

MEASUREMENT OF THE SURFACE-DIFFUSION ACTIVATION ENERGY OF POTASSIUM ON TUNGSTEN

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The average activation energy of surface-diffusion of potassium on tungsten was measured by a field emission method. Diffusion both without a sharp moving boundary and without an electric field was investigated. The value of 0.21 eV was obtained for coverage $\bar{\theta} = 0.2$. The correctness of the method used is discussed.

Introduction

Surface diffusion of potassium on tungsten is interesting not only in its own right (Schmidt and Gomer 1965), but also it is the main source of flicker noise in field emission (Kleint 1963, Timm and van der Ziel 1966, Kleint 1969). Adatoms diffusing over a monocrystal change the local work function and cause fluctuations of the field emission current. Surface diffusion of potassium on tungsten is especially appropriate for investigation of the flicker noise because of the relatively strong noise caused by the large anisotropy and large changes of the work function. It seems that some of the assumptions of the theory of the flicker noise are not fully adequate relative to the real diffusion processes, namely, on the emitter tip the real diffusion processes are more complicated.

The last decade has brought some advances in the study of the surface diffusion processes of potassium on tungsten (Naumovets 1963, 1964; Popp 1964; Schmidt and Gomer 1965) but the understanding of these processes is still incomplete. It seemed worthwhile, therefore, to continue the study of the problem.

Apparatus

The measurements were carried out in conventional, sealed-off emission tubes. The emission tubes were equipped with Bayard-Alpert ionization gauges, PTJ-4A titanium pumps and potassium sources. The potassium was cleaned by seven-fold high-vacuum distillation. Before beginning the measurements potassium was deposited onto the emitter from a thermostatically controlled source. The source and the tip assembly leads were kept

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in liquid air during the measurements. The temperature of the emitter was controlled by an electric heating loop. The temperature of the emitter was determined by means of a tungsten-molybdenum thermocouple. The residual gas pressure was less than 10^{-10} torr. There was no visible contamination of the clean emitter for many hours.

Method and results

Utsugi and Gomer (1962) observed diffusion of barium from the shank into the bare apex region of the emitter. In present investigations a similar technique was used for determining the surface-diffusion activation energy of potassium on tungsten.

The measurements were carried out as follows. After depositing the potassium and spreading it by heating over the surface, the emitter was cooled down to about 85°K and

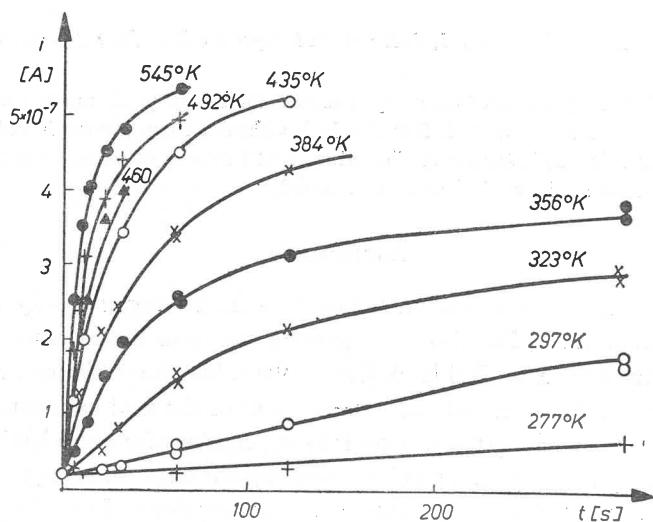


Fig. 1. The changes of emission current (at constant voltage 3660 V and at various temperatures T_d) during surface diffusion. Several points were obtained after cooling down of the emitter to $\sim 85^\circ\text{K}$

the work function was measured in order to determine the average degree of coverage. Then the temperature of the emitter was raised to the value T_d at which surface diffusion takes place. At this temperature a positive electric field was applied and potassium was desorbed from the region of the high field at the emitter, *i. e.* from the apex region. The shank remained covered with potassium because the field there was too low. The absence of potassium on the whole hemispherical part of the emitter was proved in additional experiments: at constant voltage the emission currents for this case and for clean tungsten were the same; the emission patterns were also the same. After the desorbing field was switched off surface diffusion of potassium from the shank towards the apex region without a sharp moving boundary was observed. The work function of the apex region decreased and the emission current (at constant voltage) increased. These changes of the emission current (at constant voltage 3660 V and at various temperatures T_d) are shown in Fig. 1. It is a well-known pheno-

menon that an electric field can alter diffusion processes (Naumovets 1963, 1964). In order to eliminate the influence of both the electric field and heating of the emitter by emission current (Błaszczyszyn, Błaszczyszynova and Męclewski 1967) the measurements (Fig. 1) were carried out without electric field. Potassium diffused in a given time interval at temperature T_d and then, after the emitter had cooled down to a temperature of $\sim 85^\circ\text{K}$ (at which diffusion does not take place), the emission current was measured. In consideration

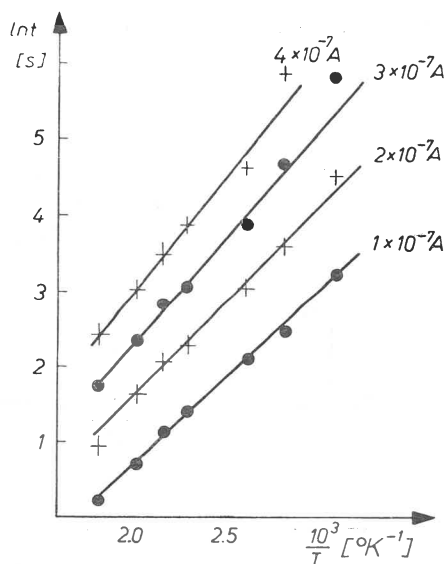


Fig. 2. Arrhenius plots corresponding to the successive endpoints of diffusion

of the thermal capacity of the tip assembly, each point of the i versus t curves was always obtained after the potassium was spread. The measurements were carried out at an initial average of coverage of the shank $\bar{\theta} = 0.2$.

Four diffusion ranges were chosen for the calculation of the average activation energies. Endpoints of diffusion were determined by suitable values of the emission current at constant voltage (3660 V), namely $i_1 = 1 \times 10^{-7}\text{A}$, $i_2 = 2 \times 10^{-7}\text{A}$, $i_3 = 3 \times 10^{-7}\text{A}$ and $i_4 = 4 \times 10^{-7}\text{A}$. Starting points of diffusion were in all cases the same: $i = 2 \times 10^{-8}\text{A}$. They correspond to the emission current for the clean tungsten tip.

Arrhenius plots corresponding to these diffusion ranges are shown in Fig. 2. The average activation energies corresponding to these diffusion ranges calculated from the slopes of the Arrhenius plots are $Q_1 = 0.21$ eV, $Q_2 = 0.22$ eV, $Q_3 = 0.24$ eV and $Q_4 = 0.26$ eV, respectively. Most of the calculations were made with a computer. The accuracy of the measurements was estimated at ± 0.02 eV. The increase of the calculated activation energy is small, but it is a little larger than the accuracy of the measurement. This increase is smaller for the initial stages of diffusion and larger for later ones.

The changes in the emission pattern during diffusion at various temperatures were the same. They corresponded to the changes in the emission pattern during an increase of co-

verage from $\bar{\Theta} = 0$ to $\bar{\Theta} = 0.2$ (Schmidt and Gomer 1965; Błaszczyszyn, Maślankówna, Męclewski and Nikliborc 1965). This seems to indicate that diffusion without a sharp moving boundary takes place in the same way in the whole range of temperatures. Therefore, it may be assumed that the distribution of the potassium concentration is determined by the emission current at constant voltage.

In the temperature range of the experiments, namely, 221°K to 545°K, very weak evaporation of potassium was observed. It may be neglected because it was detectable at very high temperature only and after a very long time had lapsed.

Discussion of results

There are different boundary and initial conditions for the initial stages of diffusion and for the later ones investigated here. In the initial stages of diffusion potassium flows over the bare cylindrical shank towards the spherical part of the emitter. The process may

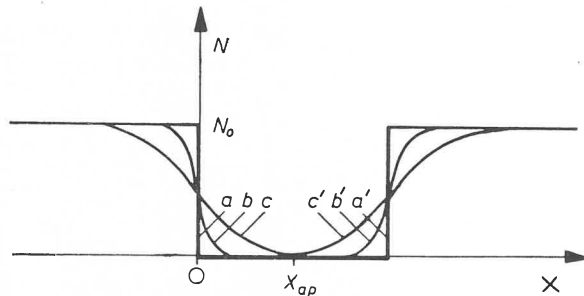


Fig. 3. One-dimensional model of diffusion towards the apex. aa' — the distribution of the concentration corresponds to the time $t = 0$, bb' — the distribution corresponds to the time t_1 (initial stage of diffusion), cc' — the distribution corresponds to the time $t_2 > t_1$, when potassium arrives at the apex. x_{ap} is the coordinate of the apex, $x = 0$ and $x = 2x_{ap}$ the coordinates of the sharp boundary after desorption on the two sides of the tip

be treated as one-dimensional diffusion along a semi-infinite cylinder. Then diffusion proceeds over the bare spherical part of the emitter. At last, in the later stages of diffusion potassium flows towards the apex over the covered surface of the sphere.

During an initial stages of diffusion potassium flows from the covered shank ($\bar{\Theta} = 0.2$) to the bare apex region ($\bar{\Theta} = 0$). Assuming both a model of one-dimensional diffusion in an isotropic medium and the existence of a sharp boundary between the covered and bare part of the emitter after desorption (Fig. 3, curve a) we have the case of diffusion along a semi-infinite straight line. The solution of this problem is to be found, for instance, in Crank's book (1956, p. 11–12) or in Bořtaks' book (1961, p. 129):

$$N(x, t) = \frac{1}{2} N_0 \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right) \quad (1)$$

(Fig. 3, curve b), with the initial conditions $N(x, 0) = N_0 = \text{const.}$ for $x < 0$ and $N(x, 0) = 0$ for $x > 0$. Here t is the time of diffusion, x the coordinate (the sharp boundary after desorption is at $x = 0$), $N(x, t)$ the concentration of the diffusing substance, N_0 the initial concen-

tration on the shank corresponding to the average of coverage $\Theta = 0.2$, D the diffusion coefficient, and $\text{erf } z = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy$ is the error function.

Since $N(x, t)$ depends only on $\frac{x}{2\sqrt{Dt}}$ and does not depend on x and t separately, we can use the square-root relationship (Crank 1956, p. 35) and, hence, for determining the average activation energy we can use the method of Arrhenius plots. For the initial stage of diffusion the starting points were the same, namely, $i = 2 \times 10^{-8} \text{ A}$, and the endpoints were also the same, $i_1 = 1 \times 10^{-7} \text{ A}$, for all curves, *i. e.* for several temperatures T_d (Fig. 1). Since for the endpoints of diffusion the distribution of the potassium concentration is the same and for a given $x = x'N(x', t)$ is the same (N_0 is constant), we have from (1):

$$\frac{x'}{2\sqrt{Dt}} = \text{const.}$$

for all curves (for several temperatures T_d). Since x' is also a constant, we have

$$Dt = K$$

(K being a constant) and, hence,

$$A \exp\left(-\frac{\bar{Q}}{kT_d}\right) = \frac{K}{t}$$

where A is a pre-exponential term of the diffusion coefficient, \bar{Q} the average activation energy, k Boltzmann's constant, and T_d the temperature of diffusion. Taking logarithms we obtain

$$\ln \frac{1}{t} = -\frac{\bar{Q}}{k} \times \frac{1}{T_d} + B \quad (2)$$

where B is a constant. Calculating the time t as a function of temperature T_d from Fig. 1, we obtain an Arrhenius plot from (2) (Fig. 2) corresponding to the endpoints of diffusion determined by the emission current $i_1 = 1 \times 10^{-7} \text{ A}$ (similar Arrhenius plots correspond to the endpoints of diffusion determined by the emission current $i_2 = 2 \times 10^{-7} \text{ A}$, $i_3 = 3 \times 10^{-7} \text{ A}$ and $i_4 = 4 \times 10^{-7} \text{ A}$).

Other initial and boundary conditions are valid at the later stages of diffusion because (i) potassium arrives at the apex and then in a finite system diffusion proceeds over the covered surface, and (ii) potassium flows over the spherical part of the emitter. Diffusion proceeds symmetrically (meridianly) towards the apex. Assuming the one-dimensional model described above we have diffusion on the right and on the left towards the apex (curve cc' in Fig. 3). Since $N(x_{\text{ap}} - x) = N(x_{\text{ap}} + x)$, where x_{ap} is the coordinate of the apex, there is no flow of diffusing substance through the apex. Therefore, when potassium arrives at the apex we have other boundary conditions, *i. e.* a finite system. Under these conditions diffusion proceeds over the covered surface from the shank towards the apex. The difference of the potassium concentration between the apex and the shank decreases. Finally, the gradient of the concentration becomes zero and diffusion is stopped (in Fig. 1 the emission current

becomes saturated). The rate of diffusion depends in this case both on the variable gradient of the concentration and on the temperature. In addition, we have other boundary conditions because diffusion proceeds over the surface of the sphere. Under new boundary and initial conditions due to (i) and (ii) the solution cannot be written as a function of the parameter x/\sqrt{t} alone. Therefore (Crank 1956, p. 14-15 and p. 35-37) we cannot use the method of Arrhenius plots for determining the activation energy. The obtained straight lines (Fig. 2) show that the deviation from the square-root relationship is still small relative to the accuracy of the measurements.

The above considerations show that the measurement of the average activation energy must be carried out only during the initial stage of diffusion. On the other hand, the increase of the calculated values of activation energy is smaller for the initial stages of diffusion than for the later ones. This indicates that the value of 0.21 ± 0.02 eV is nearest to the true value of the average activation energy. The apparent increase of the activation energy at later stages of diffusion is caused either by the change of the boundary and initial conditions or by a real increase of the activation energy due to the increase of the concentration in the apex region and adsorbate-adsorbate interactions. It is possible that this increase is caused by both a change of the boundary conditions and adsorbate-adsorbate interactions.

To describe a real system the relatively simple model presented here would have to entangle a number of other effects. (1) In initial stages of diffusion potassium flows over the conical (or hyperboloidal) shank. The assumption of cylindrical shape is correct only for a small angle of the conic (therefore in the present experiment desorption was carried out at maximum desorbing electric field). (2) The real surface is anisotropic. (3) After desorption the boundary between the covered and bare part of the emitter is not sharp because the desorbing field varies along the emitter.

The obtained value of 0.21 eV is in reasonable agreement with the results of Naumovets (1964) and Schmidt and Gomer (1965). Naumovets measured the change of the average activation energy of potassium on tungsten as a function of the applied electric field. He obtained a difference of approximately 10 per cent in the range up to -15 MV/cm and 20 per cent in the range up to $+20$ MV/cm. Such influence of the electric field on diffusion was also found in present investigations. Without electric field at $\bar{\theta} = 0.2$ (?), estimated from the emission pattern, Naumovets obtained 0.29 eV, but it seems that this value corresponds to the later stages of diffusion. Schmidt and Gomer used another method for measuring the average activation energy of potassium on tungsten. With a unilateral deposition for $\bar{\theta} = 0.2$ they obtained 0.27 eV.

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