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ADSORPTION OF H_2O ON Pt FIELD EMITTER: SURFACE DIFFUSION AND FIELD-INDUCED EFFECTS

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Adsorption of an H_2O layer onto a Pt field emitter tip under the influence of an electric field and the surface diffusion of water were studied by using the field electron microscopy method. The presence of a negative field (field electron microscopy mode of operation), examined in the range of 33–44 MV/cm, significantly reduced the water coverage on the emitter at temperatures above 120 K. The reduction could also occur upon drawing a high density field emission current when the emitter was kept at 78 K. Surface diffusion of water, which was observed in the temperature range 120–132 K, corresponded to the "unrolling the carpet" mechanism and started from a water multilayer to a surface region water- and/or hydrogen-submonolayer covered. This was accompanied by the transition process from the state of the current- and field-induced redistribution of H_2O to the state of thermal equilibrium. The activation energy of the diffusion was found to be 19 and 25 kJ/mol depending on the crystallographic direction. A positive electric field of 44 MV/cm, which was applied at temperatures of the substrate in excess of 121 K, decreased the field emission of the system and raised the desorption temperature of the layer over 720 K. It is assumed that the negative electric field causes reorientation of H_2O molecules at the surface of platinum tip. The positive as well as negative electric fields promote the field desorption of water, which is in accordance with the results reported before.

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1. Introduction

The system of water-metallic surface has been widely investigated because of its great importance in a variety of fields in science, technology and naturally occurring phenomena. A review and discussion on the experimental and theoretical results of studies of the interaction of water with solid surfaces are given in a unique monograph by Thiel and Madey [1]. Among many interesting problems there are the ones concerning the interaction of H_2O molecules with metallic surfaces under conditions of a high electric field. Stintz and Panitz [2] have studied the field desorption (in the positive field) of water from Ir, Pt and W field emitters. The main result of their study is that water is desorbed as protonated clusters $(H_2O)_nH^+$ consisting of a few molecules ($n = 1, 2, \ldots, 10$), depending on the substrate temperature. This is consistent with the results reported before that were obtained during deposition of water onto the emitter tip in the presence of electric field [2, Refs. 8–18 therein].

A very important problem to study is the kinetics of H_2O diffusion on metal surfaces where intermolecular hydrogen bonds form. The kinetics of the diffusion determines the rate at which hydrogen-bonded clusters nucleate and grow following the adsorption. There have been no direct investigations reported on the diffusion of water for H_2O molecules on metal surfaces, so far. The problem is in detail discussed by Thiel and Madey [1].

This paper presents some experimental results on the surface diffusion of H_2O multilayer over a Pt field emitter surface. This seems to be the first reported experiment for such diffusion. There are also presented results concerning the influence of electric field on a water layer condensed on the cooled Pt field emitter under conditions of field emission (FE) of electrons. The influence was examined for a negative field in the field electron microscopy (FEM) mode of operation and for a positive field (or reversed), similarly as under the conditions employed by Stintz and Panitz [2].

An attempt is undertaken to explain the reduction of the total FE current (i.e., the increase in the work function Φ) which was found during the adsorption of water on the emitter surface [3]. This result is quite different from the work function results reported for the adsorption of H_2O on the low index planes of the Pt large single crystal or a Pt polycrystal surface, which are obtained using other methods [1, 4, 5]; in the latter cases a distinct lowering of Φ occurs.

2. Experimental procedures

The experimental conditions and procedure were similar to the ones described in Ref. [3]. A glass, ultrahigh vacuum (UHV) system based on mercury diffusion pumps and equipped with a small, glass titanium pump provided a final pressure far below 1×10^{-10} torr.

Water vapor was introduced into the glass FE tube connected with the UHV system through leak valves. The water used was doubly distilled and degassed *in situ* in the usual way [2]: by several cycles of freezing it, pumping down the water container through the fully open leak valve, and melting the frozen water after closing the valve.

The tip was made from a 0.1 mm platinum wire of 99.999% purity (Johnson–Mathey) by electrolytic etching in a mixture of molten KNO_3 (80%) and NaCl (20%) at approximately 700 K. The tip assembly loop and the potential leads for the loop temperature control were made from platinum wires. The specimen temperature was stabilized using an electronic controller [6] and could be calculated from the resistance values of the central part of the Pt loop with the error of ±2.5 K.

The criteria for a clean field emitter surface are discussed by Melmed [7]. After Vanselow and co-workers [8–12] the tip was cleaned by annealing in UHV at the temperature up to 1600 K. Statistics of obtaining the clean surface was poor, it was possible to clean up one per four tips prepared in this experiment. The short-period heating (flashes) of the emitter to a temperature close to the melting point of Pt could also provide the clean FE pattern of the surface but considerable blunting made the tip useless. Vanselow and co-workers [8–11] have indicated that the main impurities of a Pt sample (C, S, P, Si) usually appear as bright spots and/or rings surrounding some plane poles in the FE micrographs. The respective intensities depend strongly on the temperature and time of heating of the Pt sample (segregation effect). An FE pattern obtained for a Pt surface and a stereographic projection of the fcc lattice (111)-oriented are shown in Figs. 1a and b, respectively. (The emitter axis was close to the direction [231].) The pattern in Fig. 1a is not essentially different from those reported earlier [7–15]. As it can be seen in the figure the surface of the Pt emitter was free of such contamination. Water desorption from the clean tip was observed in this experiment, similarly as for the large Pt single crystal [1], at 160–170 K. In the case of an unclean surface the thermal desorption of water deposited at 78 K occurs at substrate temperatures much higher than those registered for the clean surface. This phenomenon is observed owing to water dissociation [1]. In fact, desorption of water or products of its dissociation from the surface of the emitters not enough clean required much higher temperature of the substrate. Such a thermal desorption test was also employed before the experiment to find the cleaning conditions for the Pt emitters.

The amount of water deposited on the emitter is expressed in the following by the time of exposure. Measurement of water pressure near the emitter could not be carried out precisely because of a high gradient of water pressure in the tube (which was due to the freezing of water by a dewar with liquid nitrogen coolant surrounding the emitter assembly). During the course of water experiments the Bayard–Alpert gauge was switched off to avoid the possibility of dissociation of water.

As it could be expected [2, 3], high electric field significantly affected the water adsorbate. Therefore, the field was applied only for short periods (about 2 seconds) necessary to record the emission current. Exception was made for these measurements where the influence of the electric field was the subject of the study.

The field strength F at the emitter apex was estimated from the relation [6]

$$F = U/kr, \tag{1}$$

where U is the voltage (in volts) applied between the emitter and anode of the tube, k and r are a constant and the emitter tip radius, respectively. In this paper field strengths F are given for $k = 5$ [6] similarly as in the paper of Stintz and Panitz [2]. The emitter radius was about $r \approx 180 \div 190$ nm as estimated by the standard FE techniques from the emission current and voltage [6] and assuming the work function Φ to be equal to 5.32 eV for the clean Pt emitter [14, 16].

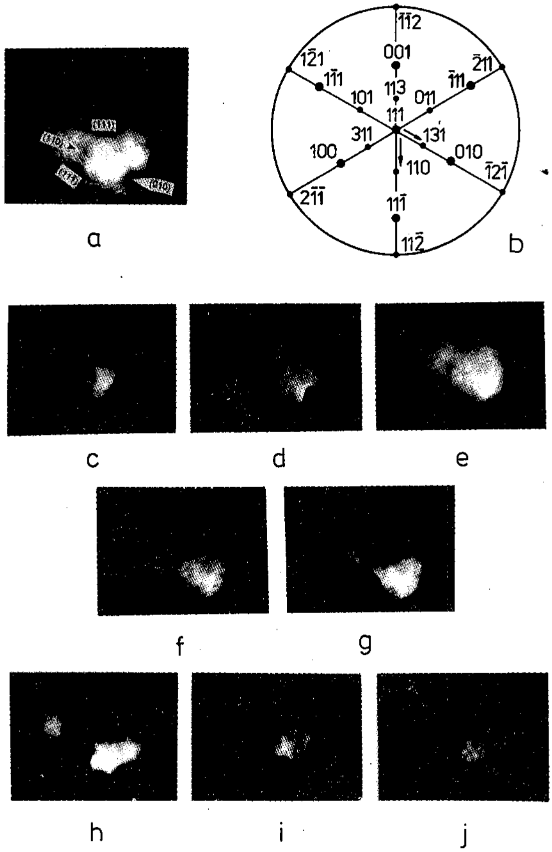


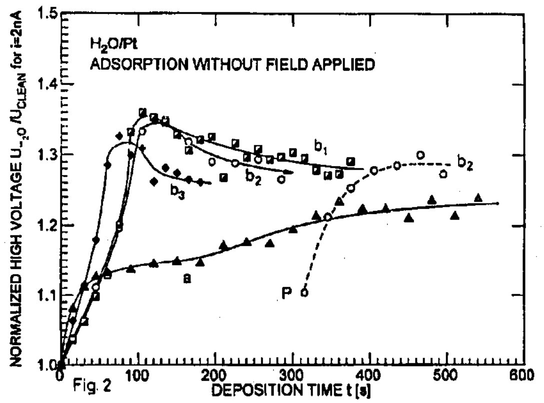
Fig. 1. FE patterns corresponding to: (*1*) desorption of multilayer water from Pt emitter under the FE conditions ($F \approx 53$ MV/cm) and diffusion (Figs. 1a–g), and (*2*) redosing of water onto the emitter after the FE desorption (Figs. 1h–j); (a) emitter after thermal cleaning, (b) stereographic projection of the fcc lattice (111)-oriented (arrows show the direction of diffusion measured, see below), (c) after condensation of water at 78 K, initial stage of the bright spot expansion (desorption), (d) next stage of expansion, (e) final stage of expansion, (f) contraction of the spot (diffusion) after heating at 125 K for 80 min, (g) the same as in (f) but for 200 min; (h) some stage of the expansion, (i) after redosing of water at 78 K, (j) for higher redosing at 78 K.

3. Results

3.1. Adsorption in the negative electric field

The influence of the electric field F and substrate temperatures on the H_2O layer condensed on the Pt emitter was examined observing the change in FE properties of the system.

Figures 2 and 3 show dependences of the normalized high voltage U_{H_2O}/U_{clean}, required to maintain a constant total emission current of 2 nA, versus time of water deposition t. The deposition was performed introducing successive H_2O doses



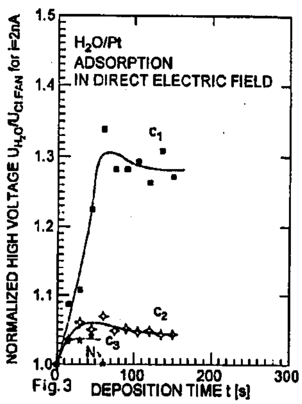


Fig. 2. Dependences of the normalized high voltage $U_{H_2O}/U_{\text{clean}}$ required to maintain a total emission current $i = 2$ nA versus water deposition time (dose by dose) in the absence of electric field F at two substrate temperatures: a — curve for 78 K, b_1 and b_2 are for a temperature of 125 K arbitrarily chosen (see text for the point P in curve b_2); b_3 for deposition at 78 K, then heating at 125 K.

Fig. 3. Dependences such as in Fig. 2 taken for the deposition made at a temperature of 125 K and in the presence of negative field: curve c_1 was taken for $F = 22$ MV/cm, c_2 — for $F = 33$ MV/cm and c_3 — for $F = 42$ MV/cm (except the point N for which $F = 44$ MV/cm).

into the field microscope with the emitter maintained at 78 K, in the absence of the electric field (Fig. 2) and, alternatively, in the presence of the negative field F (Fig. 3) at several chosen temperatures. The dependences were found as follows.

After deposition of each successive "water dose" (i.e. after shutting the leak valve) the emitter was kept under the conditions described in the figure captions for 3 to 5 minutes. At this time the water was removed from the FE tube. Then the emitter was cooled down to 78 K and the high voltage for the 2 nA emission current was applied (typically for about 2 seconds) and noted. Nonheated layers of H_2O deposit were unstable: field emission current fluctuations and the trend for an increase current during the time of the experiment (for a constant voltage) were noticed. The effect was more pronounced for a large water coverage and for a higher emission current (or electric field applied). For this reason, taking photographs of FE patterns was avoided during the course of adsorption.

It is seen in Fig. 2 that the heating of the water layer in the absence of electric field leads to the appearance of a maximum in curves b_1, b_2, b_3 in Fig. 2 and to the increase in the saturation voltage U_{H_2O} in comparison with a nonheated layer. The layer becomes more stable, i.e. the emission current is constant for a longer time. This may suggest a structural change in the condensed layer — from an amorphous state to a more ordered one when the layer is warmed. The formation process of a water layer and the structure of the latter under similar conditions are discussed in detail by Stintz and Panitz [2].

Although an absolute rate of water deposition could not be determined in these experiments, the coverage corresponding to the beginning of the saturation portion of curves b_1–b_3 in Fig. 2 likely amounts to 2–3 monolayers. From the experimental results for various systems it can be supposed that the essential changes of the emission properties (work function) typically occur for a coverage of two monolayers.

The data presented in Fig. 3 show that the effect of negative field led to a lower saturation voltage U_{H_2O}. For a higher field applied, when the electron emission already occurred, the clean emitter surface was revealed after the deposition of water (see Fig. 3 c_3, point N).

The effect of the FE current could be neglected in the case of curves c_1, c_2 and c_3. The FE currents for c_2 and c_3, estimated from the Fowler–Nordheim equation for the clean tip, were $I_e = 5.6 \times 10^{-13}$ A and $I_e = 0.5$ nA, respectively. For the point N in curve c_3, $I_e = 2$ nA and the density of current related was some 3–4 A/cm^2.

The effect of the negative field on water deposit was also observed in the case of multilayer adsorption on Pt emitter in the absence of the field. The point P in curve b_2 in Fig. 2 was obtained in such a way that the emitter with 2–3 monolayers of the water deposit was heated at 121 K for 5 minutes in the presence of the negative electric field, $F = 42$ MV/cm. Prolonged heating in the absence of F for 3 minutes did not change the emission conditions corresponding to the point P. Following depositions of water on the emitter surface in the stage represented by the point P (after switching off the field) affected the FE emission properties represented by the dashed part of curve b_2. Thus the negative field present over an adsorption layer diminishes the H_2O coverage on the Pt emitter.

3.2. Surface diffusion experiment

In the present experiment it was not possible to study the diffusion of water by the shadowing method [6, 17] because of difficulties in the one-side covering of the emitter with an H_2O layer. (The tip assembly was not thermally screened.) The gradient of water coverage could be initiated by the effect of electric field and FE current on the adsorbed multilayer.

Figure 4 presents time dependence of the field emission current for a constant high voltage ($F \approx 52$ MV/cm) from the Pt emitter with the large water coverage at 78 K. (This coverage is related to the end of the adsorption curve a in Fig. 2, i.e. it corresponds to approximately 5–6 monolayers.) For such coverages the increase in the FE current began with a current higher than 2 nA. At the origin of the curve in Fig. 4 almost the whole current was emitted from one or two small sites (that are seen in the FE micrographs as bright spots) of 50–100 Å in size. The non-uniform distribution of a polarized surface charge in the water layer, induced by the high negative electric field can be responsible for the appearance of the electron emission centers. The increase in the current was accompanied by the growth of bright spots with a sharp boundary in the central region of the FEM image where the current density was highest (Fig. 1c). Drawing a still higher emission current promoted the expansion of the spot (Fig. 1e). We think that in this case the partial or complete diminution of water coverage could be also responsible for the current increase. Inspection of the field emission micrographs indicates that the large bright spot

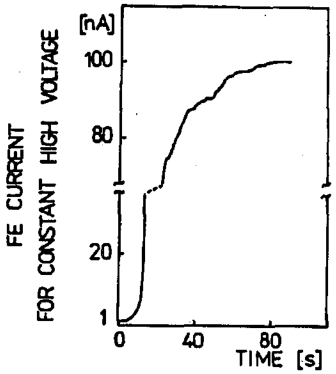


Fig. 4. Time dependence of the FE current for a constant high voltage ($F \approx$ 53 MV/cm) for the emitter with the multilayer water coverage at 78 K (the coverage corresponds to the end of curve *a* in Fig. 2, $\Theta = 5 \div 6$).

might correspond to the surface region covered by water submonolayer or products of its dissociation which were due to the negative electric field.

When the water-covered emitter of Fig. 1e was heated in the absence of the electric field, in the temperature range 120–132 K, the bright spot shrank and its sharp boundary contracted with increasing time. The trend of rising high voltage to maintain a constant emission current accompanied the shrinking of the bright spot. Photographs (f) and (g) in Fig. 1 show some stages of the contracting sharp boundary.

Redosing water onto the emitter, performed after partial reduction of its coverage, caused the bright spots in the enhanced electron emission (Fig. 1h) to diminish and a decrease in the emission current could be noticed (Figs. 1i and j) again.

The increase in the current at 78 K was also noticed for lower coverages (also for a submonolayer). It was observed for tips of other orientation and various shapes. In this case the rise of the current was not so rapid as that shown in Fig. 4. The increase was initiated at a higher value of current and no distinct spots of electric emission appeared in the relevant FE pattern. The field emission patterns became brighter and more similar to the one of the clean emitter surface. (In this case no temperature measurement was carried out because of frequent damage of the emitters.)

Typical dependences of the square displacement of the sharp boundary (or the diffusion distance) x^2 on the annealing time [17] for various substrate temperatures are shown in Figs. 5 and 6 — along the zone $\langle 011 \rangle$ between the (111)–(131) and (111)–(110) planes, respectively. Figure 7 shows Arrhenius plots (corresponding to the results in Figs. 5 and 6) from which the activation energy for the diffusion has been determined for two crystallographic zones: between the planes (111)–(131), $E_1 = 19 \pm 2$ kJ/mol and between (111)–(110), $E_2 = 25 \pm 2$ kJ/mol.

When the temperature range used for the observation of the sharp-boundary diffusion of water (contracting bright spot) was close to the thermal desorption

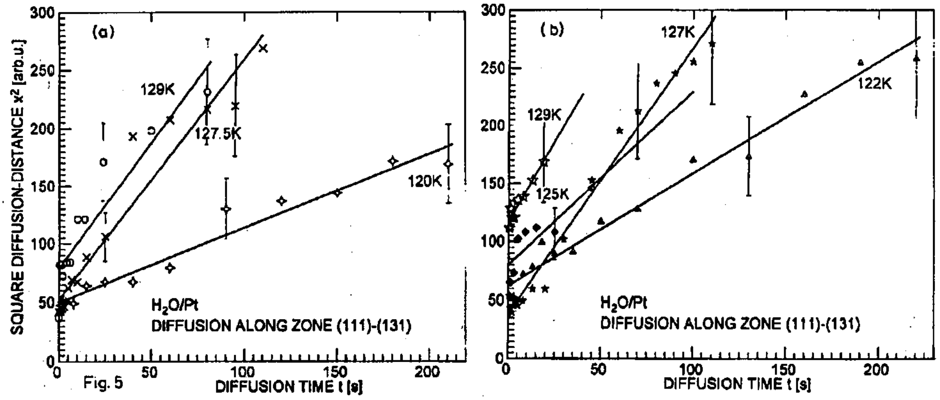


Fig. 5

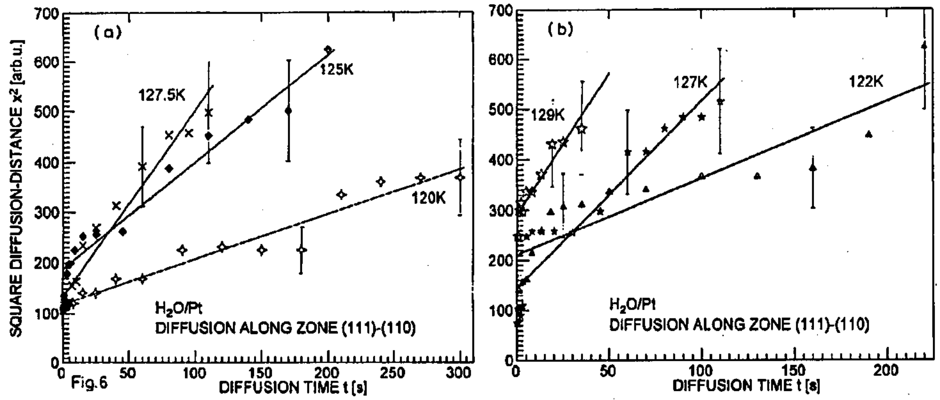


Fig. 6

Fig. 5. Dependence of the square displacement of the sharp boundary (or diffusion distance) x^2 on the heating time along the zone ⟨011⟩ between the (111)-(131) planes, (a) and (b).

Fig. 6 . The same as in Fig. 5 but between the (111)-(110) planes, (a) and (b).

temperature, the diffusion could be accompanied by the thermal desorption of water at slightly higher temperatures. At 137 K the desorption of water was explicitly seen (Fig. 8).

The average activation energy for shrinkig the sharp boundary of the diffusing water on platinum was also determined from the temperature dependence of the drop of the FE current at the constant voltage which was accompanied by contracting of the sharp boundary [18]. Average values of the activation energy E ranged between 21 and 27 kJ/mol [18].

3.3 Adsorption in the positive electric field

The results shown in Fig. 9 and illustrated by the FE patterns in Fig. 10 indicate that:

(i) The influence of the positive (or reversed) electric field on the formation of water layer is manifested by a higher value of the FE high voltage U_{H_2O} during the adsorption. Particularly this is clearly seen at temperature 121 K (curve d_1,

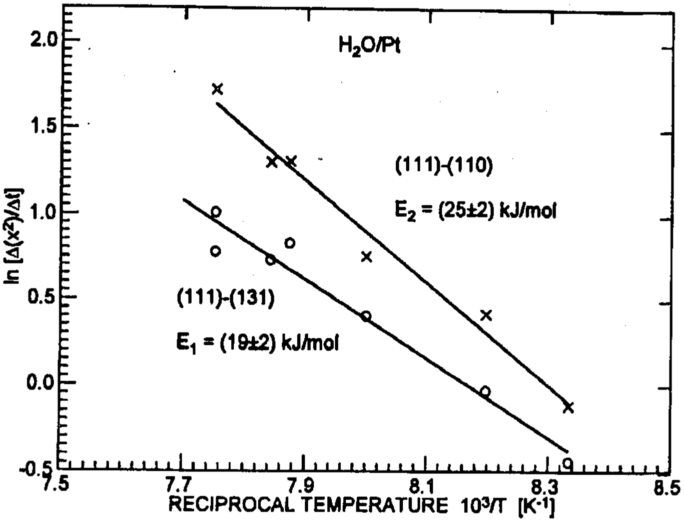


Fig. 7. Arrhenius plots corresponding to the data in Figs. 5 and 6.

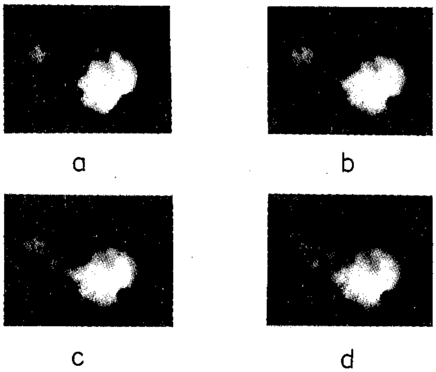


Fig. 8. FE patterns of thermal desorption of water: (a) some stage of expansion of the bright spot, $U_{H_2O} = 4365$ V at $i = 20$ nA, (b) upon warming after stage (a) at 137 K for 10 min, $U_{H_2O} = 4297$ V at $i = 20$ nA, (c) warming for 20 min, $U_{H_2O} = 4265$ V, (d) warming for 35 min, $U_{H_2O} = 4212$ V.

arrows show that in this situation the applied high voltage was too low to draw the 2 nA current; a higher voltage was not applied in order to avoid the damage of the emitter). The field emission pattern of this adsorption stage reveals black spots corresponding to the atomically rough regions of the surface (Fig. 10a). The layer formed under such conditions was more stable than the ones deposited in the absence or presence of the negative field (see Sec. 3.1.).

(ii) Voltage U_{H_2O} for large coverages decreases with increasing temperature (curves d_2 and d_3). The reduction of U_{H_2O} was also observed after an adsorption cycle had been completed, when the heating of the emitter at the reversed field applied was prolonged.

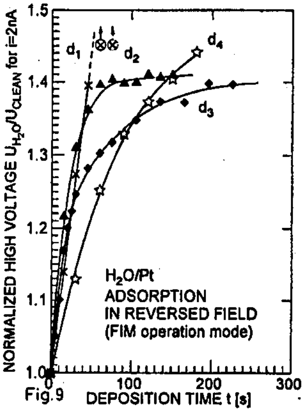


Fig.9

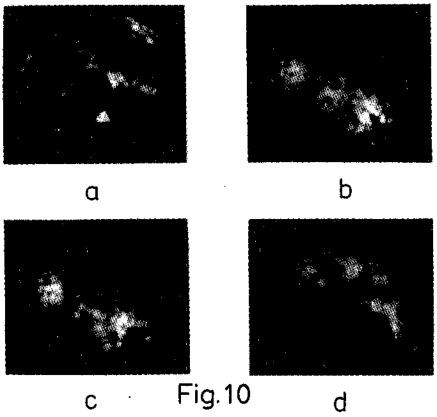


Fig.10

Fig. 9. Dependences similar as in Fig. 3, taken for the adsorption in the presence of the positive field $F = 44$ MV/cm at various substrate temperatures: d_1 is deposition curve at 121 K, d_2 at 125 K, d_3 at 133 K, d_4 represents condensation at 78 K without a field, followed by heating at 125 K with the positive field applied for one minute.
Fig. 10. FE patterns after an action of the positive field $F = 44$ MV/cm: (a) pattern taken when the field F was present during adsorption of water at 125 K, deposition time $t = 60$ s; (b) taken when the field was switched on at 125 K after condensation of water made at 78 K, $t = 60$ s; (c) field conditions the same as in (b) but for a higher water coverage, $t = 90$ s; (d) field conditions as in (b), $t = 180$ s, after heating at 290 K.

(iii) The influence of the positive field on the water layer condensed onto the emitter at 78 K without field is in general similar to the one described in point (i) (cf. adsorption curves d_4 and d_1–d_3 in Fig. 9). (Obviously, during the condensation of water with the electric field applied to the tip, the supply of water to the emitter surface is promoted by the field.) In this case FE micrographs indicate also distinct dark spots (cf. Fig. 10b), the size of which depends on the H_2O coverage (Fig. 10c corresponds to a higher coverage). Heating the emitter of Fig. 10c at room temperature provided the pattern shown in Fig. 10d. Photographs (Figs. 10a–d) were taken for the emission current of only 2 nA to reduce the influence of the imaging field on the adsorption layer.

In order to remove the layers after these adsorption runs (which are illustrated by Figs. 9 and 10) it was necessary to heat the emitter to a temperature higher than 720 K. This experiment indicates the occurrence of H_2O dissociation as a result of the presence of the positive field at the Pt surface.

4. Discussion

4.1. Adsorption in the negative electric field

4.1.1. Work function changes

An interesting question arises, why the presence of water on the Pt emitter raises its total FE work function (i.e. reduces the total FE current, Fig. 2) [3]. Although this statement should be confined to the atomically rough region of the emitter (including high index planes which contribute to the total emission current), the result is quite different from what could be expected on the basis of the results obtained in various adsorption experiments for the (111), (110), (100) planes of a large single crystal of platinum as well as for Pt polycrystalline substrate and film, which were carried out by using other methods [1, 4, 5, 19]. It is known that a molecule of water is adsorbed on a metal surface through the oxygen bond [1] with the dipole moment directed from the surface outwards. Such interaction between water and metal is responsible for the reduction of work function with increasing coverage. It is also known that the products of dissociation of water cause the increase in the work function of metals [1]. However, annealing of the H_2O covered emitter, which followed the adsorption runs that produced the data of Fig. 2 (within the temperature range 160–170 K, few seconds exposure) ensured attaining a clean emitter. This result excluded such possibility to explain the present result. The increase in the work function is supposed to be field-originated. The action of the electric field directed inwards the substrate can lead to a reorientation of H_2O admolecules which are then bound with the substrate surface owing to their configuration different than the typical one (i.e. via an oxygen atom). As a result of the field-induced reorientation the molecule may behave as the Lewis acid rather than base and, consequently, a rise of work function upon the adsorption is expected.

This argumentation is in good agreement with the results of Bonzel et al. [20]. They have shown (theoretically) that an H_2O molecule co-adsorbed with a potassium atom on a Pt_{10} cluster is tilted by an angle of 160° with respect to the surface normal, with the hydrogen atoms pointing towards the substrate. The change of the molecular orientation is caused by the electrostatic interaction with the K^+ ion. The ultraviolet photoemission spectroscopy (UPS) measurements [20] for the system of Pt(111)K–H_2O have shown that for the K coverage $\Theta < 0.1$ the adsorption of H_2O molecule on this plane is characterized by an increase in the work function Φ. Under these conditions with no positive electric field applied, no H_2O dissociation takes place. The increase in Φ should be mainly caused by a change in the H_2O molecular orientation which results in the change of the sign of the dipole moment of the molecule from "+" to "–" [20]. In the present case the driving force for the orientation change of the molecule can be that of the external electric field (applied in the FEM mode of operation).

However, a decrease in the average work function during the adsorption of water on W and Ir field-evaporated emitters at 85 K was reported by Sotola et al. [21]. Those authors used a channelplate intensifier which enabled to observe the FE patterns at a lower strength of electric field than the one typically required. Although that study concerned other substrates, it can be reasonably assumed that the strength of the electric field in the experiment was not high enough to affect the water adsorbate, and a decrease in Φ could be observed rather than an increase.

4.1.2. Field-promoted desorption

A. Submonolayer coverages

According to the very recent results of Stintz and Panitz [22] the field desorption of negative ion clusters like $(H_2O)_nOH^-$, with $n = 1, \dots, 8$, can take place in a negative electric field. The field strength F which is required for the desorption strongly depends on the substrate temperature, e.g., at 150 K the strength should be $F = 20$ MV/cm (which is below the value required for an electron emission from the clean metal surface) [22]. Although during a typical experiment done by Stintz and Panitz [22] the H_2O layer thickness was about 10 nm, i.e. much higher than in the present work, the results shown in Figs. 2 (point P), 3, 4 and 1c–e can be understood taking into account the possibility of the field desorption of negative ions from the emitter. Then, after the desorption, the residual water layer on the substrate should be protonated (hydrogen-rich) according to the reaction ([22], Ref. [31] therein)

$$(H_2O)_{n+2} \rightarrow (H_2O) \cdot H^+ + (H_2O)_n \cdot OH^- \qquad (2)$$

(where $n = 1, \dots, 8$) with the positive H^+ being solvated in the ice layer. However, in the present work, the thermal desorption of the adlayer after the action of the negative field as a result of annealing was observed at a temperature low as at 160–170 K. On the other hand hydrogen desorbs from the Pt emitter at much higher temperatures [23, 24, 25]. Also the FE pattern and electric measurements taken for the stage of the emitter surface represented by the point N in Fig. 3 indicated that the surface was clean after the negative field had been applied. It is possible that the amount of the residual hydrogen is too small to be detected in this way or mainly neutral water molecules are desorbed from a submonolayer at elevated temperature and in the presence of the electric field. It is also likely that the negative field promotes evaporation of H_2O from the Pt surface as a result of the field-induced reorientation of admolecules. The binding energy of the field-reoriented molecules on the Pt surface is expected to be much lower than the one corresponding to the typical oriented molecule [26]. In consequence, water will be desorbed at a lower temperature than in the case of the absence of field.

B. Multilayer coverages

The desorption at 78 K (Figs. 1c–e and 4) could begin for $\Theta > 4 \div 5$ at the field $F \approx 52$ MV/cm and a density of FE current estimated to amount to more than 1000 A/cm^2. FE micrographs show (compare Fig. 1a and Fig. 1e) that the water layer or rather its dissociation products were not completely removed from the apex of the emitter. In the stage to which Fig. 1e corresponds (after field reduction of the water coverage) the influence of the electric field on the residual adsorbate could be neglected and Fowler–Nordheim (F–N) characteristics were reproducible if the voltage applied (or FE current) did not exceed the ones required to obtain this stage. The F–N measurements indicated that the work function Φ of the Pt emitter of Fig. 1e (with the high-emission central part of the emitter surface surrounded by the thick water layer) was a little lower than the Φ for the clean Pt emitter ($\Delta\Phi \approx -0.1$ eV). An evidence for enhanced emission from the Pt(100) plane is also seen in Fig. 1e. This supports the supposition that the field desorption of negative ions really takes place under such conditions and the residual water layer on the substrate is protonated according to reaction (2). The remaining H^+ ions deliver the positive charge to the metal, where charge exchange can occur and the adlayer becomes hydrogen-enriched. According to Ref. [22] the hydrogen coverage after the field desorption is estimated to be below one monolayer. Hydrogen-water co-adsorbate can reduce the work function of the Pt(111) plane [27], and hydrogen can lead to the same effect on the Pt(100) [24] and Pt(110) [25] planes at low temperatures. However, hydrogen was not detected after the heating of the emitter at 170 K. This means that hydrogen deposit was small.

A satisfactory explanation of the role of FE current played in the water removal mechanism is lacking, at present.

A similar effect (of water desorption) was observed by Sotola et al. [21]. In their experiment a large water layer ($Q \gg 1$) sometimes was suddenly removed, which was followed by a tremendous increase in the FE current.

4.2. Surface diffusion

Information on the magnitude of the diffusion barrier for adsorbed H_2O is derived from the theoretical prediction: (i) the height of the diffusion barrier is approximately 10% to 40% of the value for the desorption barrier [3, 17]; (ii) the differences in binding energy between various types of sites should correspond rather closely to the diffusion barrier. This consideration leads to the conclusion that the energy barrier for the surface diffusion of H_2O molecules on metals should range from 3 to 27 kJ/mol [1]. From experimental studies of the vibration spectra of H_2O adsorbed on Pd(100) and Cu(100) it can be deduced that the barrier for the displacement of an isolated molecule of water is very low on those substrates (hydrogen-bonded clusters are formed from H_2O monomers if the surface is held at 20 K) [28]. Small clusters of H_2O are also formed at 100 K on Pt(110)(1×2) [29].

Plots of x^2 versus t in Figs. 5 and 6 show that the motion of the diffusion front does not obey well the diffusion relation $\langle x^2 \rangle / t = cD$ [17], where D is the chemical diffusion coefficient and c is a constant. Apparently a strong interaction between molecules is responsible for this. The spreading rate of the sharp boundary of diffusion is not uniform along crystallographic zones. The boundary moves fastest in the stretch between the (111) and (131) planes and is distinctly moderate (in the temperature range used it comes almost to a stop) on some regions between the (131) and (010) planes, which is clearly seen in the FE micrographs. Although the anisotropy of the activation energy is weak it indicates that the surface topography plays also a role in the transport mechanism of the multilayer water on a metal surface.

We assume that the sharp boundary diffusion has the "unrolling the carpet" mechanism proceeding from a multilayer to the water- and/or hydrogen-submonolayer covered region on the surface seen as the bright area in Fig. 1e. The diffusion of water could be accompanied by hydrogen diffusion from the emitter apex to the emitter shank but its effect on the water diffusion is difficult to estimate.

As the hydrogen bond strengths in ice and water are typically 15 to 25 kJ/mol [1], which roughly coincides with the determined activation energy for the diffusion

($E = 19$ and 25 kJ/mol), it can be suggested that during the diffusion of the water multilayer under these conditions first of all the hydrogen bond must be broken.

4.3. Effect of positive electric field

In this case, under the influence of the positive electric field, positively charged water clusters are formed on an ice surface according to the reaction $(H_2O)_{n+1} \rightarrow (H_2O)_n H^+ + OH^-$ and which was early proposed ([2], Refs. [10, 34] therein). The dissociation product OH^- is not stable. Contact with the surface leads at first to the reaction $OH + e_{Me}$ and then to $2OH \Rightarrow H_2O + O_{ad}$. Thus, it is reasonable to assume that O_{ad} is responsible for the reduction of the emission current (i.e. for the increase in U_{H_2O} in saturation curves of Fig. 9) connected with the appearance of dark spots in the patterns shown in Figs. 10a–d. According to Lewis and Gomer [14], oxygen which increases the work function of the Pt emitter is thermally desorbed at a temperature above 1000 K.

The dependence of the voltage U_{H_2O} on the substrate temperature for higher coverages (Fig. 9) can be understood taking into account the possibility of the diffusion of oxygen from the emitter apex to its surroundings.

5. Summary

The sharp boundary diffusion of a multilayer of water over the Pt emitter surface was observed in the substrate temperature range of $T = 120 \div 132$ K. The gradient of water coverage was obtained by the partial desorption of water from the apex of the emitter upon drawing a high-density FE current when the emitter was kept at 78 K. The diffusion proceeded with the "unrolling the carpet" mechanism from a surface region covered with a water multilayer to the one covered with a water- and/or hydrogen-submonolayer and needed the activation energy $E = 19$ and 25 kJ/mol depending on the crystallographic direction. The activation energy is roughly the energy of one mole of hydrogen bonds (15 to 25 kJ/mol). This suggests that the rate limiting step for the process is simply the breaking of one hydrogen bond between the diffusing molecule and its neighbor.

The presence of the negative field in the FEM mode of operation, which was examined in the range of 33–44 MV/cm, significantly lowered the desorption temperature of water. It is believed that the negative field brings about reorientation of H_2O molecules on the Pt emitter surface. This effect is assumed to be responsible for the reduction of the total FE current (i.e. the increase in the FE work function) during the adsorption of water as well as for the weakening of the binding force between the H_2O molecules and the substrate in the presence of negative field.

An effect of a positive field of 44 MV/cm, at the substrate temperature in the range of 121–133 K, was such that the field emission of electrons from the system was reduced to a higher extent than in the presence of the negative field. The positive field caused that the removing of the layer required to apply a much higher temperature, $T > 720$ K, than in the case of the absence of the positive field. Dissociation of water during the field desorption of the adlayer apparently took place under these conditions. The results are in accordance with the ones of Stintz and Panitz of [2, 22].

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