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Abstract

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PHYSICS

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CURRENT OSCILLATIONS IN β -CAROTENE FILMS

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In 1964, Cherry and Chapman (¹) first discovered current oscillations in a single crystal of the organic semiconductor β -carotene when it was heated in vacuum to a temperature of 120°C. Below we describe current oscillations that we have discovered in amorphous films of β -carotene, as well as in a mixture of carotene with protoporphyrin.

The measurements were carried out by the direct-current method in surface-type cells. The sample was connected in series with a constant-voltage source (UIP-1, VS-22) and a current meter (VI-2), from whose output the signal was fed through a divider to an electronic recording potentiometer (EPP-09). The samples were placed in a thermostated metal cuvette with an optical window which, together with the lead wires, was located in a metal shielded casing. All measurements were performed in air at room temperature. The optical part of the setup consisted of a 750-W movie lamp, focusing lenses, a heat filter (a 15-cm layer of water), and light filters. A command device (KEP-12), connected into the power-supply circuit of the movie lamp, made it possible to set a light-dark cycle for operation of the illuminator (²). The power of the radiation incident on the sample was varied by calibrated screens and monitored with a thermoelement. The principal measurements were performed at a luminous-flux power of 21 mW/cm². Surface-type cells were prepared on glass and quartz plates with deposited metallic electrodes; the width of the gap between them was 0.5 mm. A number of metals were tested as electrodes: antimony, bismuth, tin, gold, and others. Tin and gold electrodes gave ohmic contacts with the pigment. The data presented below refer to cells with tin electrodes.

The procedure for preparing the films was similar to that described earlier (³, ⁴). Onto the surface of a substrate, preliminarily heated to a temperature of 180°, there was applied in an even layer finely ground powder of synthetic β -carotene (⁴) or a mixture of carotene with protoporphyrin (Austrowaren) in an amount of 1.5 mg per sample. The molten mass was covered from above with a heated cover glass, compressed in a press at the melting temperature, and then slowly cooled to room temperature. As spectral measurements showed, the pigments were not destroyed by such treatment (⁴, ⁵). Polycrystalline

carotene films (~ 6) were prepared by evaporating a solution of the pigment in organic solvents (carbon disulfide, carbon tetrachloride, etc.). Residual solvent was removed in vacuum at $10^{-3-10^{-4}}$ mm Hg.

In studying cells prepared in this way, a difference was established in the behavior of samples with fused and evaporated films. Current oscillations arose only in fused films. Films obtained by evaporation of a carotene solution, as well as by joint deposition of a mixture of carotene with protoporphyrin, did not show this effect. The current-voltage characteristics (I-V curves) of fused carotene films and films obtained by melting a mixture of carotene with proto-

porphyrin are shown in Fig. 1. As can be seen from the figure, the current-voltage characteristics of deposited carotene films (Fig. 1, 1, 1') and of carotene films with protoporphyrin (2, 2' and 3, 3') at low field strengths are ohmic in character. Curves 2, 2' refer to a carotene film with an admixture of protoporphyrin in the ratio 20 : 1; curves 3, 3' to a film with an admixture of protoporphyrin in the ratio 10 : 1. The characteristics were recorded both for dark currents (1, 2, 3) and for photocurrents (1', 2', 3'). With increasing applied field, the current curves reach saturation. In the range of field strengths where saturation occurs both in light and in darkness, the appearance of current oscillations was observed. The threshold-voltage values for the onset of oscillations in light are lower than in darkness, and are unchanged for all films of a given composition. As the concentration of the protoporphyrin admixture in the film increased, the threshold-voltage values decreased:

β - Carotene: protopor- phyrin, wt. %	10 : 1	15 : 1	20 : 1	Pure β -carotene
Threshold voltage, V	540	850	1040	1250

The form of the current oscillations arising during one light-dark cycle is shown in Fig. 2. The oscillations have a clearly expressed period and amplitude. The amplitude of the oscillations in light and in darkness over the entire range of saturating voltages remained unchanged for a given film ($\sim 2.4 \cdot 10^{-10}$ A). The peak area characterizing the charge passing through (the current integral) was also constant. The calculated value of the charge is $\sim 2.5 \cdot 10^{-10}$ coulomb/oscillation = $1.5 \cdot 10^9$ electrons/oscillation. In Fig. 2, for comparison of the oscillation form, a light pulse (dashed line) is superimposed on the dark pulse (solid line).

Fig. 1. Current-voltage characteristics of dark current and photocurrent

Fig. 2. Form of oscillations of dark current and photocurrent

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Fig. 3. Dependence of the frequency of current oscillations on the applied voltage in light and in darkness

The frequency of the arising oscillations depended on a number of factors. In darkness it is lower than in light at a constant applied voltage. When the intensity of the light incident on the sample was decreased by a factor of two, the oscillation frequency decreased by 35-40%. With increasing applied voltage within the saturation region, the frequency of current oscillations increased, and in light it always remained higher than in darkness. Figure 3 shows the dependence of the oscillation frequency on the applied voltage in darkness (1) and in light (3), as well as the change in frequency during the light-dark cycle (2, 2').

the lamp being turned off (2, 2'). Curves 1 (lower branch) and 3 (upper branch) were taken in the direction of increasing applied voltage. Curves 1 (upper branch) and 3 (lower branch) were taken in the direction of decreasing voltage. As can be seen, hysteresis is observed in the graphs. Curves 2 were taken in the direction of increasing field during the light-dark cycle. Curve 2 corresponds to dark measurements: the upper branch to the dark interval preceding illumination, and the lower branch to the dark interval after illumination. The change in the frequency of the oscillations with the applied voltage during the illumination period of the light-dark cycle is shown by curve 2'. As can be seen from Fig. 3, the frequency of the oscillations that arise is small and amounts to tenths of a hertz.

As noted above, Cherry and Chapman ⁽¹⁾ observed low-frequency current pulsations in single-crystal samples of β -carotene when heated under vacuum conditions. Admission of oxygen lowered the temperature at which pulsations could appear to room temperature. The characteristics of the phenomenon they discovered resembled those described above, but substantial differences were also observed. The ratio of the amplitude of the oscillations to the base current in ⁽¹⁾ is less than 1; in the cells described here it is greater than 1 (see Fig. 2). The

Fig. 3. Dependence of the frequency of current oscillations on the applied voltage in light and in darkness

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threshold voltage for the onset of oscillations in single crystals was 4000 V/cm; we obtained a minimum field-strength value of 10 000 V/cm. In this connection the following fact is noteworthy. The carotene films in which oscillations arose were prepared by us by melting onto the surface of a glass substrate (see the preparation procedure). X-ray structural and electron-microscopic study of such samples showed that the structure of such films is amorphous^(5,6). The similarity of the oscillations in an amorphous glassy film to the phenomenon in single-crystal samples makes it possible to suppose that, for current oscillations to arise, the presence of a crystalline structure is not a necessary condition.

What is common in both cases is the presence of contacts that disturb the homogeneity of the film samples. It was noted above that, with increasing concentration of the protoporphyrin impurity, the value of the threshold voltage decreases (see Fig. 1). Introducing an impurity into the sample is equivalent to increasing the number of microinhomogeneities in the volume of the film, as well as in the region of contact between the pigment and the electrodes. As can be seen from the current-voltage characteristics of the films (Fig. 1), the photocurrents increase with increasing protoporphyrin concentration. This phenomenon may possibly have a common nature with the fact we previously discovered: an increase in the photovoltaic sensitivity of the chlorophyll-carotene system with increasing concentration of one of the film components^{(7)*}.

The occurrence and periodicity of oscillations in the saturating-voltage region of the current-voltage characteristics apparently indicate the appearance, in this region, of negative resistance in the films studied.

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* A separate paper, prepared for publication, is devoted to clarifying this question.

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

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