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V. M. Gryaznov, V. I. Shimulis, and V. D. Yagodovskii

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V. M. Gryaznov, V. I. Shimulis, and V. D. Yagodovskii

THE EFFECT OF ADSORPTION OF BENZENE VAPORS ON THE ELECTRICAL CONDUCTIVITY OF TRANSPARENT PLATINUM FILMS OF DIFFERENT SURFACE DENSITY*

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The electrical conductivity of metallic films, upon adsorption of various substances on their surface, usually decreases linearly with coverage ([1–9]), which is used to calculate the number of conduction electrons of the metal localized by one adsorbed molecule ([5–7]).

In such calculations, data are needed on whether the metal surface being filled by the adsorbate is homogeneous.

In the present work we studied the effect of adsorption of benzene vapor at 20° on the electrical conductivity of transparent platinum films, which were prepared by sublimation of the metal at a residual pressure of $1 \cdot 10^{-7}$ mm onto the walls of a glass cell. Benzene vapors were introduced into the cell at a constant rate of $(3.8 \div 0.3) \cdot 10^{14}$ molecules per minute, which was less than the rate of establishment of adsorption equilibrium.

On a fresh platinum film, strong adsorption first occurs, as was observed on palladium films ([10]). The amounts of benzene adsorbed after completion of strong adsorption can be removed by pumping at room temperature, whereas strongly adsorbed benzene begins to desorb only at 250°. On glass, only reversible adsorption of benzene occurs, amounting to about 50% of the reversible adsorption at the same pressure on an equal apparent surface area of a platinum film.

The electrical conductivity of all the films studied decreases during the course of strong adsorption of benzene vapors (see segments AB of the curves in Fig. 1), and upon further filling of the surface changes in different ways depending on the amount of metal per unit apparent surface area. Three typical curves of the change in $\frac{\lambda-\lambda_0}{\lambda_0}$, where λ_0 is the electrical conductivity of the film before admission of benzene vapor, are presented in Fig. 1. With a film of effective thickness about 10 Å, reversible adsorption produced an increase in electrical conductivity

Fig. 1

Figure 1: Fig. 1

up to the initial value (see segment BB, 1). The electrical conductivity of films with effective thickness from 10 to 20 Å changes little upon reversible adsorption of benzene (see segment BG, 2) and decreases upon its pumping off. For films with effective thickness from 20 to 50 Å, reversible adsorption decreases the electrical conductivity (see segment BB, 3), but to a much lesser degree than strong adsorption. Pumping off reversibly adsorbed benzene in this case leads not to a decrease but to an increase in electrical conductivity to the level corresponding to completion of strong adsorption (see segment BG, 3).

The decrease in electrical conductivity upon strong adsorption of benzene on platinum films indicates that localization of part of the conduction electrons by benzene molecules occurs at very different surface densities of the metal. The opposite effect of reversible adsorption of benzene on the electrical conductivity of films with effective thickness

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about 10 Å and 20–50 Å can be explained by a substantial difference in their structure. As is known (see (11)), at low surface density a considerable fraction of the metal granules formed on the support are not connected with one another. Apparently, the electrical conductivity of such a platinum–glass system can increase upon adsorption of benzene between the metal granules.

In denser films the granules are connected by metallic "bridges." Reversible adsorption of benzene occurs mainly on the metal and decreases its electrical conductivity owing to localization of part of the conduction electrons, while evacuation of the reversibly adsorbed benzene increases it. At a certain surface density of the film, the influence of reversible adsorption of benzene on the metal and on the glass between the granules may prove comparable, and then the electrical conductivity will not change noticeably, as shown by the segment $B\Gamma$, 2 in Fig. 1. But on evacuation benzene is removed from the glass more readily than from platinum. Therefore, during evacuation the electrical conductivity first decreases, and, as the benzene reversibly adsorbed on platinum is removed, it increases (segments ΓD and DE, 2 in Fig. 1).

Fig. 1. Dependence of the relative change in the electrical conductivity of platinum films of different surface density on the time from the beginning of admission of benzene vapor.

To determine the character of the dependence of the electrical conductivity of platinum films of different surface density on the amount of strongly adsorbed benzene, experiments were carried out, the results of which are presented in Table 1.

Table 1

Dependence of the electrical conductivity of platinum films of different surface density on strong adsorption of benzene

Film No.	Film weight, mg	Number of Pt atoms per 1 cm^2, $N \cdot 10^{-16}$	Effective film thickness, Å	Electrical conductivity before benzene admission λ_0, ohm^{-1}	Number of benzene molecules strongly adsorbed per 1 cm^2, $n \cdot 10^{-14}$	$\Delta n \cdot 10^{-14}$	$-\frac{\lambda - \lambda_0}{\lambda_0}$, %	β
1	0.21	1.3	20	1.2970	4.3	1.4	0.82	0.4
2	0.46	1.6	24	0.2752	0.6	0.2	0.06	0.4
3	0.53	1.9	29	1.4133	2.7	0.5	1.00	2.2
4	0.60	1.9	29	1.1634	1.0	0.3	0.28	1.8
5	0.82	2.2	34	0.9174	2.2	0.3	0.42	0.4
6	0.36	2.5	38	1.2372	6.6	0.9	0.25	1.5
7	0.83	2.6	39	1.2149	1.4	0.4	0.37	1.2
8	1.01	3.1	50	1.1832	2.6	0.4	0.24	1.2

The electrical conductivity of films Nos. 4, 6-8 at the end of platinum sublimation was identical, but during holding at 80-100° it changed differently; the greatest difference in the values of λ_0 was 6%. Films Nos. 6 and 7, close in surface density and electrical conductivity, differ by a factor of 4 in the amount of benzene strongly adsorbed on 1 cm^2 of visible surface. For the platinum films studied in (6) with effective

with a thickness of 77-85 Å, the values of λ_0 also varied in a complicated way with increasing surface density and, even at the same density, differed by 4%. These facts indicate that the structure of platinum films depends strongly on the difficult-to-control features of the processes of their evaporation and formation.

Despite the differences in properties, for each of the films listed in Table 1, the curve of the dependence of electrical conductivity on the number of adsorbed benzene molecules has a linear segment. As can be seen from Fig. 2, on the linear segment, for strong adsorption of $\Delta n = 1.4 \cdot 10^{14}$ benzene molecules per 1 cm^2 of film No. 1,

$$\frac{\lambda - \lambda_0}{\lambda_0}$$

Fig. 2

Figure 2: Fig. 2

is 0.8%. The corresponding values of

$$\frac{\lambda - \lambda_0}{\lambda_0}$$

and Δn for the remaining films are given in Table 1.

Fig. 2. Dependence of the relative change in the electrical conductivity of platinum film No. 1 on the number of benzene molecules adsorbed on 1 cm^2 of the visible surface

There are also given the values of β—the average numbers of conduction electrons of platinum localized by one benzene molecule. The calculation of β was carried out according to the formula used in works ([5–7]). The values of β range from 0.4 to 2.2, and no simple dependence on surface density is observed.

In the adsorption of benzene vapors on nickel films ([7]), for three films the values of β turned out to be close to 6, and the conclusion was drawn that 6 covalent bonds are formed between the benzene molecule and the film. However, for two other nickel films prepared under the same conditions ([7]), the slope of the linear segment of the dependence of electrical conductivity on adsorption differs significantly from the average for the first three films.

It can be shown that the simplifying assumptions made in calculating β do not correspond to reality. The linear dependence of the electrical conductivity of films on adsorption does not prove the uniformity of the centers being filled; it will also be observed on films with centers of different adsorption potential. It is necessary only that the relative numbers of these centers be the same for all parts of the film and that transfer of adsorbed molecules from center to center not take place, or take place sufficiently slowly. Under these conditions, the change in the electrical conductivity of the film attributable on average to one adsorbed molecule will prove to be constant over a certain range of coverages, but it will be only an effective average with respect to some range of true values of the electronic interaction of adsorbate molecules with the metal. The width of this range should increase with decreasing temperature because of the increase in the "lifetime" of molecules on adsorption centers. We found that at 20° the adsorption of benzene vapors on platinum films occurs simultaneously on centers with different adsorption potentials even at small coverages. Especially illustrative are the experiments with a cylindrical cell, in which the contact wires for measuring electrical conductivity (a, b in Fig. 3) were located only under the upper half of a continuous platinum film of length bc. When benzene vapor was admitted into the cell through tube d, the electrical conductivity of the upper half of the film did not change until

Fig. 3

Figure 3: Fig. 3

adsorption of benzene occurred on the lower half of the film (see segment AB in Fig. 3). After this, a linear drop in electrical conductivity was observed, corresponding to strong adsorption of benzene (segment BG), and a less rapid decrease (segment GD) during reversible adsorption.

When benzene vapor was admitted through tube e, the electrical conductivity decreased at once (H_1 on curve 2 in Fig. 3). If the admission of vapor was stopped before the completion of strong adsorption (P_1 in Fig. 3), the electrical conductivity changed hardly at all. If, however, strong adsorption on the upper part of the film had ended, then after the admission of vapor was stopped (P_2, P_3, P_4) the electrical conductivity increased, as when reversibly adsorbed benzene was pumped off (cf. segment DE of curve 1). The same results were obtained in the absence of contact between the two parts of the film (see the diagram in Fig. 3). These facts are difficult to explain by anything other than the migration of benzene molecules that had occupied sites with a low adsorption potential on the upper part of the film to sites of stronger adsorption not yet filled on the lower part of the film, whose electrical conductivity was not measured.

Fig. 3. Dependence of the relative change in the electrical conductivity of platinum films on the conditions of supplying benzene vapor

The foregoing shows that, in the portions of the film adjacent to the place where vapor is admitted, not only strong but also reversible adsorption occurs earlier than strong adsorption begins on the more remote portions of the film. About 10 min is required for redistribution of the adsorbed molecules at 20°. It is easy to see that in experiments carried out at 90 or 77°K ([7]), this redistribution practically did not occur, and the observed dependence of the film electrical conductivity on the amount adsorbed is not sufficient for quantitative estimates of the electronic interaction of benzene molecules with the metal. Study of changes in the electrical conductivity of metallic films during adsorption and desorption makes it possible to detect redistribution of the adsorbate among sites with different adsorption potentials and to estimate the mean residence time of molecules on them.

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.