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Collective processes in thermal ionization on the surface of $NaAu_x$ intermetallic compound

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A mechanism is proposed for the decomposition of molecular clusters of diethylamine $(C_2H_5)_2NH$ on the surface of the $NaAu_x$ intermetallic compound with the formation of decomposition products desorbed from the surface, including in the form of ions with m/z from 58 to 197, during heating of the intermetallic compound at a rate of 20 K/s. Exposure of the $NaAu_x$ surface at a temperature of 320 K in diethylamine vapor leads to the formation of molecular clusters on it. Rapid heating of $NaAu_x$ at a rate of 20 K/s leads to the decay of clusters, desorption, and ionization of the decay products due to the redistribution of internal energy over the degrees of freedom of the cluster. The study of thermal ionization processes during heating of $NaAu_x$ at a rate of 20 K/s in the temperature range from 600 to 1000 K made it possible to establish that the surface stoichiometry during heating is quasi-stationary, dehydrogenation and ionization of individual diethylamine molecules occur under equilibrium conditions, while for compounds formed in the process of cluster decay, the conditions are not equilibrium.

Keywords: thermal ionization, diethylamine, intermetallics, sodium, gold.

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Introduction

Studies of thermal ionization (TI) of atoms and molecules on the surface of heated metals and their oxides made it possible to create a consistent theory of the process of desorption of adsorbed particles in the form of ions [1,2]. The practical application of the TI phenomenon was ionization sources for mass spectrometry of organic molecules [2–12], for isotope analysis [13–18] and highly sensitive selective air detectors of organic compounds [19–26]. The study of the TI process on emitters made of refractory metals and their oxides made it possible to use TI both as a method for studying the surface of a solid body and processes in the adsorbed layer, and for determining the characteristics of adsorbed compounds [2–4].

TI studies are carried out mainly under equilibrium conditions, when at given values of the temperature of the solid body (T), particles flow to the surface (ν), and electric field strength at the surface (ε) a constant concentration is set of each the type of adsorbed particles that are desorbed in charged (ν_i^+) and neutral (ν_i^0) forms. The value T must exceed the threshold temperature T_0, at which the concentration of the substance adsorbed on the surface changes the emission characteristics of the surface so that TI stops [1,2]. The ratio of flows of desorbed charged and neutral particles of each type under the condition of thermal and charge equilibrium of adsorbed particles with solid body is determined by their ionization efficiency $(\alpha_i(T))$, which can be written in accordance with [4] as

$$\alpha_i(T) = \frac{\nu_i^+}{\nu_i^0} = A_i \exp\left(\frac{1}{kT}\left(\varphi - E_i + e(e\mathscr{E})^{1/2}\right)\right), \qquad (1)$$

where e is electron charge, φ is work function, E_i is ionization energy of i-particles, A_i is the ratio of total statistical sums for charged and neutral i-particle, k is the Boltzmann's constant.

The TI study of organic compounds on emitters made of metals and their oxides showed that the TI mass spectra are mainly composed of ions of products of dehydrogenation and decay of adsorbed organic compounds [2,4]. At the same time, the TI mass spectra of the studied organic compounds on emitters coated with $NaAu_x$ intermetallic compound (where x is not necessarily integer) differ in the presence of peaks corresponding to both decay reactions and reactions of synthesis of new compounds on the surface [5]. For example, the TI mass spectrum of tetramethyltetrazene $(CH_3)_2NN{=}NN(CH_3)_2$ on tungsten oxide WO_x contains only one primary peak [4,6], while on the surface of $NaAu_x$ there are many primary peaks corresponding to ions with the mass both less and more M up to $2M$, where N is the molecular mass of adsorbed molecules [5]. Studies of the TI of tetramethyltetrazene on $NaAu_x$ carried out in the paper [7] showed that the complex form of the mass spectrum is associated with the formation of new compounds on the surface as a result of tetramethyltetrazene adsorption, these compounds are thermally ionized. These new compounds are formed due to the dissociative adsorption of tetramethyltetrazene on $NaAu_x$, which results in the appearance of long-lived radicals on the surface. These radicals interact with each other, creating new compounds on the surface.

To confirm the role of synthesis reactions in the adsorbate layer in the formation of the mass spectrum of thermal ionization on $NaAu_x$, studies of the TI of diethylamine $(C_2H_5)_2NH$ (DEA) were made. The choice of DEA was due to the fact that the TI of amines, including DEA, was studied in detail [2,4], which made it possible to compare the mechanisms of ions formation for different emitter materials. For emitters coated with $NaAu_x$ we studied the effect of temperature, partial pressures of oxygen, DEA, and the flow of sodium atoms on the surface [8] on the formation of the mass spectrum of diethylamine TI. These studies showed that the composition of the mass spectrum of diethylamine TI on $NaAu_x$, as in the case of tetramethyltetrazene, is mainly determined by reactions in the adsorbed layer between co-adsorbed DEA molecules, as well as between DEA molecules and their decay products.

When organic compounds are adsorbed due to decay and synthesis reactions, i-types of new compounds can be formed on the surface, each of which is desorbed in charged ν_i^+ and neutral ν_i^0 form. For equilibrium conditions, as in [4], one can write

$$\nu_i = \gamma_i(\nu, T, \mathscr{E})\nu,$$

$$\nu_i = \nu_i^+ + \nu_i^0, \qquad (2)$$

where $\gamma_i(\nu, T, \mathscr{E})$ is individual coefficient for i-compounds, depending on the interacting pair adsorbed compound-emitter that reflects the reactions in the adsorbed layer leading to the formation of i-compounds.

While the efficiency of (M−H) and $(M-CH_3)$ ionization during diethylamine TI on emitters made of $NaAu_x$ and oxidized W practically coincides and amounts to 0.3 A/(cm^2·Torr), the dependencies $\gamma_i(\nu, T, \mathscr{E})$ differ [5,8]. For the reaction of amine dehydrogenation during TI on tungsten oxides (WO_x), the value γ_i was often taken close to 1 [9]. The value γ_i of the products of exchange reactions between co-adsorbed molecules on tungsten oxides (WO_x) was determined mainly by the probability of meeting the co-adsorbed compounds and was proportional to the square of pressure [10]. During diethylamine TI on $NaAu_x$, the value γ_i corresponding to the products of reactions between co-adsorbed compounds did not have a quadratic dependence on pressure, which gave grounds to conclude that the exchange and synthesis reactions occur in separate areas of the surface [8]. The temperature dependences of the ionic currents of the products formed as a result of reactions between co-adsorbed diethylamine molecules during the diethylamine TI on $NaAu_x$ are close to each other. Considering the difference and influence on the shape of the temperature dependences of the current of ions of the ionization energy E_i and the energy of ionizable products formation in [8], it was concluded that formula (1) is not fully applicable for TI on $NaAu_x$.

Paper [11] studied the TI mechanism on $NaAu_x$ of urotropine ($C_6H_{12}N_4$), which has a spatial structure in the form of an irregular decahedron, and it was concluded that the theory of organic compounds TI, presented in the review [2], does not give a complete description of TI for the $NaAu_x$ intermetallic compound, and ionization efficiency and temperature dependences of the ion current during TI on $NaAu_x$ are largely determined by the features of activation and deactivation of complexes adsorbed particle-surface.

To determine the reasons of feature of organic compounds TI on the surface of intermetallic compound, it is necessary to separate the influence of the variable parameters $\nu, T, \mathscr{E}$ on the ionization efficiency a from their influence on the reactions on the surface leading to the desorption of ionizing products. However, it is not possible to do this under equilibrium conditions of TI. Studies of the kinetic parameters of desorption and reactions on the surface are carried out under nonequilibrium conditions of TI, when change in one of the TI parameters i.e. $\nu, \mathscr{E}$ and T leads to a violation of the equilibrium conditions on the surface, namely to the formation of nonequilibrium concentration of adsorbed particles. This occurs when the time, during which one of the parameters $\nu, \mathscr{E}$ and T changes, is less than the time of transient processes on the surface leading to equilibrium conditions. Determining the kinetics of changes in the ion current during these transient processes makes it possible to obtain information on the kinetic parameters of particles desorption and reactions on the surface, as well as on their activation energy [27]. The change with time of the adsorbed particles concentration N in this case can be determined by the equation [27]:

$$\frac{dN}{dt} = \nu - K(\nu, \mathscr{E}, T)N(t), \qquad (3)$$

where $K(\nu, \mathscr{E}, T)$ is the sum of the rate constants of all processes on the surface that affect the concentration of the adsorbed substance. When i-products are formed on the surface, the change with time in the concentration of the i-product N_i under nonequilibrium conditions, taking into account equation (2), can be determined as

$$\frac{dN_i}{dt} = \gamma_i(\nu, T, \mathscr{E})\nu - K_i(\nu, \mathscr{E}, T)N_i(t). \qquad (4)$$

Equation (4) is valid for adsorbed reaction products at constant in time emission and catalytic characteristics of the surface. The papers [5,28,29] show the influence of external factors, such as a weak electric field with a strength of up to 10^3 V/cm and illumination, on the emission and catalytic characteristics of $NaAu_x$ surface. This effect is associated with a change in the surface stoichiometry under the influence of external factors, namely, the concentration of alkaline centers on it, which are responsible for reactions on the surface of organic compounds [5]. The concentration of these centers is determined by the diffusion exchange of Na atoms between the volume and surface of the intermetallic compound, which depends on T and $\mathscr{E}$ [5,28,29]. Therefore, to fulfill equation (4) it is necessary that the change in the parameters $T, \mathscr{E}$ under the experimental conditions does not affect the stoichiometry of the $NaAu_x$ surface, which can be achieved if the time of changing the parameters is much shorter than the characteristic time of diffusion exchange of Na atoms in the intermetallic compound, i.e. during the time of changing the parameters, a possible change in the emission and catalytic properties of the surface has practically no effect on the measured dependences. In this case, the surface can be considered as quasi-stationary.

The purpose of this work was to study the temperature dependences of the ions current of diethylamine $(C_2H_5)_2NH$ thermal ionization on the surface of NaAu$_x$ at the emitter temperature change rate, which provides the TI of the reaction products under nonequilibrium conditions. The studies were carried out at constant flows of adsorbed substances (diethylamine, oxygen, and sodium), constant electric field intensity, and emitter temperature above the threshold temperature — $T > T_0$.

1. Experiment

This work was carried out in a 90-degree sector magnetic mass spectrometer with a radius of 300 mm with a dual ion source: TI and electron ionization. The TI emitter in the mass spectrometer was a gold ribbon with a purity of 99.99 and size of $0.05 \times 2.5 \times 50$mm with a NaAu$_x$ intermetallic compound film formed on it. The NaAu$_x$ layer was formed *in situ* according to the method presented in [5,7]. In the process of layer formation by this method, a tape coating with NaAu$_x$ intermetallic compound with a thickness of several atomic monolayers with sodium deficiency is formed. Its stoichiometry is close to NaAu$_2$ [7]. The NaAu$_x$ alloy is stable and retains its physical and chemical properties at the emitter temperature up to 1250 K.

The emitter was heated by direct heating with direct current.

A high-vacuum multichannel inlet valves system was used for adding gases into the mass-spectrometer. Oxygen in the inlet valves system was produced by thermal decomposition of $KMnO_4$.

The flow of sodium atoms was obtained by thermal decomposition of a standard mixture of sodium dichromate with zirconium. A mixture of sodium dichromate with zirconium in the form of tablets was placed in a heated quartz ampoule with a hole. The flow of Na atoms to the emitter was formed by a system of diaphragms.

In the present work diethylamine Purisisumum grade was used. Vacuum training of the by DEA sample freezing and heating up under vacuum pumping was performed for its dehydration and degassing prior to adding the DEA into the inlet valves system. The mass spectrum of diethylamine during electron ionization coincided with known reference data (NIST). The mass spectrum contains no impurities with a mass greater than the molar mass of diethylamine.

For the treatment of the emitter surface from possible contamination with the decomposition products oxygen was fed up to the pressure of $2 \cdot 10^{-6}$ Torr into the mass-spectrometer. The oxygen influence on the processes on the surface and TI is considered in [8].

The emitter temperature in the range 970–1300 K was determined using an optical pyrometer. To determine the emitter temperatures in the range 350–1100 K, the FD-226 photodiode was used, which was preliminarily calibrated according to the radiation of oxidized stainless steel in air.

The electric field intensity in the gap between the tape-extracting electrode did not exceed 200 V/cm, which made it possible to exclude the electric field effect on the efficiency of ion formation in accordance with the Schottky effect [1,2], since the value of $(e\mathscr{E})^{1/2}$ did not exceed 0.005 eV.

The study of TI under nonequilibrium conditions with the temperature change was carried out after the adsorbed compounds accumulation on the surface with the emitter ribbon turned off. This accumulation occurred during the emitter exposure under steady partial pressures of oxygen and DEA vapors with the emitter heating turned off. Its temperature in this case was determined by the temperature of the parts of the TI source, which after 8 h of the emitter heating was close to 320 K, so the lower temperature of the emitter with the ribbon turned off was taken close to $T_{\min} = 320$ K. After the emitter exposure at diethylamine pressure of $P = 3 \cdot 10^{-7}$ Torr maximum for $t = (300-900)$ s at $T_{\min}$, the filament current of tape was switched on, the its value increased linearly with time until the specified maximum current value was reached, which corresponded to the emitter temperature T_{m0} close to 1000 K. After reaching the emitter temperature T_{m0}, the temperature of the tape continued to increase almost linearly by 10–20 K for $\sim$ 20 s due to heating of the ribbon holder. Thus, $T_{\max} = T_{m0} + \Delta T$, where T_{m0} is close to 1000 K and ΔT does not exceed 10–20 K. The time of temperature rise from $T_{\min}$ to T_{m0} (temperature sweep time) was 30 s, which provided the emitter temperature change rate $\nu_T \sim 20$ K/s. In the emitter temperature range from $T_{\min}$ to T_{m0}, the temperature dependence on time was parabolic.

During the emitter temperature change, the emitter temperature and ion current were automatically recorded. Considering that the amount of compounds desorbed from the emitter surface is negligibly small to create a noticeable pressure increasing in the vacuum chamber of the mass spectrometer, the measurement of particles desorption by their ion current during the emitter temperature rise can be considered as thermal desorption at an infinitely high pumping rate.

To monitor the fulfillment of the conditions of quasi-stationary surface stoichiometry at a rate of temperature change $\nu_T \sim 20$ K/s, we compared the dependences of the ion current change with the emitter temperature rise from $T_{\min}$ to T_{m0}, and temperature decreasing from $T_{\min}$ to T_{m0}. The rate of the emitter temperature change as it decreased was $\nu_T \sim 2$ K/s.

To determine the effect of the surface stoichiometry change on the TI, the temperature dependences of the ion currents were measured under stationary conditions, i.e., for each emitter temperature the ion current was measured after the ion current complete stabilized in time.

2. Results and discussion

With the emitter heating turned off with $T = T_{\min}$ and diethylamine pressure from $3 \cdot 10^{-07}$ to $9 \cdot 10^{-06}$ Torr, the thermal ionization ion current was not registered. As the temperature rise from $T_{\min}$ at a rate of $\nu_T \sim 20$ K/s, the ion current was recorded from $T_{\min}$ to 400 K, depending on the type of ions. This indicates that under the experimental conditions there are no threshold TI processes at emitter temperatures $T > T_{\min}$.

Fig. 1 shows the current of $[\mathrm{MH}]^+$ ions of dehydrogenated diethylamine $[\mathrm{MH}]^+$ with m/z 72 vs. time at the emitter temperature rise from $T_{\min}$ to $T_{\max}$ after emitter exposure at $T_{\min}$ for 300 s and diethylamine pressure $P = 3 \cdot 10^{-07}$ Torr. The graph shows the start time of the emitter temperature sweep (t_0) at a rate of $\nu_T \sim 20$ K/s, the time of the temperature sweep stop when the emitter temperature is $T_{m0}(t_1)$, as well as the time until the emitter temperature stabilization and reaching the maximum emitter temperature $T_{\max}(t_{\max})$. Fig. 2 shows current of $[\mathrm{MH}]^+$ ion vs. the emitter temperature at the temperature rise at a rate of $\nu_T \sim 20$ K/s after emitter exposure at $T_{\min}$ for 300 s and diethylamine pressure $P = 3 \cdot 10^{-07}$ Torr. The ion current for each curve in Fig. 2 is normalized to the value of the current at $T = 1000$ K.

In the emitter temperature range 400–600 K the ion current peak is observed, which can be associated with the thermal desorption peak of dehydrogenated DEA. With a further rise of the emitter temperature from 600 K to $T_{\max}$, the rise of ion current is observed, which is characteristic for the case of „hard ionization“, when $(E_i - \varphi) \gg kT$ [2,4]. For comparison, Fig. 2 shows the temperature of $[\mathrm{MH}]^+$ ion current vs. temperature at the emitter temperature decreasing at a rate of $\nu_T \sim 2$ K/s at diethylamine pressure of $P = 8 \cdot 10^{-07}$ Torr.

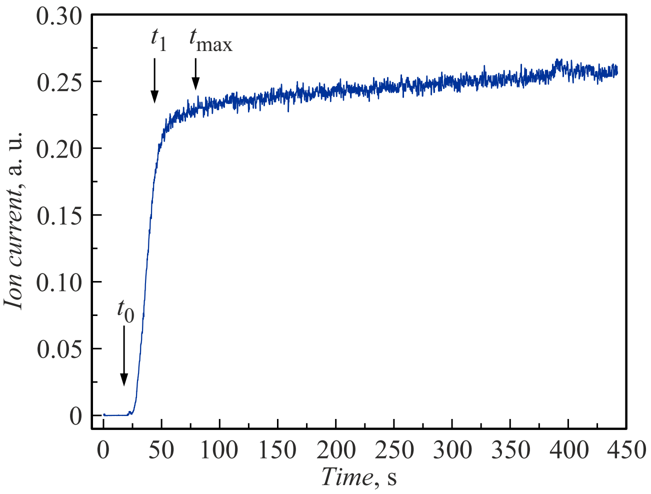

Figure 1. Current of $[\mathrm{MH}]^+$ ions of diethylamine vs. emitter temperature sweep time; t_0 is start time and t_1 is end time of temperature sweep; $t_{\max}$ is time to reach the maximum emitter temperature.

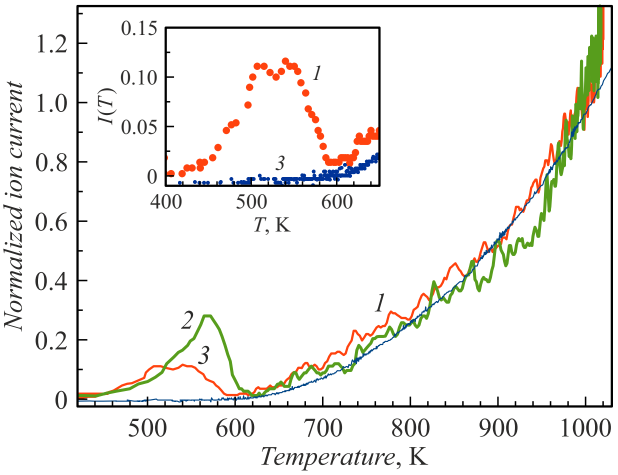

Figure 2. Current of $[\mathrm{MH}]^+$ ions of diethylamine vs. emitter temperature during its sweep to $T_{\max}$ after its exposure at $T_{\min}$ 300 (curve *1*) and 600 s (curve *2*), as well as with decreasing of emitter temperature (curve *3*).

Under equilibrium conditions, the temperature dependence of $[\mathrm{MH}]^+$ ion current is determined by the dependence on T of the ionization efficiency $\alpha_i(T)$ according to equation (1) and the formation of (M-H) $\gamma_i(T)$ as per equation (2) [2,4]. Under nonequilibrium conditions, the temperature dependence of the ion current is additionally affected by the processes of establishing the equilibrium concentration (M-H) on the surface in accordance with equation (4). According to [27] the nonequilibrium adsorbate concentration is formed if the average time constant of the processes in the adsorbed layer (τ_a), that determine the formation and desorption of the adsorbate, is greater than the temperature change time dt by dT. In this case, with T rise an excess of the ionizable adsorbate is desorbed relative to the equilibrium conditions, and in the case of T decreasing — a deficiency [27]. Therefore, the curves of ion current vs. temperature, measured with T decreasing and increasing, under nonequilibrium conditions should show a difference — hysteresis, and under equilibrium conditions, while maintaining the emission and catalytic properties of the surface with temperature change, they should coincide. The similarity of the temperature dependences of the ion current $[\mathrm{MH}]^+$ during T increasing and decreasing at $T > 600$ K indicates that on the surface with T increasing and decreasing no nonequilibrium concentration of the ionizable compound (M-H) is formed, and the conditions of TI (M-H) at $T > 600$ K can be considered as equilibrium. Since for (M-H) at $T > 600$ K, at temperature rise with a rate of $\nu_T \sim 20$ K/s, no nonequilibrium concentration is formed, it can be concluded that the formation and desorption rates (M-H) are higher than the rate of T change, and the time constant of these processes is less than $\tau_a(T) < 1/\nu_T = 0.05$ s. At $T < 600$ K the curves of the temperature dependence of the ion current with T decreasing and increasing show a significant difference: T

decreasing leads to the desorption of the excess of ionizable dehydrogenated diethylamine (M-H), which forms a thermal desorption peak. It follows from this that at $T < 600$ K and the emitter temperature rise at a rate of $\nu_T \sim 20$ K/s the TI (M-H) conditions are nonequilibrium.

Under equilibrium conditions at $\varphi < E_i$ the temperature dependence of the $[\mathrm{MH}]^+$ ion current is determined by the product of $\alpha_i(T)\gamma_i(T)$ [2,4]. Assuming, in accordance with [11,30,31], that the formation of (M-H) occurs as a result of dissociative adsorption of DEA molecules, the $\gamma_i(T)$ dependence can be determined using the Arrhenius equation:

$$\gamma_i(T) = \mathrm{const} \cdot \exp(-E_{ai}/kT), \qquad (5)$$

where E_{ai} is the effective activation energy of DEA molecules dehydrogenation during adsorption. Taking into account the equations (1), (2) and (5), as well as the small value of $e(e\mathscr{E})^{1/2}$ under the experimental conditions, the temperature dependence of the $[\mathrm{MH}]^+$ ion current in the temperature range from 600 K to $T_{\max}$ can be approximated by the dependence:

$$I(T) = \mathrm{const} \cdot \exp\big((\varphi - E_i - E_{ai})/kT\big). \qquad (6)$$

The temperature dependences of the $[\mathrm{MH}]^+$ ion current with emitter temperature increasing and decreasing (Fig. 2, curves *1–3*) can be approximated in the coordinates $\ln I$ from $1/kT$ straight line with slope $a_v = (\varphi - E_i - E_{ai}) = -(0.42)-(-0.45)$ eV. Approximation of the temperature dependence of the $[\mathrm{MH}]^+$ ion current by equation (6) confirms the equilibrium conditions for the TI of dehydrogenated DEA (M-H) when the emitter temperature changes at a rate of $\nu_T \sim 20$ K/s.

As can be seen from Fig. 1, when T increases, $[\mathrm{MH}]^+$ ion current after reaching $T_{\max}$ continues to increase for a long time. Considering that at $T > 600$ K the TI (M-H) conditions are equilibrium, i.e. there is no excess (M-H) on the surface, which can be desorbed with time, the change in the ion current after reaching $T_{\max}$ can be associated with change with time of the catalytic and emission characteristics of the surface. To determine the effect of this change of surface properties on the temperature dependence of the $[\mathrm{MH}]^+$ ion current, it was determined under stationary conditions, i.e. the value of the ion current after the emitter temperature change was measured after the current stabilization with time, which occurred for tens of minutes. The temperature dependence of the $[\mathrm{MH}]^+$ ion current under stationary conditions in the coordinates $\ln I$ on $1/kT$ can also be approximated by a straight line. The slope of this straight line was $a_s = -1.67$ eV. The difference between a_v and a_s is associated with the fact that in the stationary current measurement mode, in the process of the ion current stabilization after the emitter temperature change, the surface stoichiometry is rearranged and, consequently, its catalytic and emission characteristics change. Since the surface stoichiometry is determined by the slow diffusion exchange of Na atoms between the surface and the bulk of NaAu$_x$ layer [5,28,29], at emitter temperature change rates of $\nu_T 2$ and 20 K/s the change in the surface stoichiometry, if it takes place, is insignificant, which does not affect the ion current. On this basis, and also taking into account the similarity of the temperature dependences with T increasing and decreasing, we can consider the surface stoichiometry upon the emitter temperature change at a rate of 2 and 20 K/s as quasi-stationary, and the surface characteristics are unchanged. Thus, at the emitter temperature change rate of $\nu_T \sim 20$ K/s, TI on NaAu$_x$ occurs under conditions of quasi-stationary surface stoichiometry, and the surface concentration of compounds involved in the formation of (M-H) at $T > 600$ K satisfies the equilibrium conditions.

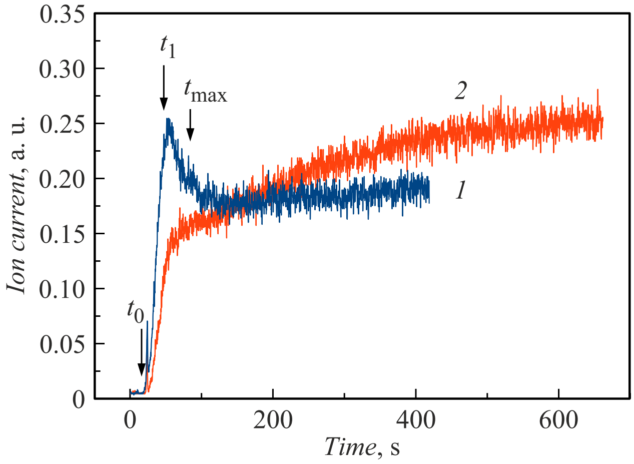

Figure 3. Ion current: *1* — with m/z 86, *2* — with m/z 58 vs. time as the emitter temperature increases; t_0 — start time and t_1 — end time of temperature increasing; $t_{\max}$ — time to reach maximum emitter temperature.

When DEA is adsorbed on NaAu$_x$, as a result of exchange reactions during DEA dimerization or in the reactions of DEA molecules with their decay products DEA molecules are methylated $((\mathrm{MH})+\mathrm{CH_3}))$ [8]. Methylated DEA with molecular weight of 87 Da during TI is registered as $[((\mathrm{MH})+\mathrm{CH_3})\text{-H}]^+$ ions with m/z 86 [8]. In the exchange reaction during DEA methylation the ethylmethylamine $((\mathrm{M\text{-}CH_3})+\mathrm{H})$ paired with methylated DEA is formed with molecular weight of 59 Da, which is registered during TI in form of $[((\mathrm{M{-}\text{-}CH_3})+\mathrm{H})-\mathrm{H}]^+$ with m/z 58 [8]. However, the formation of ions with m/z 58 also occurs during the decay of DEA molecules with the formation of $[\mathrm{M-CH_3}]^+$. Fig. 3 shows the dependence of current of ions with m/z 58 and 86 on time as the temperature increases from $\nu_T \sim 20$ K/s. These dependences were measured after 600 s exposure of the emitter at $T = T_{\min}$ at diethylamine pressure $P = 3 \cdot 10^{-07}$ Torr. The graph shows the start time of T increasing, as well as the time when the emitter reaches T_{m0} and $T_{\max}$.

The emitter temperature rise from $T_{\min}$ to T_{m0} is accompanied by rise of current of ions with m/z 58 and 86. After reaching T_{m0}, the ion current change is observed for a long time until it stabilizes. In this case, the ion current change from T_{m0} to $T_{\max}$ for ions with m/z 58 and 86 is multidirectional. Peaks (Fig. 4) are observed in the emitter temperature range 500–630 K, which can be associated with thermal desorption. The temperature of the maxima of these peaks is close to $T = 580$ K. After the stop of temperature change with rate ν_T and T_{m0} achievement, the current of ions with m/z 86 decreases with time. This indicates that by the time the emitter temperature reaches $T_{m0} = 1000$ K, there is excessive concentration of methylated DEA $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ on the surface, and, consequently, at $T < T_{m0}$ at sweep T with $\nu_T \sim 20$ K/s the conditions of its TI are nonequilibrium. The latter confirms that the temperature dependence of the current of ions with m/z 86 in the range T from 630 K to T_{m0} with T increasing can not in accordance with expression (6) be approximated with a straight line in coordinates $\ln I$ from $1/kT$. Assuming that this excess $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ is provided by exceeding the mean lifetime on the surface $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ of value dT/dt [28], from the ratio of the average lifetime on surface (M-H) at $T = 600$ K and $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ at $T = 1000$ K it follows that the value of energies of their desorption should differ by several times. Assuming such a difference to be unlikely, we can assume that the kinetics of the ion current change is determined by the concentration of DEA dimers responsible for the formation of $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ [8]. In this case, the kinetics of the ion current change after reaching T_{m0} is determined by the kinetics of establishing the equilibrium concentration of dimers, and the nonequilibrium conditions of TI of $(((\mathrm{M{-}H}){+}\mathrm{CH_3}){-}\mathrm{H})$ at $T < T_{m0}$ at sweep T with $\nu_T \sim 20$ K/s is provided with a significant lifetime on the surface of DEA dimers.

Fig. 4 shows the dependences of current of ions with m/z 58 and 86 on temperature as the temperature increases. Dependencies are determined under the same conditions as for Fig. 3. The ion current is normalized to the value of the current at $T = 940$ K. As can be seen, the temperature dependences of the current of ions with m/z 58 and 86 in the range from $T_{\min}$ to 940 K practically coincide. This confirms the conclusion of the paper [8] about the formation in the exchange reaction of a pair of — methylated diethylamine and methylethylamine. On this basis, we can conclude that the temperature dependence of the current of ions with m/z 58 in the range from $T_{\min}$ to 940 K, as well as the temperature dependence of the current of ions with m/z 86 are determined mainly by the concentration of DEA dimers on the surface.

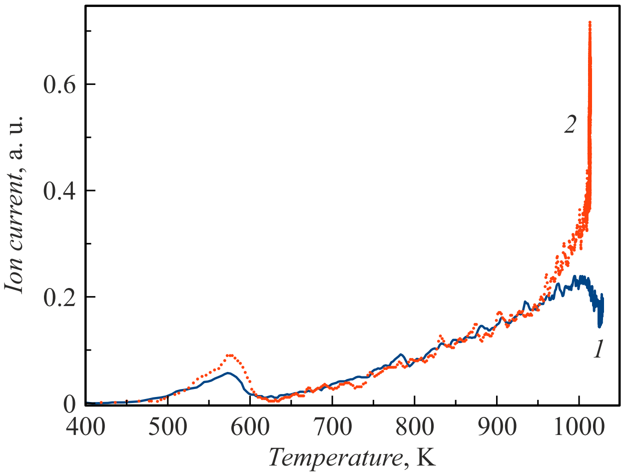

Figure 4. Ion current: *1* — with m/z 58, *2* — with m/z 86 vs. emitter temperature at emitter temperature increasing.

At $T > 940$ K the rate of current increasing of ion with m/z 58 increases with temperature rise, which is apparently associated with the temperature activation of the decay of diethylamine molecules $\mathrm{M} \rightarrow (\mathrm{MR}) + \mathrm{R}$. This decay occurs at higher T than the dehydrogenation reaction occurs, which is confirmed by the results of studies of amines TI [4], which showed that the temperature of the start of registration of ions formed as a result of the decay with the detachment of $\mathrm{CH_3}$ radical is by several hundred degrees higher than the beginning of registration of dehydrogenated compounds. Therefore, in the range from $T_{\min}$ to 940 K, ions formed during the methylethylamine dehydrogenation predominate, and at $T > 940$ K ions from DEA decays make a greater contribution to the ion current. The larger contribution to the current of ions with m/z 58 at $T > 940$ K of ionized products $(\mathrm{M{-}CH_3})$ of the direct decay of diethylamine molecules explains the difference in the change with time of the current of ions with m/z 86 from the current of ions with m/z 58 after reaching T_{m0} and $T_{\max}$. When the emitter reaches $T_{\max}$, the current of ions with m/z 58 increases for a long time, similarly to the current of ions with m/z 72. Consequently, ions with m/z 58 and 72 at $T > 940$ K are formed from individual adsorbed DEA molecules, while ions with m/z 86 and 58 in the temperature range from $T_{\min}$ to 940 K are formed mainly in exchange reactions from DEA dimers, whose lifetime on the surface is long.

In the association reactions of DEA molecules on NaAu_x diamines can be formed, for example, N,N'-diethyl-2-butene-1,4-diamine with a molecular weight of 142 Da, as well as hydrazones (compounds containing C=NN group) with molecular weight of 114 and 100 Da [8]. The TI mass spectrum of these compounds includes peaks corresponding to ions with m/z 97 and 99. Dependences of the current of ions with m/z 97 and 99 on the emitter temperature as the temperature rises from $T_{\min}$ to $T_{\max}$ at rate of vT 20 K/s after emitter exposure for 300 s at diethylamine pressure $P = 3 \cdot 10^{-07}$ Torr are shown in Fig. 5. These dependences at emitter temperature $T_{\min}$ show peaks (Fig. 5) corresponding to thermal desorption peaks of ionizable compounds. In contrast to ions with m/z 58, 72, and 86, the ion current intensities at the peak maximums of the ion current significantly exceed the ion current intensity at $T_{\max}$. This may be due to both weak temperature dependence of the ionization efficiency of these ions, and to the higher efficiency of dimer decay with the formation of compounds desorbed as ions with m/z 97 and 99. The temperature dependence of the current of

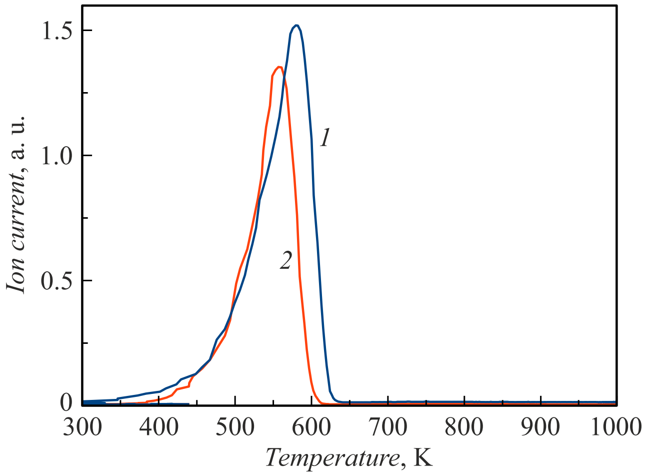

Figure 5. Current of ions with m/z 97 (curve *1*) and 99 (curve *2*) vs. emitter temperature as its temperature rises.

ions with m/z 97 and 99 in the range from 640K to T_{m0} is growing, and the shape of the temperature dependence is close to the temperature dependence of ions with m/z 86 in the same temperature range. The latter indicates that a significant peak amplitude of the temperature dependence of the current of ions with m/z 97 and 99 is determined by the desorption flow of the corresponding ionizable substances, and hence the greater efficiency of the formation of compounds ionized with the formation of these ions.

In the stationary mode the temperature dependences of the current of ions with m/z from 97 to 141 are similar: the ion current increases with temperature up to $T = 980-1100$ K, and with a further temperature increasing the ion current practically does not depend on it [8]. Based on this, a conclusion was made about the general nature of the mechanism of ions formation of this group. For ions of this group the temperature dependences with temperature rise after the emitter exposure at $T_{\min}$ in DEA vapor are similar to the temperature dependences of ions with m/z 97 and 99 i.e. have a peak with current value at the maximum significantly exceeding the ion current at $T_{\max}$. This confirms that the formation of this group of ions occurs during the decay of dimers, which are effectively formed and accumulated at $T_{\min}$.

The DEA mass spectrum on NaAu$_x$ contains peaks corresponding to ions with a mass exceeding the dimer mass, namely, ions with m/z from 151 to 197 [5,8]. These heavy ions are formed in the decay of molecular clusters formed on the surface of NaAu$_x$ in the reactions of association of dimers with diethylamine molecules and dimers between themselves [8]. The efficiency of dimers formation, i.e. of the molecular clusters with the number of molecules in the cluster $n = 2$, and molecular clusters with $n > 2$ should increase with the emitter temperature decreasing [4,10]. Therefore, after the emitter exposure in DEA vapor at $T_{\min}$, one can expect thermal desorption of heavy compounds, including those ionized by TI. Fig. 6 shows the current of „heavy" ions vs. emitter temperature as the temperature rises from $T_{\min}$ to T_{m0} at a rate of $\nu_T \sim 20$ K/s after emitter exposure at emitter temperature $T_{\min}$ 300 s at diethylamine pressure $P = 3 \cdot 10^{-07}$ Torr on the example of ions with m/z 183 and 197. This dependence shows ion current peaks corresponding to thermal desorption peaks of ionizable compounds, which confirms the formation of molecular clusters with $n > 2$ at $T_{\min}$. Just as for ions with m/z 97 and 99, the value of the current of ions with m/z 183 and 197 at the maximum is much greater than the value of the ion current at $T_{\max}$.

Thus, the value of the maximum ion current of the thermal desorption peak for ions with $m/z < 97$ is less than the value of the ion current at $T_{\max}$, and vice versa for ions with $m/z > 97$ the ion current at the maximum of the thermal desorption peak is much larger than the current at $T_{\max}$. The area under the curve of the ion current peak reflects the number of compounds desorbed during T increasing, which depends on the exposure time of the emitter in DEA vapor at $T_{\min}$. Fig. 7 shows examples of current peak area of ions with $m/z < 97$ and > 97 vs. exposure time of the emitter at $T_{\min}$ at diethylamine pressure of $P = 3 \cdot 10^{-07}$ Torr.

The peak area for ions $m/z < 97$ decreases with exposure time, and increases for ions with $m/z > 97$. Considering that ions with m/z 58 are formed mainly due to the decay of dimers, and ions with m/z 72 are formed due to the decay of DEA molecules, it can be assumed that ions with $m/z > 97$ are formed due to the decay of molecular clusters with $n > 2$. As the adsorbate accumulates at $T_{\min}$ on the surface, the role of molecular clusters increases, as a result of this the number of individual molecules and dimers decreases. In the process of the molecular clusters decay, the ionizable compounds are formed, mainly ions

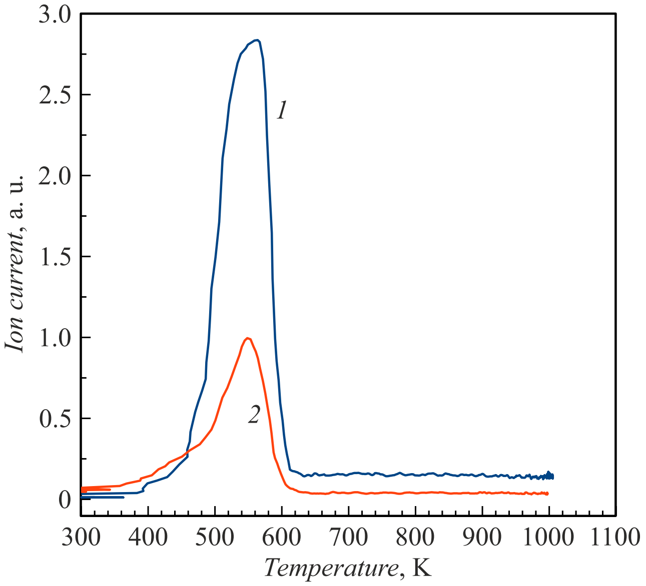

Figure 6. Current of ions with m/z 183 (curve *1*) and 197 (curve *2*) vs. emitter temperature as emitter temperature rises.

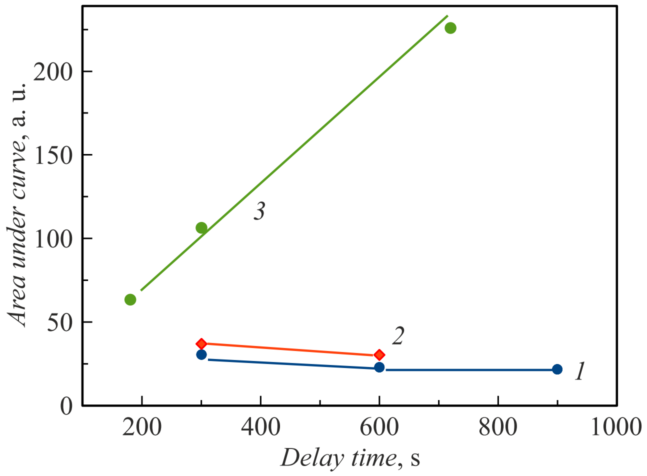

Figure 7. Peak area of the temperature dependence of the current of ions with m/z 58 (*1*), 72 (*2*) and 99 (*3*) vs emitter exposure time at $T_{\min}$.

with $m/z > 97$. This assumption can be confirmed by the closeness of the temperatures of the maxima of the peaks of the temperature dependence of the ion current. These temperatures discrepancy within 50 K is due to the fact that the shape of the peaks is determined by the shape of the thermal desorption peak and the temperature dependence of the compounds ionization efficiency.

The effective formation of molecular clusters at $T_{\min}$ and their presence at high emitter temperatures up to 1300 K [8] indicate that molecular clusters are formed in specific areas of the surface, the number of which weakly depends from temperature. This gives grounds to assume that during the emitter exposure in DEA vapors at $T_{\min}$ not the number but the size of these clusters (the number of DEA molecules in the cluster) changes. The cluster size is determined by the DEA pressure and the exposure time of the emitter. At $T_{\min}$ and constant DEA pressure, the size of molecular clusters increases with exposure time, while the number of individual molecules and dimers on the surface decreases.

In accordance with the theory of monomolecular decays [32], the efficiency of decay reactions of compounds, other things being equal, is determined by the temperature and the number of degrees of freedom in the compound, on which energy can accumulate. As a result, the decay efficiency at $T = \text{const}$ increases from molecules to molecular clusters and grows by n times. The relationship between the efficiency of formation of ionizable compounds and the combination of adsorbed molecules into dimers was confirmed in the study of the mechanism of TI of urotropin on NaAu_x [11]. It was also shown that during the desorption and ionization of the products of cluster decay, the thermal equilibrium of the desorbed compound with the solid can be violated. From this, it can be assumed that the decay of clusters and the desorption of decay products can occur with the violation of thermal equilibrium in the adsorption system.

It can be concluded that DEA adsorption on NaAu_x at $T_{\min}$ results in the formation of molecular clusters on the surface. The thermal energy of the emitter is distributed over numerous degrees of freedom of the cluster. The more molecules are in the cluster, the more energy is accumulated in it. At a constant temperature, the equilibrium energy distribution over the degrees of freedom is achieved due to the energy exchange of the cluster molecules with the solid body, as a result of which the ion current at constant temperature $T_{\min}$ is not recorded. Rapid heating of the emitter at a rate of $\nu_T \sim 20$ K/s violates the equilibrium distribution of the energy accumulated at the degrees of freedom in the cluster, leads to the redistribution of energy, possibly due to wave processes stimulated by rapid heating of the emitter both in the intermetallic compound layer and in the cluster. This leads to the energy release on individual bonds of the cluster, as a result of which decays and desorption of the decomposition products occur, and thus a thermal desorption flow of various types of compounds is formed, some of which are ionized. This collective process of energy accumulation and its release on individual bonds in the process of violation of the thermal equilibrium of the adsorption system during rapid heating of the emitter leads to numerous decomposition, desorption of decomposition products and their ionization. The consequence of this collective process is that at a temperature close to $T_{\min}$, with rapid heating of the emitter, the ion current begins to be recorded, and the formation, desorption and ionization of various kinds of compounds, that differ significantly in mass, structure and electrochemical properties, occurs almost at the same sufficiently low temperature. This mechanism also explains the large values of the ion current at the peaks of the temperature dependences.

Conclusion

Exposure of gold emitter coated with NaAu_x intermetallic compound at $T_{\min} \sim 320$ K in diethylamine vapor leads to the formation of molecular clusters on the surface with more than two molecules in the clusters. As exposure increases, clusters increase due to the decreasing of number of molecules and their dimers. Rapid heating of the emitter at a rate of $\nu_T \sim 20$ K/s, starting from emitter temperature close to $T_{\min}$, causes clusters decay, desorption, and ionization of decomposition products. The process of clusters decay is reflected in the registration of current peaks of ions with m/z from 58 to 197 in the emitter temperature range from $T_{\min}$ to 620 K. The temperatures of the peak maxima of ion current are in the range 520–600 K. A mechanism for the molecular clusters decay is proposed, which is associated with the start by emitter rapid heating of wave processes in a system of coupled oscillators — degrees of freedom in molecular cluster, causing energy redistribution in it. This wave process ensures the release of energy on individual bonds in the cluster in an amount sufficient for decay, desorption and ionization of decomposition products — a collective process in thermal ionization.

The study of the temperature dependences of the ion current during thermal ionization of diethylamine on the surface of $NaAu_x$ at emitter temperature $T > 600\,K$ and the emitter temperature rise at a rate of $\nu_T \sim 20\,K/s$ allowed to determine that the dehydrogenation of diethylamine and ionization (M-H) occurs under equilibrium conditions, the value of the activation energy for the formation and ionization of dehydrogenated diethylamine is $(\varphi - E_i - E_{ai}) = -(0.42)-(-0.45)$ eV. The $NaAu_x$ surface remains quasi-stationary in the temperature range $600-1000\,K$ as the emitter temperature changes at a rate of $\nu_T \sim 2\,K/s$. The formation and ionization of compounds formed as a result of the decay of dimers of diethylamine molecules and molecular clusters in the temperature range $600-1000\,K$ with the emitter temperature change at a rate of $\nu_T \sim 20\,K/s$ occurs under nonstationary conditions due to their long lifetime.

Conflict of interest

The authors declare that they have no conflict of interest.

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