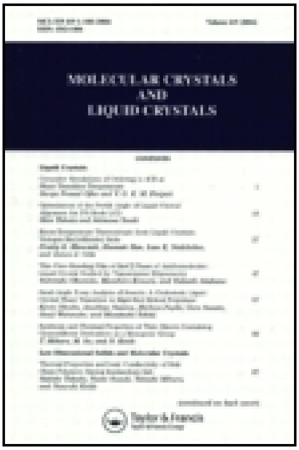

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STUDY OF PHOTOELECTRIC PROPERTIES IN THE SYSTEM INORGANIC SEMICONDUCTOR - LANGMUIR-BLODGETT FILM

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Abstract Effect of Langmuir multilayers of amphiphilic viologen, cyanine and triphenylmethane dyes, and stearic acid upon the spectral dependence of the Si photosensitive diode with p-n junction is discussed.

Monomolecular Langmuir-Blodgett films and their functional ensembles are of great interest for molecular electronics, nano- and biotechnologies, electronic devices of new generations.

One of the promising ways is to obtain LB films on different semiconductor and metal substrates, including SIS and MIS structures. Many papers consider photoelectric properties of the structure "inorganic semiconductor - Langmuir-Blodgett film", e.g.,effect of monolayers on the Schottky barrier height in CdTe and GaP[1,2], on the surface potential in GaP[3], on the optical sensitization of the photoeffect in AgBr[4].

In this paper we studied effects of LB films of a number of amphiphilic compounds with different donor and acceptor properties upon the photocurrent in the silicon photosensitive diode.

Photoelectric measurements were carried out on a heterostructure of single crystalline silicon with p-n junction and n-base. The face side of the photosensitive diode was a p-type layer, 0.4 µm thick, with carrier concentration

$2\cdot10^{19}$ cm^{-3}. The base layer is of n-type, 320 μm thick, with carrier concentration $1.2\cdot10^{16}$ cm^{-3}. Multilayers of different amphiphilic compounds were deposited onto the surface of the diode: stearic acid (I), viologen (A) - an acceptor, cyanine dye (S) - a spectral sensitizer, triphenylmethane dye (D) - a donor. As a subphase we used $CdCl_2$ solution (2.5 10^{-4} M) for surface monolayers stabilization in the twice distilled water, pH=6.2. Solutions of the above-mentioned substances in hexane and chloroform were spread onto the subphase surface. Studies of π - A isotherms have shown that LB films of good quality could be formed at surface pressures 25 - 35 mN/m. Transfer efficiency both on dipping and pulling out of the subphase was close to unity. After cleaning by organic solvents, 5 monolayers of the corresponding substances were deposited onto the Si surface, forming a Y-type multistructure.

Spectral dependencies of the photodiode current were carried out using a MDR-12 monochromator. The total radiation energy of the light source was 150 W/m^2. Measurements were carried out in the short circuit current regime. To make data analysis more convenient, experimental dependencies of the photocurrent on wavelength $I(\lambda)$ were converted into the form $(I'(\lambda) - I(\lambda))/I(\lambda) = \Delta I(\lambda)/I(\lambda)$, where $I'(\lambda)$ and $I(\lambda)$ are photocurrents, respectively, with and without LB-film on the diode surface.

On Fig.1 $\Delta I(\lambda)/I(\lambda)$ dependencies for the substances studied are presented. For LB(I) $\Delta I/I$ is nearly zero in all spectral region, except short wavelength region. For LB(A) $\Delta I/I$ changes its sign: in the region $\lambda<400$ nm $\Delta I/I<0$, while at $\lambda>400$ nm $\Delta I/I>0$. For LB(S) and LB(D) the character of $\Delta I(\lambda)/I(\lambda)$ is similar to that of LB(A), except for the central part of the spectrum, where a "gap" is observed. This gap is evidently caused by light absorption in the dye multilayers.

Analysis of the experimental data within a framework of the Garrett-Brattain theory[5] for the initial model (photosensitive diode with p-n junction, thickness of the face

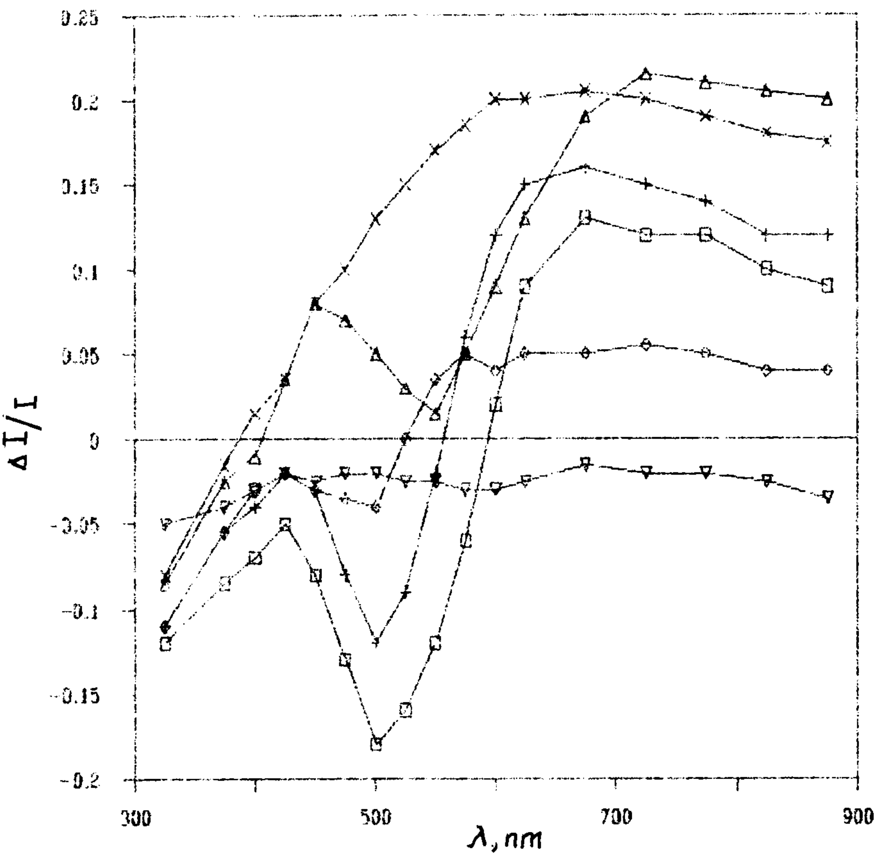

FIGURE 1. The spectral dependencies $\Delta I(\lambda)/I(\lambda)$ of photosensitive diode with LB films of stearic acid (▽), viologen (×), triphenylmethane dye (△), cyanine dye with concentration (mol.%): 5 (◇), 25 (+), 100 (□) in the stearic acid matrix.

layer W much lower than the diffusion length L of the extrinsic carriers, the case of low injection level) leads to an expression for $\Delta I(\lambda)$ depending both on bulk and surface properties of the semiconductor.

Let us assume that as a result of the adsorption of the monolayer molecules the surface recombination rate Si on the illuminated surface is changed. In this case, according to [6] we obtain

for $\alpha W \ll 1$

$$\Delta I/I \approx \begin{cases} -\frac{\Delta S}{S}\cdot\frac{W}{DS}, & \text{at} \quad W \ll D/S, \qquad (1a)\\ -\frac{\Delta S}{S}\cdot\frac{D}{SW}, & \text{at} \quad W \gg D/S, \qquad (1b)\end{cases}$$

for $\alpha W \gg 1$

$$\Delta I/I \approx \begin{cases} -\frac{\Delta S}{S}\cdot\frac{WS}{D}, & \text{at} \quad W \ll D/S, \qquad (2a)\\ -\frac{\Delta S}{S}, & \text{at} \quad W \gg D/S, \qquad (2b)\end{cases}$$

where α is the absorption coefficient, S is the surface recombina-tion rate, D is the diffusion coefficient of the extrinsic carriers in Si.

It follows from expressions (1) and (2) that both in the long- and short-wavelength parts of the spectrum $\Delta I/I > 0$ af-ter the change in surface properties , if $\Delta S < 0$, and $\Delta I/I < 0$, if $\Delta S > 0$, which is contrary to experimental data.

As shown in [7], the validity conditions of the Garret-Brattain theory can be violated for a number of semiconductors including Si, due, in particular, to the high surface recombination rate. This implies the necessity of accounting for the effects of the space-charge region upon non-equilibrium processes in the surface-adjacent region. Skipping the exact calculations, the qualitative picture of the behavior of $\Delta I/I$ at low and high α values is the following: for $\alpha W \gg 1$ $\Delta I/I$ has the same form as (2), and for $\alpha W \ll 1$ (1a) and (1b) should be multiplied by $(1-SLf(z))^{-1}$, where f(z) is function dependent upon the surface bending of the bands, the diffusion coefficients and concentrations of non-equilibrium charge carriers, the distance from the surface to the border of the space-charge region, and the quasineutral vo-lume. If $S < (Lf(z))^{-1}$ the $\Delta I/I$ dependence is similar in character to (1): however, if $S > (Lf(z))^{-1}$, $\Delta I/I$ changes sign in (1).

It follows that experimental data are in qualitative agreement with the theory, if the surface recombination rate in Si exceeds the critical value $(Lf(z))^{-1}$.

It is known[6] that at the Si - SiO_2 phase boundary (thermooxidated silicon) rapid surface states are localized, which determine the surface recombination rate in Si. At the Si-SiO_2 / air phase boundary the slow surface states are localized, being of adsorption nature and responsible for the bending of bands .

Let the Si-SiO_2 surface potential be changed by $\Delta e\varphi/kT \ll 1$ due to adsorption of the monolayers. Then we obtain from the Steven-Keyes formula for S [8]

$$\Delta S/S \sim \Delta\varphi, \qquad (3)$$

with the sign of ΔS/S depending on the initial value of the surface potential without the LB-film. Assuming that after a standard chemical processing of the p-type Si surface the bending of bands is negative (accumulation), we find from (3) and the experimental ΔI/I dependence that $\Delta\varphi > 0$. Thus, as a result of monolayer adsorption for the compounds (A), (S),(D) the exhaustion regime is realized.

It follows from Fig.1 that ΔI/I does not depend upon whether multilayers on the silicon surface are formed by donor or acceptor molecules, but depends upon magnitude of the molecular dipole moment. For the solution of (S) in (I) it was found in the LB films that on increasing the concentration of (S) ΔI/I reaches maximum at 25%, and then begins to decrease. From these data it can be assumed that in the monolayers with oriented adsorption of molecules with large dipole moments the surface bending of bands is decisively affected not by donor or acceptor nature of the molecules, but by the magnitude and orientation of their dipole moments.

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