# Dye-Sensitized Photoconductivity and Photovoltaic Effect in Silicon

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Keywords: Internal Photo Effect, Powdered and Monocrystalline Silicon, Dye Sensitization.

Abstract: In this paper we investigate the influence of organic dyes applied to the semiconductor surface on the effectiveness of the direct current photoconductivity of powdered silicon and photovoltaic effect in the monocrystalline silicon. Dyes on the semiconductor surface effectively increase the photoconductivity of powdered samples in the dye absorption band. The effectiveness of the monocrystal sensitization is smaller because the specific surface area of finely divided powders is several orders of magnitude larger than it is in monocrystals. The optimum concentrations of dye molecules on the semiconductor surface for the internal photo effect sensitization are determined. We also discuss the mechanism of the sensitization based on the theory of non-radiative resonant inductive energy transfer.

## 1 INTRODUCTION

Organic dyes effectively sensitize the photoconductivity and photolysis in broad-band semiconductors (ZnO, AgHal, $TiO_2$, etc) in the dye absorption range (Akimov, et al, 1980, Goryaev, 2013). In the silver halide photography dye sensitization is the most effective method of varying the sensitivity level and spectrum of photographic materials (James, 1977). Photoelectrochemical cells based on the dye-sensitized titanium dioxide provide an alternative to silicon solar batteries (Gratzel, 2003). The thickness of solar cells based on crystalline silicon must be hundreds of microns, because the extinction coefficient of the semiconductor is relatively low in the range of indirect electron transitions (Alferov, et al, 2004, Afanasyev, et al, 2011, Duffie and Beckman, 2013). Modern electron photography systems have the silicon CCD matrices as image sensors in (Boyle, 2010), and using light filters for color separation system leads to the loss of energy and valuable information (Goryaev and Dudnikov, 1990). In the present study we investigated the internal photo effect in silicon and the influence of the application of organic dyes to the semiconductor surface on its effectiveness.

## 2 EXPERIMENTAL

Silicon powdered samples with micron-sized microcrystals and flat monocrystals of 1-2 $cm^2$ with a thickness of 0.5 mm were used for the investigation. The semiconductor surface was covered with dyes from the ethanol solution with a definite concentration by means of a natural evaporation of the solvent at room temperature. The direct current (DC) photoconductivity measurements were performed in special surface type cells for investigating the electro-physical properties of powder semiconductors (Povkhan, et al, 1974), in which the sample in the pellet form was pressed to a quartz plate under constant pressure (approx. 10 kg/$cm^2$). The quartz plate was covered with a raster of platinum electrodes; the distance between the electrodes was 0.1 mm, and the effective length of electrodes was 80 mm. The photocurrent $\Delta I_{ph}$ measured under the conditions of a constant sweeping electric field was normalized to number of light $E$ (Goryaev, 2015). The method used for the investigation of the monocrystalline samples was the measurement of the photo-EMF at the modulated irradiation (Akimov, 1966). To estimate the effectiveness of the photovoltaic effect, the measured signals $\Delta U_{ph}$ were normalized to number of light quanta $E$.

# 3 RESULTS AND DISCUSSION

## 3.1 DC Photoconductivity

The photoconductivity spectra of powdered silicon are shown on figures 1 and 2: the undyed sample (curve 1) and the samples with the dyes applied to the semiconductor surface (curve 2). The results demonstrate that the photoconductivity of dyed samples in the absorption range of the dyes (curve 2, Fig. 1 and Fig. 2) is higher than the photoconductivity of the original silicon sample (curve 1, Fig. 1 and 2) by more than an order of magnitude.
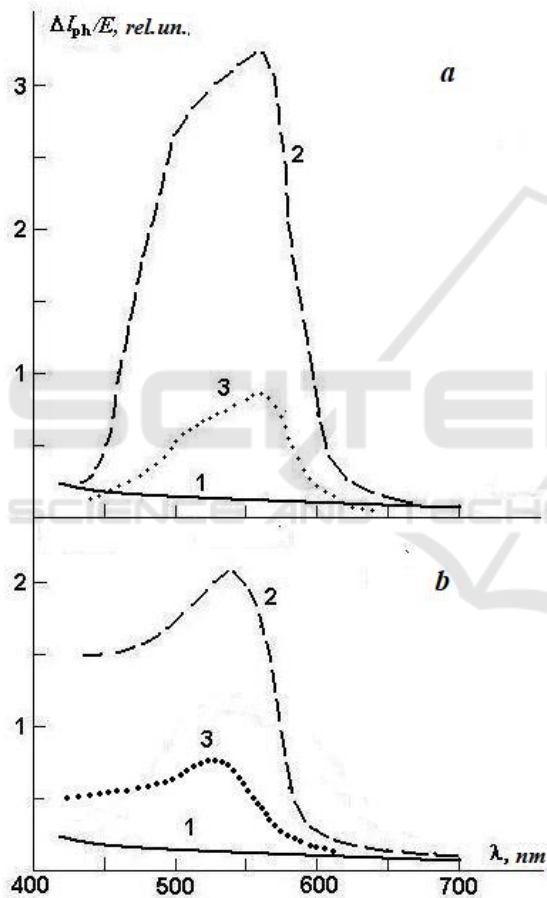


Figure 1: Photoconductivity spectra of undyed silicon (1) and samples dyed with Rhodamine 6G (a) and Erythrosine (b) with concentrations of $10^{-4}$ Mole/g of Si (2) and $2\times10^{-4}$ Mole/g of Si (3) with concentrations of $10^{-4}$ Mole/g of Si (2) and $2\times10^{-4}$ Mole/g of Si (3).

The increase in photoconductivity in the absorption range of the dye cannot be related to the carrier generation in the dye layer because the dark conductivity of both the powdery dye layers and the thin dye films deposited from a solution on a quartz plate with electrodes is several orders of magnitude smaller than the conductivity of undyed silicon samples, while the photoconductivity is absent altogether. This circumstance explains the decrease in the photocurrent for the dye deposited in a large amount on the semiconductor surface (Goryaev, 2015).

The magnitude of the observed photocurrent sensitization effect depends on the amount of dye applied to the semiconductor surface non-monotonely: when the dye concentration is increased, the photoconductivity at first increases and then decreases (curves 2 and 3, Fig. 2). The decrease in the photocurrent when the large amount of dye is deposited on the semiconductor surface is explained by the fact that a solid insulating dye film is formed on silicon, and it hinders the transition of charge carriers among the microcrystals. The optimum concentration of dye molecules on the semiconductor surface for the photocurrent sensitization of powdered samples is about of $10^{-4}$ Mole/g of Si.
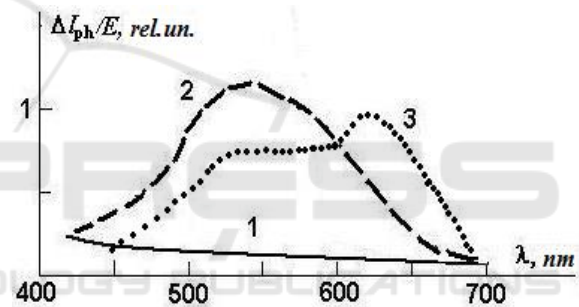


Figure 2: Photoconductivity spectra of undyed silicon (1) and samples dyed with Crystal Violet with concentrations of $10^{-4}$ Mole/g of Si (2) and $2\times10^{-4}$ Mole/g of Si (3).

The investigation of photoconductivity spectra shows the interesting results for the samples with the dye crystal violet applied to the semiconductor surface (Fig. 2). On increasing dye concentration not only a decreasing photoconductivity in the dye absorption band due to the insulating dye film formation is observed, but an additional absorption band appears in the long-wave region (curves 2 and 3, Fig. 2). This fact may be explained by the J-aggregates formation at the large amount of dye on the semiconductor surface. The absorption band of dye J-aggregates lies in the longer wave region and their sensitization effectiveness is larger than that for the dye in a non-aggregated state (James, 1977).

## 3.2 Photovoltaic Effect

For the monocrystalline silicon the spectral sensitization of condenser photo-EMF is also

observed in the absorption band of the dye (curves 2 and 1, Fig. 3). In comparison to powdered silicon the magnitude of the sensitized photo effect in silicon monocrystals is significantly smaller than in polycrystalline samples (Goryaev, 2017). This is a consequence of the fact that the specific surface area of monocrystals is several orders of magnitude smaller than in microcrystals of finely divided powders. It should also be noted that during a characteristic absorption the absorption and carrier generation happens rather deep in the crystal because of a small extinction coefficient of silicon. The role of near-surface photoelectron generation increases during the light absorption by dyes because the efficient energy transfer radius during the dye sensitization is several nanometers large (Akimov, et al, 1980). The thickness of monocrystals is very significant, therefore the number of such near-surface photoelectrons is small in comparison with the carriers generated due to the characteristic absorption in the volume of the semiconductor.
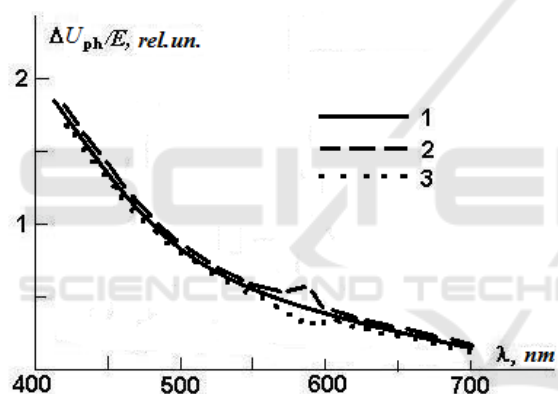


Figure 3: Photo-EMF spectra of undyed silicon monocrystals (1) and samples dyed with Rhodamine 6G with dye molecule concentrations of 30 nm$^{-2}$ (2) and 60 nm$^{-2}$ (3).

The magnitude of the observed photo effect sensitization depends on the amount of dye applied to the semiconductor surface non-monotonely as well: when the dye concentration is increased on monocrystals the photo-EMF at first increases and then decreases in an absorption band of the dye (curves 2 and 3, Fig. 3). Dye sensitization is observed at the optimum concentration of dye molecules on the monocrystal surface about of 30 nm$^{-2}$. Taking into account the fact that the surface density of molecules in the dye monolayer is 0.7-1.4 nm$^{-2}$ (James, 1977), the optimum thickness of the dye film formed on the monocrystal surface is around 30 monolayers or 10-15 nanometers. As the length of the efficient radius of energy transfer at the spectral dye sensitization is 5-7

nanometers (Akimov, et al, 1980), part of the energy absorbed by the dye does not reach the semiconductor for the larger film thickness. Besides, increasing the film thickness increases the role of the intramolecular energy conversion rate on the vibrational and rotational degrees of freedom during light absorption by the dye. Those processes lead to the filter effect in an absorption band of the dye applied on the solid surface, as it is observed for the photophysical and photochemical processes in the dye – aluminum hydride system (Goryaev and Pimenov, 1975, Goryaev, 1980; 2000).

## 3.3 Mechanism of Sensitization

The efficiency of spectral sensitization for the photoelectron formation in a solid after the light absorption by the dye applied on the surface is determined by the following ratio:

$$P_s = P_a \cdot P_{tr} \cdot P_{ph} , \qquad (1)$$

where $P_a$ – the efficiency of absorption determined by the dye extinction coefficient and its concentration; $P_{tr}$ – transfer efficiency of excitation energy from dye to semiconductor; $P_{ph}$ – the efficiency of photoelectron formation in a solid as a result of the excitation energy transfer from dye.

Some processes occur in the dye-semiconductor system during light absorption by the dye. After the dye photoexcitation non-radiative and radiative electron transitions can realize in molecules. The possibility of electron excitation energy exchange between the vibrational and rotational degrees of freedom and the rate of the internal energy degradation are determined by the rigidity of the dye molecule skeleton. For dyes applied on the solid surface the molecular structure becomes more rigid and intramolecular conversion probability becomes insignificant. As result the luminescent quantum yield of dyes is measured in tens of percent on the dielectrics surfaces (Goryaev, 1980; 1981; 1997, Goryaev and Smirnov, 2015). But the luminescence is completely absent on metals, narrow-band semiconductors and well-sensitizable photosensitive broad-band semiconductors (for example, silver halides and zinc oxide) because of the effective photoexcitation energy transfer from dyes to the solids (Akimov and Goryaev, 1984).

After the light absorption the photoexcitation energy received by the dye can be transferred to the semiconductor, be observed as luminescence and degrade within the molecule with the corresponding transition constants $k_1$, $k_2$ and $k_3$. Transfer efficiency

of the excitation energy is determined by the following ratio:

$$P_{tr} = \frac{k_1}{k_1 + k_2 + k_3}. \tag{2}$$

The intramolecular energy conversion rate $k_3$ becomes insignificant when compared to $k_1$ and $k_2$ for the majority of dyes applied on the solid surface because of the hardening of the molecule structure. Therefore the luminescence becomes the main competing process with the effective electronic excitation transfer to the semiconductor. The fluorescent state lifetimes of dyes applied on the solid surface are $10^{-11} - 10^{-10}$ s (Akimov and Goryaev, 1984, Goryaev, 2013), and photoexcitation transfer rate constant $k_1$ in effectively sensitized semiconductors exceeds $10^{12}$ s$^{-1}$ (Akimov, et al, 1980, Goryaev, 2013), so the quantum effectiveness of the photophysical and photochemical processes sensitization in the semiconductor approaches unity under such circumstances.

According to the theory of non-radiative resonant inductive energy transfer, the transfer probability depends on the overlap integral of the donor luminescence spectrum and the acceptor absorption spectrum (Ermolaev, et al, 1996):

$$P = \frac{Cq_{0d}}{n^4 \tau_{od} R^6} \int I_d n(v)\, \varepsilon_a(v) v^{-4} dv. \tag{3}$$

In equation (3): $q_{0d}$ and $\tau_{0d}$ – are, accordingly, the quantum yield and duration of luminescence decay of the donor in the absence of quenching, $I_d$ – quantum radiation spectral density of luminescence, $\varepsilon_a(v)$ – molar decimal absorption coefficient, $R$ – distance between the donor and the acceptor, $n$ – the environment refractive index, $v$ – wave number, $C$ – constant.

Local electronic states of the forbidden band play the role of the energy acceptors in broad-band semiconductor sensitization (Akimov, et al, 1980, Akimov and Goryaev, 1984, Goryaev, 2013). The existence of such local states in the semiconductors capable of accepting energy from the dye is the main reason for the luminescence quenching in these systems. The integrated density $10^9$ -$10^{10}$ cm$^{-2}$ of the surface states occupied by electrons is sufficient for the complete luminescence quenching (Goryaev, 2013). This is the necessary requirement for the sensitization of broad-band semiconductors. Such surface states are responsible for the weak absorption and photoconductivity in the impurity region of the semiconductors. The dyes applied on the solid surface

provide the spectral sensitization of the photophysical and photochemical processes in the semiconductors because of increasing the absorption in this region.

In silicon this spectral region corresponds to electronic transitions from the valence band to the conduction band. The densities of states in these bands are quite sufficient for the complete dye luminescence quenching because of accepting the photoexcitation energy. The intrinsic light absorption by the semiconductor is formed by indirect electronic transitions, and free carriers obtained by the intrinsic absorption are generated in the volume of the semiconductor. The near-surface free carriers generation during the light absorption by dyes produces a significant increase in the efficiency of the photoelectric effect (Fig. 4).
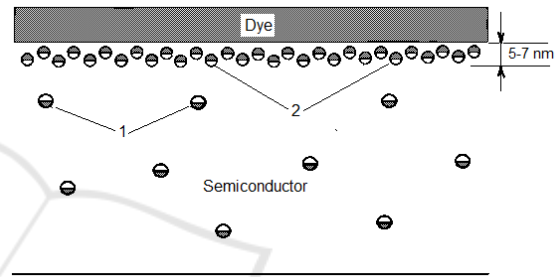


Figure 4: The generation of free carriers in the volume of the semiconductor due the intrinsic absorption in silicon (1) and in the subsurface region due the energy transfer from the dye (2).

The sensitization process efficiency after the transfer of excitation from a dye to the semiconductor is determined by the fate of an electron appearing in the semiconductor conductivity band. This electron may remain free for a sufficient period of time, enabling the sensitized photoeffect, or may quickly recombine. If the free carriers are formed with a constant $k_4$ and recombination of carriers in a semiconductor occurs with constant $k_5$, the effectiveness of the photoelectron formation in a solid after electronic excitation transfer is determined by the formula:

$$P_{ph} = \frac{k_4}{k_4 + k_5}. \tag{4}$$

The additional reason for the large differences of sensitized photoelectric effect in monocrystalline and powder silicon is that photo-EMF has both drift and diffusion components (Akimov, 1966). If the spectrum of the drift component repeats the photoconductivity spectrum, the diffusion photo-EMF is determined not by the concentration of carriers but by their gradient. Depending on the

subsurface band bending, drift and diffusion currents have different signs. At the dye – silicon heterojunction the change of photopotential character during illumination in different spectral regions was discovered (Komolov, et al, 2006). The subsurface band bending in semiconductors can be controlled by an external electric field or an additional illumination (Akimov, 1966), as well as the adsorption of the electron-acceptor and electron-donor molecules on the semiconductor surface (Pimenov and Goryaev, 1976).

## 4 CONCLUSIONS

Observed effective dye sensitization of the internal photoelectric effect in silicon can be used in such semiconductor devices for converting the light energy into electric energy as solar panels or image sensors in modern electronic photography systems. In the case of silicon solar batteries increasing the near-surface free carriers generation may decrease the thickness of cells. The application of dye sensitization in CCD matrices will enable the improvement of the color separation system during the recording of colored images as in traditional silver halide photography. Selecting appropriate dyes to provide an effective increase in sensitivity in the required spectral range instead of using light filters can decrease losses of energy and of valuable information in electronic photography.

## ACKNOWLEDGEMENTS

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