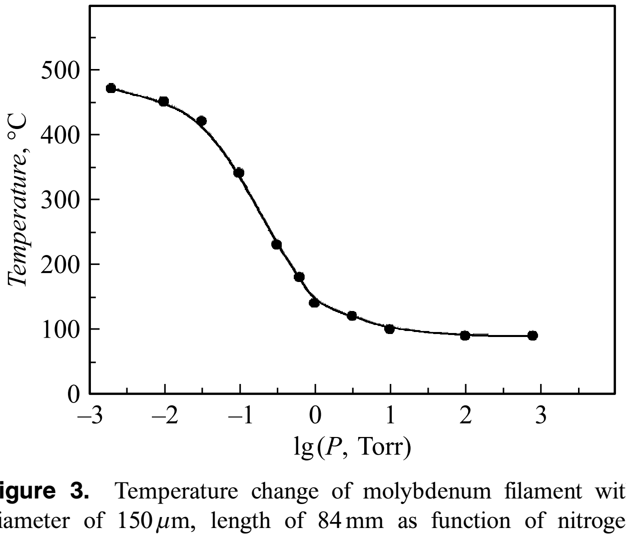

Figure 3. Temperature change of molybdenum filament with diameter of 150 μm, length of 84 mm as function of nitrogen pressure in the chamber in the coordinates lg(P [Torr]). Current through filament — 0.8 A.

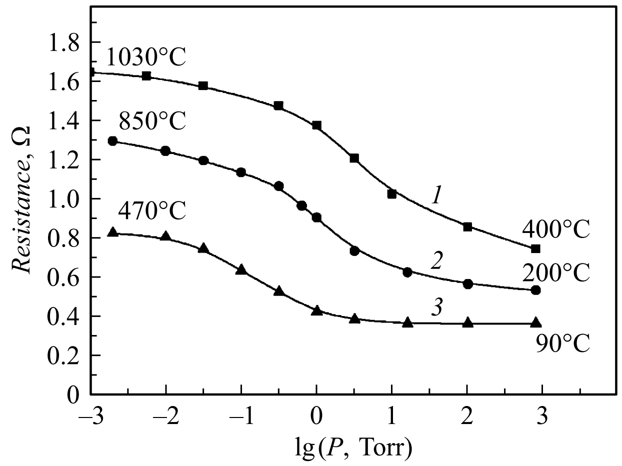

Figure 4. Change in resistance of molybdenum filament with diameter of 150 μm and length of 84 mm as function of the (decimal) logarithm of nitrogen pressure in the chamber. Current through filament (A): *1* — 1.7; *2* — 1.4; *3* — 0.8.

molecules weakly bound to the surface is reached on it, and now the heat loss from the filament is determined not by the external gas flow to the surface, as happens at low pressures (below 10^{-1} Torr), but by the flow of N_2 molecules thermally desorbed from the surface of the molybdenum filament. In the considered case, the flux density from the surface is $\nu_s = N/\tau$, where $\tau = \tau_0 \exp(E_2/kT)$, E_2 — energy of N_2 molecules binding with molybdenum when all strongly bound sites are occupied by nitrogen atoms. Note that the majority of N_2 molecules arriving at the surface no longer participate in heat transfer (nitrogen N_2 on nitrogen).

If we assume that, for example, for $P = 1$ Torr, the maximum concentration of nitrogen molecules on the surface is $N \approx 10^{15}\,\mathrm{cm}^{-2}$, $T = 140°\mathrm{C}$ (Fig. 3), then under the equilibrium conditions $\nu = \nu_s = N/\tau$ under the assumption $\tau_0 = 10^{-13}$ s we can determine $E_2 = 0.5$ eV, which perfectly matches the published data for the system N_2-molybdenum. Processing curves of the type presented in Fig. 3 for different filament currents, we obtained the value $E_2 = 0.55 \pm 0.05$ eV.

Fig. 4 shows the dependences of the molybdenum filament resistance on the nitrogen pressure in the chamber for different filament currents — different power consumption $W_1 = IU = I^2R$. It can be seen that for $I \geq 1.4$ A the „plateau"observed for $I = 0.8$ A (curve *3*) is no longer observed. In this case, the dissipated power W_1 on the filament does not allow to reach low temperatures and the maximum possible concentration of nitrogen N_2 (Fig. 4). Under these conditions, the molybdenum filament can work as pressure sensor in the range of 10^{-3}–760 Torr.

Fig. 5 shows the calculated dependence of the concentration of surface nitrogen N_2 in a weakly bound state on the gas pressure in the chamber for two cases: $I = 0.8$ and 1.7 A; the nitrogen desorption energy was assumed to be $E_2 = 0.55$ eV. It can be seen that in the case of $I = 1.7$ A, the maximum coverage is achieved only at $P = 760$ Torr.

Fig. 6 shows the dependence of the power $W_1 = I^2R$ for the case $I = 0.8$ A on the gas pressure in the chamber (curve *1*) and the calculated curve *2* for the power „carried away" by nitrogen. The flux ν_s of nitrogen molecules was determined by formula (1) taking into account the real area s of the filament surface $s = \pi dl = 0.4\,\mathrm{cm}^2$, where d — filament diameter (150 μm), l — its length (84 mm). For example, for the case $P = 1$ Torr, the real flux of nitrogen molecules is $\nu_s = 8.8 \cdot 10^{19}\,\mathrm{s}^{-1}$. If we assume that each N_2 molecule „carries away" energy $E_1 = kT$ from the filament surface, then the power „carried away" by nitrogen will be equal to $W_2 = \nu_s E_1$.

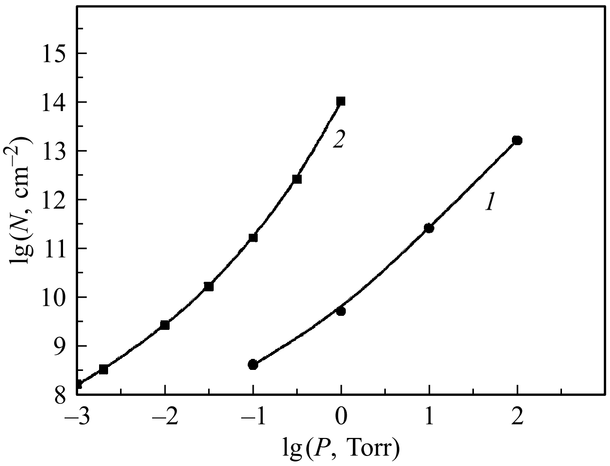

Figure 5. Calculated change in nitrogen coating lg(N) for molybdenum filament with diameter of 150 μm and length of 84 mm depending on nitrogen pressure in chamber lg(P [Torr]). Current through filament (A): *1* — 1.7; *2* — 0.8.

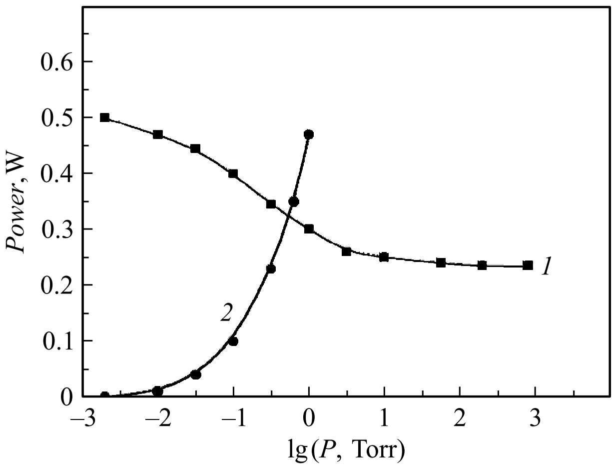

Figure 6. *1* — change in the power released on molybdenum filament with diameter of 150 μm and length of 84 mm depending on the air pressure in the chamber lg(P [Torr]). Current through the filament is 0.8 A. *2* — calculated value of gas flow power from the surface from lg(P [Torr]).

For the case $I = 0.8\,\mathrm{A}$, Fig. 6 (curve *2*) shows the dependence W_2 on the gas pressure considering the filament temperature (Fig. 3). It can be seen that for $P < 10^{-3}$ Torr $W_2 \ll W_1$, the molybdenum filament also cannot be used as a pressure sensor. At $P > 10^{-3}$ Torr W_2 becomes comparable to the value of W_1, which leads to a change in temperature (resistance) of the filament.

Note once again that at $P > 1$ Torr the filament cooling mechanism changes — the power „carried away" is now determined by the nitrogen flow ν_s from the surface (the lifetime of nitrogen on the surface). It is also clear that there is a region of transfer from one cooling mechanism to another, depending on the gas pressure and the filament temperature.

Obviously, the operation of Pirani-type pressure sensor most often occurs in air, which is a mixture of various gases. Therefore, it was interesting and important to repeat the experiments under conditions when air will be replaced in the chamber by nitrogen. It is known that the main contribution to the composition of atmospheric air is made by nitrogen ($\sim 78\%$). As expected, the results obtained almost completely coincided with the experiments when pure nitrogen was injected into the chamber. The gas with second concentration in the air is oxygen, which on metals is close to nitrogen in terms of adsorption-desorption properties [17,18]. The remaining impurity gases, apparently, do not make any significant contribution to the physics of the operation processes of the Pirani-type sensor.

Conclusion

The physical picture is reviewed during the interaction of the heated metal (filament) with gas (nitrogen, air), which leads to a change in the filament resistance, its temperature depending on the gas pressure in the chamber.

In the case of nitrogen, there are several mechanisms of heat „loss" from the heated sample. At low pressures ($1-10^{-3}$ Torr) the heat „loss" is determined by the gas flow from outside to the surface. At pressures greater than 1 Torr, nitrogen can occupy not only strongly bound sites ($E \approx 3\,\mathrm{eV}$), but also occupy all weakly bound sites ($E \approx 0.5\,\mathrm{eV}$). In this case the heat „loss" is determined by the lifetime of nitrogen N_2 molecules on the surface.

Conflict of interest

The authors declare that they have no conflict of interest.

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