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Abstract

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Study of the Formation of Semiconducting Films of the Polymeric Complex of Tetracyanoethylene on Metals by the Method of Volta-Potential Measurement

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The present work was undertaken in connection with the study of the electrophysical properties of films of the polymeric complex of tetracyanoethylene (TCE) on various metals.

It seemed of interest to determine how the work function and the adsorption capacity change as the film grows.

The change in the work function during film formation was studied by the vibrating-capacitor method ([1]). The film was obtained by the interaction of TCE vapors with the surface of copper and nickel, previously reduced in hydrogen.

The Volta potential was measured in an apparatus in which the reference electrode was a molybdenum plate sealed in glass ([2]). The Volta potential of such an electrode relative to gold, according to data obtained in R. Kh. Burshtein' s laboratory, is 0.2 V.

Copper (99.99%) and nickel (99.99%) plates were used as the electrodes under investigation. Preliminary treatment of the electrodes consisted of repeated reduction with hydrogen at a temperature of 350° and subsequent degassing, usually to $1—2 \cdot 10^{-5}$ mm Hg at the same temperature. Similar results were obtained in experiments in which the system was evacuated to a residual pressure of $3 \cdot 10^{-6}$ mm Hg. TCE vapor was introduced into the cell from a special side arm, which was connected to the apparatus by means of a break seal. The pressure of TCE vapor in all experiments corresponded to its vapor pressure at 20° and was $5—6 \cdot 10^{-3}$ mm Hg. All Volta-potential measurements were carried out at room temperature, regardless of the reaction conditions. When measuring the Volta potential in TCE vapor it was necessary to take into account the magnitude of the change in Volta potential resulting from adsorption of TCE on the glass-covered reference electrode. To determine this value, experiments were carried out to measure the Volta potential in TCE vapor, with

the reference electrode capable of being heated very rapidly to temperatures above 200°, while the electrode under investigation was heated in practice to no more than 50–70°. In this case a decrease in the Volta potential by 0.15 ± 0.05 V was observed in comparison with the values obtained without heating the reference electrode. As will be shown below, adsorption of TCE in the case of a copper surface, with which TCE reacts most readily, is to a considerable extent reversible. It was therefore assumed that, upon heating the reference electrode, its surface could be made free of adsorbed TCE, whereas adsorption on copper remains almost unchanged because of the insignificant change in the temperature of the electrode under investigation. The correction thus obtained was subtracted in all cases where measurements were made in the presence of TCE. In control experiments, the film thickness was determined by weighing at the initial stage of growth, when changes in weight began to be observable, and at the final point, when the Volta potential ceased to change as the film grew. The maximum values of the Volta potential in the experiments differed by no more than 0.15 V. At zna-

measurements of the Volta potential close to zero, the relative error reached 25%, since the accuracy of measurement in this region was 0.05 V.

The process of film formation may conventionally be divided into a number of stages: adsorption of TCE on the surface of the metal reduced in hydrogen; the initial moment of film formation, when the work function from the electrode under study is maximal; film formation noticeable from the change in color and weight of the electrode under study, while the work function begins to decrease; attainment of such a thickness at which further heating of it in TCE vapors does not lead to a change in the work function.

At each of these stages, experiments were carried out on the desorption of TCE from the electrode surface in order to determine what part of the total change in the work function can be attributed to film formation, and what part to adsorption of TCE on it. By the latter is meant that part of the change in the Volta potential which is due to desorption of TCE from the electrode at 200°.

Table 1

Effect of adsorption of TCE vapors on the change in the work function during formation of a polymer film on copper (relative to a clean copper surface)

Electrode treatment	after adsorption of TCE at 20°C	after heating in TCE vapors for 15 min.	with a film $2 \cdot 10^{-6}$ thick present
Adsorption at 20°	0.74	1.1	0.98
Desorption at 20°	0.55	0.80	0.85

Electrode treatment	after adsorption of TCE at 20°C	after heating in TCE vapors for 15 min.	with a film $2 \cdot 10^{-6}$ thick present
Desorption at 200°	0.35	0.67	0.70
Repeated adsorption at 20°	0.65	—	0.98

The reversibility of TCE adsorption at different stages of film formation was also investigated. Desorption of TCE vapors was carried out at the temperature of film formation (not above 200°) in order to avoid noticeable changes in the film itself.

Upon adsorption of TCE on copper and nickel at room temperature, the magnitude of the Volta potential changed, respectively, by 0.74 V and 0.51 V on the surfaces of copper and nickel reduced in hydrogen. An increase in the work function upon adsorption of TCE was observed for 20-30 min after admission of the vapors, after which it became constant.

Table 1 gives the results for the adsorption of TCE on copper at room temperature and its desorption during evacuation. From the data of Table 1 it is seen that during evacuation for three days the work function from the electrode decreases by 0.19 V. After heating to a temperature of 200° with simultaneous evacuation of TCE vapors, the electron work function is only 0.35 V greater than from the surface of copper reduced in hydrogen. Upon thawing, the electrode again adsorbs TCE vapors, and the work function increases to 0.65 V.

Heating the cell in TCE vapors for 15 min at 200° increases the work function still more (second stage). For copper the maximum change in the work function reaches 1.1 V, and for nickel +0.87 V. At this stage there are no visible changes in the electrode, and the film, if it has formed, is not determined by weighing (at a thickness of $2—3 \cdot 10^{-6}$ cm, the change in weight of plates with an area of 6 cm^2 was $2—3 \cdot 10^{-5}$ g and was measured with an accuracy of up to $5 \cdot 10^{-6}$ g).

From the data of Table 1 it is also seen how the Volta potential changes upon evacuation of the cell under conditions where the work function from the electrode is maximal. At room temperature, desorption of TCE decreases the work function by 0.3 V. Upon heating in vacuum, the Volta potential decreases by another 0.13 V.

The results obtained for adsorption-desorption of TCE on a film $2 \cdot 10^{-6}$ cm thick (third stage) are presented in Table 1. From the data given it is seen that the magnitude of the work function upon desorption of TCE can

be decreased by 0.28 V. Repeated adsorption of TCNE again increases the work function, which proves to be close to the initial value. From this it may be con-

cluded that adsorption of TCNE on the film, as on the "clean" metal, is reversible to a considerable extent. The presence of reversible and irreversible adsorption was also found in studying the influence of adsorbed organic substances on the electron work function of metals and semiconductors.*

Figure 1 shows the change in work function during formation of the film. The shaded part in Fig. 1 corresponds in magnitude to the increase in work function after desorption of TCNE from the electrode upon heating and characterizes the change in work function from the degassed surface of the film during its operation. From Fig. 1 it is evident that, as the film becomes thicker, the work function

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Fig. 1. Change in the work function from the surface of the electrode under investigation during formation of a film on copper after desorption of TCNE (shaded region); the same during adsorption of TCNE on the surface of the electrode under investigation (unshaded region).
1 —treatment with TCNE vapor at 20°; 2 —heating in TCNE vapor for 15 min. at 200°; 3 —formation of a film of thickness $2 \cdot 10^{-6}$ cm; 4 —formation of a film of thickness $9 \cdot 10^{-5}$ cm

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passes through a maximum, whereas the effect of TCNE adsorption (unshaded part) at the first and second stages of film formation almost coincides, and then continuously decreases and becomes constant only on a film of thickness of the order of 10^{-4} cm, not exceeding 0.1-0.15 V.

After heating for 15 min., the work function reaches its maximum value (Fig. 1, 2). Further heating of the plate in TCNE vapor leads to a gradual decrease in the work function. At this stage, film formation is noticeable from the weight gain. In this case the color of the film on copper changes from yellowish to reddish-violet and finally becomes black. At a film thickness of about $2 \cdot 10^{-6}$ cm (Fig. 1, 3), the increase in work function is 0.70 V, and at a thickness of the order of 10^{-4} cm, 0.55 V. This value does not change with further thickening of the film. The resulting film is very inert. The change in work function is imperceptible even when air is admitted or when heating in hydrogen at 350°. When the cell was heated for 2 hours at 400° with removal of TCNE vapor, the decrease in work function was only 0.05-0.1 V.

The increase in work function upon adsorption of TCNE is apparently associated with the formation of dipoles Me^{+}—$TCNE^{-}$. As the film forms, access to the metal ceases and dipoles $film^{+}$—$TCNE^{-}$ are formed. However, whereas the effect of reversible adsorption of TCNE on a clean metal is +0.40 V, on a thick film the increase in work function due to reversible adsorption does not exceed +0.15 V. This indicates that the film is a weaker electron donor than the metal. Intermediate states corresponding to a thinner film show how the metallic substrate stimulates the donor properties of the film. This effect may

be interpreted in light of works ([3,4]), where the possibility is shown of changing the work function, adsorption capacity, and catalytic–

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* To be published elsewhere.

activity owing to a change in the position of the Fermi level for films whose thickness is less than the Debye screening radius.

As is known, observation of the Hall effect in organic semiconductors is at present difficult. It therefore seemed of interest to estimate the concentration of free carriers n in the film, using the known formula for the Debye screening length d

$$d = \sqrt{\frac{\varepsilon kT}{8\pi e^2 n}},$$

where ε is the dielectric constant, e is the electron charge, k is Boltzmann' s constant, and T is the absolute temperature. Taking $\varepsilon = 5$, $d \sim 10^{-5}$ cm, we obtain $n \sim 10^{15}$ cm^{-3}. The correlation we have found between the change in the electrical properties of the films and the change in the Volta potential will be published in the near future.

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