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Current-voltage characteristic of the thermal ion emission of Na from the Na$_x$Au surface

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In a high-vacuum diode, the volt-ampere characteristic of the thermionic emission of Na$^+$ with surface of Na$_x$Au intermetallide. Its hysteresis was found, which is associated with changes in the surface Na$_x$Au caused by the action of an external electric field. In accordance with the Schottky effect, analysis of the current-voltage characteristic and the value of the work function of the Na$_x$Au surface was estimated. Suggested mechanism of thermionic emission of Na$^+$ from the surface of Na$_x$Au.

Keywords: intermetallic compound, thermal ionization, Schottky effect.

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Dependence $\alpha(T)$ of the degree of ionization of particles desorbing from heated metals on the temperature of a solid body follows the Saha–Langmuir equation

$$\alpha(T) = \nu^+/\nu^0 = A\exp\left[\left(\varphi - \varepsilon_i + e(eE)^{1/2}\right)/kT_{em}\right], \quad (1)$$

which holds true under the condition of thermal and charge equilibrium between adsorbed particles and a solid body [1]. Here, ν^+ and ν^0 are the fluxes of particles desorbing in charged and neutral states, respectively; φ is the work function of the surface; ε_i is the ionization energy of the particle; T_{em} is the temperature of a solid body; E is the electricfield (EF) strength; A is the ratio of complete partition functions for charged and neutral states of desorbing particles; and k is the Boltzmann constant. The results of experimental studies of thermal ionization (TI) with metallic (W, Mo, Pt, Ir, Re, Ni), semiconductor (Si), and oxide (W, Mo, Ni, oxides) emitters confirmed that thermal equilibrium is established between desorbing particles and the surface and that the Saha–Langmuir equation holds true [1,2].

Thermionic Na$_x$Au emitters have demonstrated a degree of ionization of organic compounds comparable to the one characterizing the most efficient emitters known [3]. According to (1), this is possible only at high values of φ [2]. Record-high estimates of φ were obtained in the study of TI of hexamethylenetetramine molecules on Na$_x$Au: $\varphi \sim 7.6-7.9$ eV [4]. However, thermal equilibrium between desorbing particles and the emitter is not established in TI of hexamethylenetetramine, making Eq. (1) inapplicable. High α values in TI of organic compounds on Na$_x$Au may be induced by non-equilibrium processes due to reactions between coadsorbed particles [4]. The determination of φ in accordance with (1) for TI of atoms is made difficult by their dissolution in Na$_x$Au [5]. The estimate of φ obtained using the contact potential difference method in the process of Na$_x$Au coating formation is ~ 5.1 eV [5]; i.e., the φ value of Na$_x$Au is insufficient for efficient TI of organic compounds at operating Na$_x$Au emitter temperatures $T_{em} < 1200$ K [2–4]. According to (1), the ratio of α on Na$_x$Au with $\varphi = 5.1$ eV to α on W oxide with $\varphi = 6.8$ eV [2] at $T_{em} \sim 1000$ K should be much lower than 10^{-8}. This contradicts the results reported in [3,4].

The distribution of Na ions desorbing from a Na$_x$Au surface over the initial energy was found to correspond to a Maxwellian one, but distribution temperature T_{M} was significantly (by a factor up to 2) higher than T_{em} [6]. The value of T_{M} at $T_{em} =$ const depended exponentially on the cube root of E, while T_{M} for the emitters studied earlier was independent of E [1,2]. Dependence $\alpha(E)$ (the so-called Schottky effect) follows from (1) [1,2,7,8]. In accordance with it, ion current i at $E < 10^7$ V/cm an a constant particle flux to the surface is written as

$$i = \mathrm{const}\exp\left[\left(e(eE)^{1/2}\right)/kT_{em}\right]. \quad (2)$$

The Schottky effect is related to the impact of the external EF on separation of a charge (ion) from the surface [1,2,7,8]. This provides an opportunity to examine the specifics of ion emission from a Na$_x$Au surface with no allowance being made for the probable non-equilibrium nature of processes inducing ion desorption and for the dissolution of particles in the emitter. Since the Schottky effect for Na$_x$Au has not been investigated earlier, the present study was aimed at examining the current-voltage characteristics (*I-V*) of Na ion emission from a Na$_x$Au surface.

(*I-V*) measurements were performed in a high-vacuum diode with its cathode being a 2.5-mm-wide gold ribbon coated with Na$_x$Au in accordance with the procedure detailed in [3–6]. A metal plate with a width of 20 mm and a gold layer deposited onto it was the anode, which was positioned 8 mm away from the ribbon. The pressure in the diode was $< 1 \cdot 10^{-7}$ Torr. A flux of Na atoms with a density of $10^{12}\,\mathrm{s}^{-1} \cdot \mathrm{cm}^{-2}$ was deposited onto the

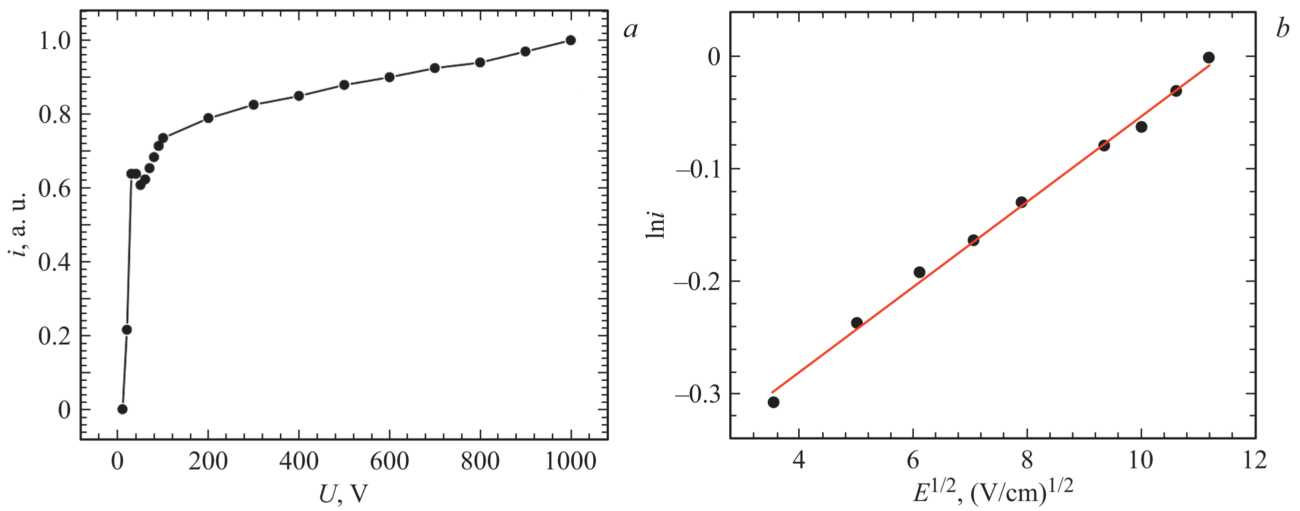

Figure 1. *a* — Current-voltage characteristic for the current of Na ions from the Na_xAu surface; *b* — dependence of the current of Na ions on the strength of the electric field at the Na_xAu surface at $U > 100$ V.

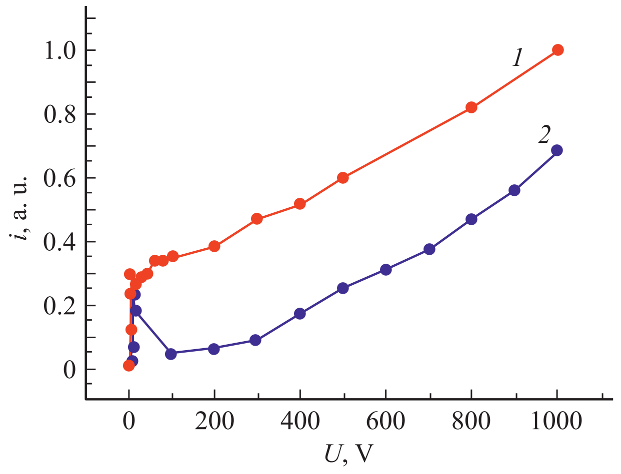

Figure 2. Current-voltage characteristic for the current of Na ions from the Na_xAu surface under increasing (*1*) and decreasing (*2*) voltage.

ribbon heated to 1000 K. The working volume was filled with oxygen to a pressure of $1 \cdot 10^{-6}$ Torr in order to clean the surface of organic contaminants [3–5]. The current of Na ions in the diode was measured as a function of voltage across the electrodes.

Figure 1, *a* shows an example *I-V* curve for Na^+ current *i* under voltage *U* across the electrodes increasing from 0 to 1000 V. This voltage adjustment corresponded to an EF strength at the surface varying from 0 to 125 V/cm. The shape of the dependence corresponds to the one for metals with a nonuniform surface and Eq. (1) at $\varepsilon_i > \varphi$ [1]. Figure 1, *b* presents dependence of Na^+ current $\ln i$ on $E^{1/2}$ in the diode at $U > 100$ V ($E > 12.5$ V/cm). It corresponds to Eq. (2) (normal Schottky effect [1]). At $U < 100$ V, the Na ion current is lower than the one derived from Eq. (2) (anomalous Schottky effect [1]). Strength E_0 at which the anomalous Schottky effect switches to a normal one is $E_0 = 10^3{-}10^4$ V/cm for metals and $E_0 = 10{-}10^2$ V/cm for semiconductors [1,7,8]. This transition is associated with the influence of the contact field of surface patches with different φ values on the resulting EF at the emitter surface [1,7,8]. It follows from Fig. 1 that $E_0 \sim 10$ V/cm. This E_0 values corresponds to semiconductor emitters [7]. The agreement between the measured *I-V* curve and the one determined earlier for emitters with $\varphi < \varepsilon_i$ [1] suggests that the same condition ($\varphi < \varepsilon_i = 5.14$ eV) is satisfied for Na_xAu. This estimate agrees with the φ assessment obtained using the contact potential difference method in the process of Na_xAu coating deposition.

Figure 2 shows the *I-V* for the Na ion current in the diode under increasing (i_1) and decreasing (i_2) voltage measured after the emitter was exposed to $E = 125$ V/cm for several hours. It can be seen that current i_1 is higher than i_2, and dependence $i(U)$ forms a hysteresis. When *U* drops below 100 V, ratio i_1/i_2 of Na currents decreases, but the initial Na ion current value is restored after the emitter is exposed to $E = 0$ V/cm.

In the process of exposure in a field with $E = 125$ V/cm, cations Na^+ [9] and, possibly, holes move to the surface of the Na_xAu layer, thus producing a positively charged layer on the surface. This leads to a decrease φ of the surface [1] and, consequently, induces a reduction in the Na ion current (see Fig. 2). When the emitter is exposed at $E = 0$ V/cm, the initial charge distribution restores. This is the reason why the *I-V* of sodium ion emission from Na_xAu is markedly hysteresis.

Calculations of the electron structure of Na_xAu [10–15] shows that Au atoms act as anions, while Na atoms are cations. The electron-density excess (near Au) and deficiency (near Na) depend on the concentration of Na atoms in the intermetallic compound. The external EF, which pulls positive ions from the surface, raises the concentration of

Na^+ cations in the surface Na_xAu layer, thus increasing the Na^+ cation charge in the surface layer [9]. Sodium atoms are adsorbed on Na_xAu in a neutral state (this is confirmed by their short lifetime on the surface [9]). The interaction of sodium with a sodium cation of the Na_xAu surface may result in transfer of an electron from a Na atom to a Na cation with subsequent charge exchange in neutralization by a hole or electron escape into Na_xAu. Several closely spaced Na ions repel each other. Depending on the position of a sodium atom on the surface relative to surface cations and anions, the produced Na ion either desorbs from the surface or diffuses into Na_xAu, combining with an anion. In the case of desorption, the conversion of an adsorbed atom to an ion and its transfer to the repulsion curve violate thermal equilibrium between desorbing ions and the emitter; consequently, $T_{\mathrm{M}} \gg T_{em}$. The increase in concentration of Na cations on the Na_xAu surface and, consequently, in their charge in stronger fields E translates into strengthening of the repulsive force acting between a Na ion and a Na surface cation. This explains the $T_{\mathrm{M}}(E)$ dependence.

The volt–ampere characteristic of sodium ion emission from Na_xAu has a well-marked hysteresis related to a change in the concentration of Na cations on the surface under the influence of an EF. The agreement between the I-V for Na^+ ion emission from Na_xAu and I-V observed for metals and semiconductors gives reason to believe that the surface work function is definitely below 5.14 eV. The desorption of ions from Na_xAu is induced by the transition of adsorbed particles into an ionic state and the Coulomb repulsion of like-sign charges: Na^+ ions and Na_xAu surface cations, the charge of which depends on the external EF strength. This leads to a nonthermal distribution of desorbing ions over initial energy $T_{\mathrm{M}} \gg T_{em}$ and to a dependence of this distribution on the EF strength $(T_{\mathrm{M}}(E))$. This mechanism of TI on Na_xAu cannot be characterized by the Saha–Langmuir equation and the concepts developed for metal and oxide emitters.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] E.Ya. Zandberg, N.I. Ionov, *Surface ionization* (Jerusalem, 1971).
[2] U.Kh. Rasulev, E.Ya. Zandberg, Prog. Surf. Sci., **28** (3-4), 181 (1988). DOI: 10.1016/0079-6816(88)90003-2
[3] M.V. Knatko, M.N. Lapushkin, Rapid Commun. Mass Spectrom., **35** (17), e9144 (2021). DOI: 10.1002/rcm.9144
[4] M.V. Knatko, M.N. Lapushkin, Tech. Phys., **92** (3), 397 (2022). DOI: 10.21883/TP.2022.03.53271.236-21.
[5] M.V. Knatko, V.I. Paleev, E.Ya. Zandberg, Phys. Low-Dim. Struct., N 7/8, 27 (1996).
[6] M.V. Knat'ko, M.N. Lapushkin, Fiz.-Khim. Aspekty Izuch. Klasterov, Nanostrukt. Nanomater., No. 10, 352 (2018) (in Russian). DOI: 10.26456/pcascnn/2018.10.352
[7] L.N. Dobretsov, M.V. Gomoyunova, *Emissionnaya elektronika* (Nauka, M., 1966), pp. 154–160, 180–195 (in Russian).
[8] L.K. Hansen, J. Appl. Phys., **37** (12), 4498 (1966). DOI: 10.1063/1.1708068
[9] M.V. Knat'ko, M.N. Lapushkin, V.I. Paleev, Tech. Phys., **50** (4), 498 (2005). DOI: 10.1134/1.1901791.
[10] G.H. Grosch, K.-J. Range, J. Alloys Compd., **233** (1), 30 (1996). DOI: 10.1016/0925-8388(96)80030-2
[11] G.H. Grosch, K.-J. Range, J. Alloys Compd., **233** (1), 39 (1996). DOI: 10.1016/0925-8388(96)80031-4
[12] C. Xiao, L.L. Wang, R.V. Maligal-Ganesh, V. Smetana, H. Walen, P.A. Thiel, G.J. Miller, D.D. Johnson, W. Huang, J. Am. Chem. Soc., **135** (26), 9592 (2013). DOI: 10.1021/ja403175c
[13] C. Koenig, N.E. Christensen, J. Kollar, Phys. Rev. B, **29** (12), 6481 (1984). DOI: 10.1103/PhysRevB.29.6481
[14] R.E. Watson, M. Weinert, Phys. Rev. B, **49** (11), 7148 (1994). DOI: 10.1103/PhysRevB.49.7148
[15] X. Du, H. Lou, J. Wang, G. Yang, Phys. Chem. Chem. Phys., **23** (11), 6455 (2021). DOI: 10.1039/D0CP06191C