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Abstract

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PHYSICS

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SPECTRAL MANIFESTATIONS OF THE INTERACTION OF ORGANIC MOLECULES WITH THE SURFACE OF THE HOLE SEMICONDUCTOR TlJ

(Presented by Academician A. N. Terenin, 25 XI 1966)

In A. N. Terenin' s 1955 review, devoted to donor-acceptor intermolecular interaction, the prospect of finding charge-transfer complexes in surface phenomena was first pointed out (ˆ1). In the present work we have attempted to detect the spectral manifestations of such interactions on the surface of the hole semiconductor TlJ.

Donor-acceptor interactions belong to specific and strong interactions. To realize them, we carried out the adsorption

Fig. 1. Spectral distribution of the capacitor photo-emf, V_ϕ/E.
1 –standard–pure high-vacuum TlJ; 2 –TlJ + N-MDPA ($t = 150^\circ,\ \tau = 15$ min.); 3 –TlJ + TCE ($t = 150^\circ,\ \tau = 15$ min.). Here and below, the temperature and duration of adsorption are indicated in parentheses. The ordinate scale for the sensitization region is increased 100-fold.

of organic molecules under high-vacuum conditions from vapors onto a TlJ sample previously degassed at a temperature of 150° in a vacuum of the order of 10^{-6} mm Hg for 3 h. Details of the experiment on vacuum adsorption of molecules from the gas phase in sealed systems and on measurement of the photoeffect have been described in previous works (^{6,}7). The organic molecules used as electron-donor and electron-acceptor adsorbates were: tetramethyl-*n*-phenylenediamine (TM-*n*-PDA), N-methyldiphenylamine (N-MDPA), which have a very small ionization potential (ˆ8), and tetracyanoethylene (TCE), *n*-chloranil and *n*-benzoquinone, which are distinguished by a high electron affinity (ˆ9).

1. Effect of adsorption of electron-donor molecules on the photo-

Fig. 2. Spectral distribution of photoconductivity I_ϕ/E: 1 –standard –pure vacuum-treated TlJ; 2 –TlJ + N-MDF ($t = 150°,\ \tau = 15$ min.); 3 –TlJ + n-chloranil ($t = 150°,\ \tau = 15$ min.); 4 –absorption spectrum of n-chloranil on TlJ ($t = 150°,\ \tau = 15$ min.).

Figure 2: Fig. 2. Spectral distribution of photoconductivity I_ϕ/E: 1 –standard –pure vacuum-treated TlJ; 2 –TlJ + N-MDF ($t = 150°,\ \tau = 15$ min.); 3 –TlJ + n-chloranil ($t = 150°,\ \tau = 15$ min.); 4 –absorption spectrum of n-chloranil on TlJ ($t = 150°,\ \tau = 15$ min.).

semiconductor properties of TlJ. Powdered TlJ, subjected to high-vacuum treatment at elevated tempera-

···temperature, possesses a capacitor photo-emf (Fig. 1, 1) and transverse photoconductivity (Fig. 2, 1). Upon adsorption of electron-donor molecules, the spectra of the capacitor photo-emf and photoconductivity change in appearance (Figs. 1, 2 and 2, 2). In the spectrum of the capacitor photo-emf (Fig. 1, 2), at the absorption edge of TlJ there is a spectral maximum at 445 mμ. Taking into account the origin of the capacitor photo-emf (4,5) in the presence of hole conductivity in TlJ, the appearance of such a maximum at the absorption edge indicates an accumulation of a large positive charge on the surface. This accumulation leads to considerable band bending at the semiconductor surface, making the spectrum of the capacitor photo-emf similar to the photoconductivity spectrum. In other words, the band bending becomes so large that, in the region of weak absorption by the adsorbent, the motion of charges is determined not by the Dember effect (10), but by the magnitude and direction of the field near the surface. In the photoconductivity spectrum (Fig. 2, 2), a distinct maximum is observed at the absorption edge.

Fig. 2. Spectral distribution of photoconductivity I_ϕ/E
1 –standard–pure vacuum-treated TlJ; 2 –TlJ + N-MDF ($t = 150°,\ \tau = 15$ min.); 3 –TlJ + n-chloranil ($t = 150°,\ \tau = 15$ min.); 4 –absorption spectrum of n-chloranil on TlJ ($t = 150°,\ \tau = 15$ min.).

The interaction with the surface may be represented schematically as follows:

$$D + S \rightarrow \frac{D}{S} \overset{t^\circ}{\underset{t_{\text{room}}}{\rightleftarrows}} \frac{D^{+\delta}}{S^{-\delta}}; \qquad |\delta| < |e^-|.$$

If adsorption is carried out at elevated temperature, or if a TlJ sample with an adsorbate weakly bound to the surface is heated, the molecules pass into a more stable (charged) form. However, $|\delta| \neq |e^-|$, since neither the ESR signal nor the absorption bands of the corresponding cation-radical, described in works (11,12), were detected by us. The lower arrow indicates that, upon cooling the sample after adsorption to room temperature, a slow partial transition of the molecules into the weakly bound state is observed. This leads to a decrease in the surface charge, to a decrease in the magnitude of the band bending, which manifests itself in a certain decrease of the spectral maximum of the capacitor photo-emf located at the absorption edge of TlJ. Heating of the sealed···

part of the capacitor cuvette partially restores the initial spectrum.

II. The influence of adsorption of electron-acceptor molecules on the photoconductive properties of TlJ. Adsorption of electron-acceptor molecules on the surface of TlJ also leads to strong spectral manifestations in the spectra of capacitor photo-emf and photoconductivity. In the spectrum of capacitor photo-emf (Fig. 1, 3) a change in the sign of the effect and a decrease in photosensitivity are observed in the region of intrinsic absorption of TlJ. As in the preceding case, a spectral maximum appears at the absorption edge of TlJ at 450 mμ. When the capacitor photo-emf is measured by passing illumination from the side of short wavelengths, in the spectral region where the change of sign begins, the photoresponse from TlJ indicates the existence of at least two different photoprocesses in time. The fastest process exists and is manifested, apparently, uniformly over the entire spectrum (Fig. 1, 3). When the sample is illuminated for several minutes with monochromatic light from the spectral region in which "repolarization" begins, the capacitor photo-emf decreases (Fig. 1, 3′). This circumstance indicates a decrease of charge on the surface and may be interpreted as follows. Upon illumination in the region of weak absorption of TlJ, the majority carriers—holes—according to the direction of band bending, move toward the surface, leading to the discharge of part of the negatively charged chemisorbed molecules. This probably occurs both in the region of weak absorption ($\lambda > 460$ mμ) and in the region of strong absorption ($\lambda < 430$ mμ). However, the capacitor photo-emf is most sensitive to changes in the concentration of chemisorbed molecules in the region where the sign of the photoeffect changes. In the dark, equilibrium between physisorbed and chemisorbed molecules is restored.

Most remarkable is that in the spectra of photoconductivity and photo-emf, sensitization of the photoeffect to longer-wavelength light is observed. From Figs. 1, 3 and 2, 3 it follows that the sample has an absorption that lies in the region 490–570 mμ, depending on the acceptor. It is accompanied by an e.p.r. signal in the region of the g-free electron.* It is characteristic that neither TlJ nor any of the acceptors used by us has an absorption band in this region. Therefore it is natural to attribute this band to an optical transition corresponding to the adsorbent–adsorbate system as a whole, and, apparently, it corresponds to a charge-transfer complex between the adsorbed molecule and the adsorption center on the surface of TlJ. Formation of such a complex requires a certain activation energy. The existence of "repolarization" (Fig. 1, 2) and of the spectral maximum at 460 mμ (Fig. 1, 3) is difficult to interpret unambiguously. The following explanations are proposed:

1. Since the spectral maximum of the capacitor photo-emf at the absorption edge of TlJ, which is a measure of the magnitude of band bending, is very intense, it may be assumed that inversion of the Fermi level is observed

Fig. 3. Dependence of the capacitor photo-e.m.f. of TlJ on the adsorption temperature of TM-*n*-PDA, 1—TlJ + TM-*n*-PDA ($t = 150^\circ$, $\tau = 15$ min.); 2—TlJ + TM-*n*-PDA ($t = 120^\circ$, $\tau = 15$ min.)

Figure 3: Fig. 3. Dependence of the capacitor photo-e.m.f. of TlJ on the adsorption temperature of TM-*n*-PDA, 1—TlJ + TM-*n*-PDA ($t = 150^\circ$, $\tau = 15$ min.); 2—TlJ + TM-*n*-PDA ($t = 120^\circ$, $\tau = 15$ min.)

in the near-surface layer, which gives rise to the aforementioned spectral manifestations.

2. If it is assumed that the rate of recombination of carriers at the surface of TlJ after adsorption of molecules is greater than in the bulk, then at sufficiently high concentrations of chemisorbed molecules (Fig. 3) an anomalous Dember effect is observed ([14]), manifesting itself in the region of sufficiently weak absorption of TlJ.
3. The behavior of the capacitor photo-emf in the region of sufficiently weak absorption of TlJ can also be understood if it is assumed that, in the sample, in addition to the hexagonal (yellow-green) form of TlJ that has been discussed so far, there are traces of another, cubic form (the so-called red modification of TlJ), which gives rise to the electronic type of conductivity. However, the possibility of stabilizing such a TlJ phase by adsorption of molecules is not known to us. The interactions occurring on the surface of TlJ with electron-acceptor molecules may be represented by the following schemes:

$$A + S \to \frac{A}{S} \underset{t_{\text{room}}}{\overset{t^\circ}{\rightleftarrows}} \frac{A^{-\delta_1}}{S^{+\delta_1}}; \qquad |\delta_1| < |e^-|.$$

Fig. 3. Dependence of the capacitor photo-e.m.f. of TlJ on the adsorption temperature of TM-*n*-PDA, 1—TlJ + TM-*n*-PDA ($t = 150^\circ$, $\tau = 15$ min.); 2—TlJ + TM-*n*-PDA ($t = 120^\circ$, $\tau = 15$ min.)

If the adsorption temperature is sufficiently low, the adsorbed molecules are either in an uncharged or in a weakly charged form. During adsorption at an elevated temperature (up to 150°), the charged form of adsorption is realized. A charge-transfer complex appears on the surface. The lower arrow indicates that cooling the sample after adsorption to room temperature may lead to the transition of part of the molecules from the chemisorbed to the physisorbed state. The middle arrow indicates that an analogous slow reversible transition can be obtained by illuminating the TlJ sample,

* All e.p.r. measurements of the samples were performed by V. E. Kholmogorov, to whom the author expresses his gratitude.

$$\frac{A^{-\delta_1}}{S^{+\delta_1}} \underset{\tau}{\overset{h\nu_{\text{st}}}{\rightleftarrows}} \frac{A^{-\delta_2}}{S^{+\delta_2}}; \qquad |\delta_2| \to |e^-|.$$

Under the action of a photon in the spectral region of the new band, a more complete transfer of an electron from the adsorption center to the adsorbed molecule evidently occurs, and hole injection into TlJ is effected. The sign of the capacitor photo-e.m.f. in the sensitization region (Figs. 1, 3) is in agreement with this representation. The phototransfer of the electron is reversible, as is the case for not very strong charge-transfer complexes. In 10^{-9} sec. ($^{2-3}$) the system returns to its initial state.

I consider it my duty to note, with sincere gratitude, the constant interest and attention shown by Academician A. N. Terenin in the supervision of this work.

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