EFFECT OF VAPORS AND GASES ON THE ELECTRICAL CONDUCTIVITY, PHOTOCONDUCTIVITY, AND PHOTO-EMF OF COPPER POLYPHENYLACETYLIDE

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Figure 1

Figure 1: Figure 1

Abstract

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V. S. MYL’ NIKOV

EFFECT OF VAPORS AND GASES ON THE ELECTRICAL CONDUCTIVITY, PHOTOCONDUCTIVITY, AND PHOTO-EMF OF COPPER POLYPHENYLACETYLIDE

(Presented by Academician A. N. Terenin, February 8, 1965)

Investigation of the photosemiconducting and photoluminescent properties of copper phenylacetylide (PAM) (^{1}), which is a coordination-type polymer (^{2}-^{5}), led to the conclusion that the surface plays an important role in the processes studied. During adsorption of organic dyes on the surface of PAM, spectral sensitization of the photoeffect is observed in the visible region of the spectrum (^{6}, ^{7}).

In the present work the influence of adsorption of electron-acceptor gases and vapors on the electrical conductivity, photoconductivity, and condenser photo-emf of PAM is investigated (oxygen, water vapor, quinone, chloranil, and others). Let us note that the action of electron-acceptor molecules on the properties of low-molecular organic semiconductors is widely studied (^{8}-^{12}). The influence of oxygen on the electrical conductivity of polymeric organic materials has been reported in works (^{13}-^{15}). The use of additives to increase the photosensitivity of organic polymers has been patented in electrophotography.

Fig. 1. Influence of oxygen on the electrical conductivity (a) and photoconductivity (b) of copper phenylacetylide. **I** –evacuation of air to $5 \cdot 10^{-5}$ torr, **II** –admission, **III** –evacuation, **IV** –admission of oxygen, **V** –discharge in oxygen, **VI** –evacuation.

The method for measuring photoconductivity and photo-emf was described in previous works (^{1}, ^{4}, ^{7}). PAM was studied in the form of a finely dispersed powder which, as the X-ray pattern showed, consists of macrocrystallites. Oxygen was obtained from potassium permanganate and, after drying with liquid air or phosphorus pentoxide, was admitted into a cell evacuated to $5 \cdot 10^{-5}$ torr with a sample.

Figure 1 shows the typical character of the change in the electrical conductivity and photoconductivity of PAM upon admission of oxygen. Removal of air to $5 \cdot 10^{-5}$ torr (**I**) leads to an increase in the dark current and photocurrent by 3–2 orders of magnitude; in this case the increase in the dark current is more significant. Admission of dry oxygen (**II**) suppresses both currents, but this suppression is reversible, since the subsequent removal (**III**) and admission (**IV**) of oxygen repeat the entire cycle. The suppressing effect on the electrical conductivity and photoconductivity—

conductivity is enhanced if a discharge is carried out in an atmosphere of dry oxygen (V). The ions formed as a result of the discharge possibly partially oxidize PAM, but nevertheless, upon subsequent pumping out, the electrical conductivity and photoconductivity increase. An analogous effect of oxygen was also found for the photo-emf. The photoconductivity (Fig. 1) was recorded under illumination with light of $\lambda = 455$ mμ, which corresponds to the maximum of the PAM absorption spectrum. An analogous effect of oxygen on the photoconductivity and photo-emf was found over the entire spectrum. Figure 2 shows the (not recalculated for an equal number of photons) photo-emf spectrum of PAM in air (curve 1), in vacuum (curve 2), immediately after admission of oxygen (curve 3), and after a discharge in oxygen (curve 4). The character of the spectrum is preserved in all cases, which indicates the absence of chemical and photochemical interactions of PAM with oxygen.

For a *p*-type semiconductor, which PAM is [1], it is generally assumed that adsorption of molecules having an affinity for an electron should lead to an increase in photosensitivity. In our case, oxygen suppresses both the electrical conductivity and the photoconductivity of PAM. Apparently, oxygen creates new effective recombination centers, reducing the lifetime of the majority carriers (holes). The photo-emf should also decrease in this case, which is what is observed experimentally. Most likely, the new recombination centers created by oxygen are predominantly surface in nature. The surface character of the levels associated with oxygen is confirmed by the following experiment. As reported earlier, exposure of PAM to ultraviolet light in air leads to suppression of photoluminescence and an increase in the photo-emf, without a substantial change in their action spectra. Figure 3 gives the photo-emf spectrum of PAM (not recalculated for an equal number of photons) before (curve 1) and after its irradiation in vacuum for 30 min with light of $\lambda = 365$ mμ, selected by a light filter (curve 2). In contrast to irradiation in air, the appearance of the photo-emf spectrum after irradiation in vacuum changes, shifting into the long-wavelength region. The magnitude of this shift depends on the intensity and time of irradiation of PAM. The activity of wavelengths was checked down to 405 mμ. The phenomenon is reversible. After admitting air into the evacuated vessel, the photo-emf spectrum instantly returns to a form practically coinciding with curve 1 of Fig. 3, but with a correspondingly lower intensity. To

Figure 2

Figure 2: Figure 2

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

clarify the question of what such changes in the photo-emf spectrum are associated with, experiments were carried out on the separate admission of water vapor and dry oxygen and on their combined action on the photo-emf spectrum changed by exposure in vacuum (curve 2). It was found that admission of water vapor practically does not change the form of the spectrum, but only slightly suppresses the photo-emf in amplitude. Let us note that in this case the action of water vapor is opposite to that which it exerts on the photo-emf spectrum not changed by exposure in vacuum. The admission of oxygen, in contrast to water vapor, helps return the spectrum to its initial form. Curve 3 shows the photo-emf spectrum 5 min after admitting oxygen onto a sample with the spectrum characterized by curve 2. The combined action of water vapor and oxygen promotes a more effective return of the photo-emf to the unexposed form of the spectrum. The results obtained make it possible

Fig. 2. Photo-emf spectra of copper phenylacetylide (not recalculated for an equal number of photons).
1 —in air, 2 —in vacuum, 3 —after admission of oxygen, 4 —after a discharge in oxygen.

one may conclude that in vacuum, under the action of UV light, effective photodesorption of oxygen occurs, leading to a change in the conditions at the PAM surface. The capacitor photo-emf is determined by the diffusion of the majority carriers, on which is superimposed the drift of carriers in the field of surface charges (16–17). A change in the conditions at the PAM surface

Fig. 3. Spectra of the photo-emf of copper phenylacetylide (not recalculated to an equal number of photons). **1**—in vacuum, **2**—after 30 min irradiation in vacuum with light $\lambda = 365$ mμ, **3**—spectrum 2, 5 min after the admission of oxygen, **4**—spectrum of the photoconductivity of copper phenylacetylide, **5**—spectrum 2 with simultaneous illumination by light $\lambda = 365$ mμ

Fig. 4. Effect of mercury vapor 10^{-3} torr on the electrical conductivity (*a*) and photoconductivity (*b*) of copper phenylacetylide. **I**—evacuation of air, **II**—admission of mercury vapor, **III**—freezing out of mercury vapor ($T = 77^\circ$K), **IV** —evacuation, **V**—admission of air

as a result of photodesorption of oxygen leads to sharp suppression of the diffusion part of the photo-emf. This is evidenced by comparison of the spectra represented by curves 1 and 2 in Fig. 3. After irradiation in vacuum, the photo-emf in the region of light strongly absorbed by PAM, where there is a maximum concentration gradient of photocarriers generated by the light, falls sharply. The determining role begins to be played by carriers participating in photoconductivity under the action of the field of the surface charge, which also determines the fictitious shift of the spectrum of the capacitor photo-emf (curve 2). The fact that this spectrum (curve 2, Fig. 3) is determined mainly by photoconductivity is confirmed by its good agreement, especially in the region of weak absorption, with the PAM photoconductivity spectrum (curve 4) (1). The above-mentioned suppressing action of water vapor on the spectrum (curve 2) also confirms that it is determined by photoconductivity in the field of the surface charge. Water vapor decreases the photoconductivity and increases the photo-emf of PAM. Moreover, if, simultaneously with measurement of the modulated photo-emf signal (spectrum 2), constant illumination is applied at the absorption maximum of PAM, then in the region of weak absorption the appearance of a photo-emf of the opposite polarity is observed (curve 5, Fig. 3). Constant illumination of the photo-emf, characterized by curve 1, with light strongly absorbed by PAM, also leads to a decrease in the amplitude of the photo-emf. The appearance in the photo-emf under illumination of an inversion band indicates the anti-barrier character of the double layer on the PAM surface after UV exposure in vacuum.

In this work, the influence of electron-acceptor molecules (quinone, chloranil) on the semiconducting properties of PAM was investigated. Vapors of quinone and chloranil do not exert a substantial influence on the photo-emf and suppress the conductivity and photoconductivity of PAM. The character of the photoconductivity spectrum in quinone vapor does not change relative to the spectrum in vacuum, but the suppression of photoconductivity is more effective in the region of strong absorption. The invariance of the spectrum indicates the absence of

the chemical interaction between PAM and quinone, while the change in the ratio of the photocurrent amplitudes of the long-wavelength and short-wavelength parts of the spectrum is probably associated with a change in the nature of charge-carrier recombination. When PAM was treated with quinone from solution, an increase in the photo-emf was observed. The formation, upon contact with the solvent, of additional centers promotes adsorption of quinone molecules, which, possessing a high electron affinity, serve as traps for them, correspondingly increasing the photo-emf of the p-type.

It should be noted that, when experiments with PAM are carried out in vacuum using a mercury diffusion pump, mercury vapor must be carefully removed from the system, since experiment has shown that even at low pressures it suppresses the conductivity and photoconductivity of PAM. The nature of the change in the conductivity and photoconductivity of PAM at a mercury-vapor pressure of 10^{-3} torr is demonstrated in Fig. 4. Upon evacuation, the conductivity and photoconductivity are restored, which indicates the weak nature of the adsorption. We note that the action of mercury vapor on photoconductivity has previously been observed for certain dyes (9,18).

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