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Spectra and kinetics of dye-sensitized photovoltaic effect in silicon

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Abstract. This paper investigates the action of organic dye molecules placed on the surface of semiconductors on the manifestation of the photovoltaic effect in silicon samples with different types of conductivity. Spectral sensitization is observed in the dye absorption band of the photo-EMF for monocrystal samples with n-type conductivity, and a desensitizing effect of the dye is found in samples with p-type conductivity. In addition, the kinetics of the photovoltaic effect in the region of dye absorption in semiconductors with different types of conductivity is different: in n-type silicon, a monotonic increase of the photo-EMF is observed, while in p-type silicon, the photo-EMF first increases and then decreases. In powder samples, effective sensitization of DC photoconductivity is observed for both n-type and p-type semiconductors. The difference of contributions of electrons and holes generated during nonradiative inductive-resonant energy transfer from a dye to a semiconductor to different types of photoelectric effect is discussed.

Keywords: silicon with different types of conductivity, silicon with an adsorbed dye, spectral sensitization, photo-EMF, DC photoconductivity, dye sensitization of photovoltaic effects

Introduction

Spectral sensitization by dyes with an absorption band in the visible and near-infrared spectral region is widely used to increase the sensitivity of photophysical and photochemical processes in various solids (AgHal, ZnO, TiO_2 and others) (Akimov et al 1980; Goryaev 2015; 2016; 2018; 2019; Goryaev, Pimenov 1975; 1980; James 1977). The application of organic dyes provides effective control of the photosensitivity spectrum and increases the sensitivity of classical silver halide photographic materials (James 1977). Photoelectrochemical cells based on titanium dioxide particles with sensitizing dyes are proposed as an alternative to silicon solar cells (Gratzel 2003). The efficiency of using organic dyes is primarily determined by the high extinction coefficient in the absorption band. One of the significant deficiencies of silicon solar cells is the relatively low extinction coefficient of this semiconductor in the region of indirect transitions; therefore, converters of light energy into electrical energy manufactured on its basis must have a sufficiently large thickness (Alferov et al 2004). Effective dye sensitization of DC photoconductivity was found in powdered silicon (Goryaev 2015; 2016) and in monolithic silicon (Goryaev 2018; 2019). In this paper, the photovoltaic effect in silicon samples with different types of conductivity and the influence of organic dyes on its surface on its spectra and kinetics are investigated.

Results and discussion

The investigations were carried out on samples with electron conductivity, doped with phosphorus at a concentration of 10^{15} cm^{-3}, and with hole conductivity, doped with boron at a concentration of 10^{15} cm^{-3}. Photo-EMF spectra on flat monocrystalline samples with an area of about 1 cm^2 and a thickness of 360–450 μm were measured using the capacitor method (Akimov 1966) at modulated illumination. The block schematic diagram of this measuring complex is shown in Fig. 1.

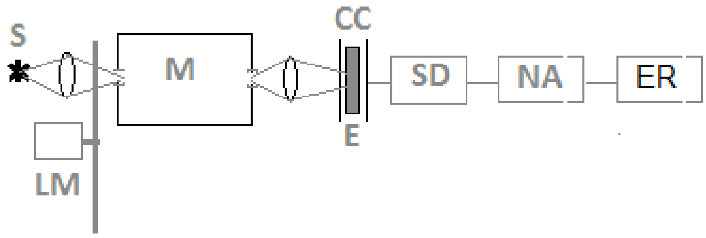

Fig. 1. Block schematic diagram of the laboratory complex for measuring photo-EMF spectra by the capacitor method. S — light source, LM — light modulator, M — monochromator, CC — capacitor cell, E — sample, SD — synchronous detector, NA — narrow-band amplifier, ER — curve-tracer Enregistreur

DC photoconductivity was studied in powdered samples of silicon with a microcrystal size of several microns, obtained by grinding the original single-crystal samples. It was measured in special surface-type cells in order to study the electrophysical properties of powder semiconductors, in which a sample in the form of a tablet is pressed by constant pressure (about 10 kg/cm^2) to a quartz plate. Platinum electrodes were applied to a quartz plate in the form of a raster so that the distance between the electrodes was 0.1 mm with an effective electrode length of 80 mm. The ethanol solution of the required dye of a certain concentration was used for placing the dye molecules on the surface of a semiconductor. The effect of the dye on the photoelectric properties of samples was studied after the adsorption of the dye and the non-stimulated evaporation of the solvent at room temperature. To assess the efficiency of the internal photoelectric effect in different spectral regions, the photo-EMF signals U_{ph} and the DC photocurrents I_{ph} were normalized to the same number of light quanta E falling on the sample. The results, illustrated in Fig. 2, show that the dye applied on the surface of the semiconductors at different concentrations significantly influences the spectra of the capacitor photo-EMF of monocrystal silicon samples with different types of conductivity in the absorption band of the dye.

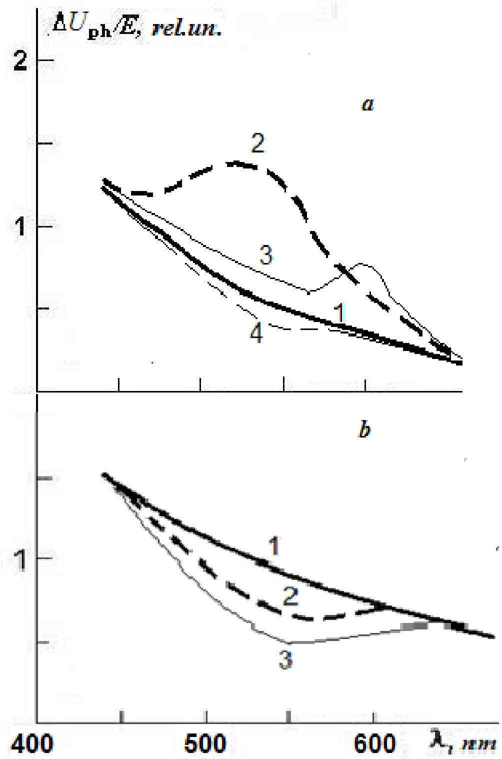

Fig. 2. Photo-EMF spectra of a silicon sample without dye (1) and samples dyed with rhodamine 6G at dye molecule concentrations of 40 nm^{-2} (2), 70 nm^{-2} (3) and 110 nm^{-2} (4); a — n-type semiconductor, b — p-type semiconductor

When rhodamine 6G is placed on the surface of a semiconductor with electronic conductivity, the photo-EMF initially increases with growth dye concentration (Fig. 2a, curves 1 and 2), and spectral sensitization of the photoelectric effect occurs. The maximum value of the recorded signal in the dye absorption band increases almost twofold. The resulting sensitized photoelectric effect is determined by the different contribution of charge carriers generated due to energy transfer from the dye. In silicon, when light is absorbed in a given region, both additional electrons and holes appear when electrons transfer between the valence band and the conduction band. The studied samples were homogeneous. They did not contain heterojunctions, and no conditions for the implementation of the valve component of the photo-EMF were created. Therefore, the observed capacitor photo-EMF has a diffusion nature and is caused by the diffusion of generated charge carriers in the semiconductor due to the gradient of their concentration during light absorption (Dember effect) (Akimov 1966; Bonch-Bruevich, Kalashnikov 1977). The Dember EMF is determined by the relationship:

$$U_{ph} = \frac{kT}{e} \frac{\mu_n - \mu_p}{\mu_n + \mu_p} ln \frac{\sigma_1}{\sigma_2},$$

where μ_n and μ_p are the mobilities of electrons and holes, while σ_1 and σ_2 are the conductivities at the front and back surfaces of the sample. The magnitude of the EMF will be determined by the difference in the mobilities of electrons and holes. In silicon, the mobility of holes is several times lower than that of electrons (Bonch-Bruevich, Kalashnikov 1977); therefore, the main contribution to the change in photo-EMF is made by electrons generated during the transfer of energy from the dye.

In n-type silicon without dye, the photo-EMF is caused by electrons; therefore, when the dye is applied at small concentrations, an increase in the EMF is also observed due to additional electrons appearing as a result of the transfer of photoexcitation energy from the dye to the semiconductor (Fig. 2a, curves 1 and 2). Further, with an increase in the amount of the applied dye, the value of the photo-EMF decreases (Fig. 2a, curves 3 and 4) since part of the energy hitting the sample does not reach the semiconductor due to an increase in the thickness of the dye film on the surface of this semiconductor, and a filter effect is observed in the absorption band of the dye (Goryaev 1980; 2015; 2019).

It should be noted that the filter effect manifests itself primarily in the short-wave region of the dye absorption band (Fig. 2a, curve 3). This is due to the fact that, according to the theory, the efficiency of inductive-resonant nonradiative energy transfer depends on the overlap integral of the luminescence spectrum of the donor and the absorption spectrum of the energy acceptor (Ermolaev et al 1996):

$$K = C \int I_d n(\nu) \varepsilon_a(\nu) \nu^{-4} d\nu,$$

where I_d is the quantum spectral density of the donor luminescence radiation, $\varepsilon_a(\nu)$ is the molar decimal absorption coefficient of the energy acceptor, n is the refractive index of the medium, ν is the wave number and C is a constant. The overlap integral strongly depends on the wave number, which is confirmed by the more noticeable luminescence quenching of dyes in the long-wavelength region of the spectrum during the transfer of energy to the solid (Goryaev, Akimov 1979). Therefore, the spectra of the sensitized photoelectric effect are shifted relative to the absorption spectra of the dye, and with an increase in the dye concentration, the filter effect is first noticeable in the short-wave region of the absorption band; in addition, sensitization of the photo-EMF is observed in the long-wave region (Fig. 2a, curve 3) and it is only with a further increase in the dye concentration that merely the filter effect is observed. (Fig. 2a, curve 4).

The magnitude of the photo-EMF of p-type monocrystal silicon samples decreases monotonically from the beginning in the absorption band of the dye if its concentration on the surface of the semiconductor increases (Fig. 2b, curves 1–3). As already noted, the photo-EMF, due to the carriers of the charge generated when the transfer of photoexcitation energy occurs from the dye to the semiconductor is ultimately determined by additional electrons. The polarity of this component is opposite to the photo-EMF caused by the majority charge carriers of p-type silicon, i. e. holes. All this, together with the filter effect described above, leads to a desensitizing effect of the dye on the photovoltaic effect in p-type silicon (Goryaev 2024a; 2024b).

The different influence of the dye on the photovoltaic effect in silicon with different types of conductivity is confirmed by kinetic investigations (Goryaev 2025). Fig. 3 shows kinetic curves of the photo-EMF of n-type (a) and p-type (b) silicon samples upon excitation by light in the absorption band of the dye.

When the dye is applied to the surface of silicon, an increase in the photo-EMF value is observed at low concentrations since the main contribution to the change in EMF is made by the electrons generated during the transfer of energy from the dye and it coincides with polarity of the photo-EMF in the original n-type silicon (Fig. 3a, curves 1 and 2). An increase in the dye concentration is further accompanied by a decrease in the signal (curve 3), associated with a filter effect in the absorption band of the dye.

The photo-EMF of silicon samples with hole conductivity in the steady state decreases in the absorption band of the dye as its concentration on the surface of the semiconductor increases (Fig. 3b, curves 1–3). This is due to the fact that the additional photo-EMF during the transfer of photoexcitation energy from the dye is determined by electrons and its polarity is opposite to the photo-EMF caused by the main

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carriers of p-type silicon, which leads to a desensitizing effect of the dye: the photoelectric effect almost completely disappears (curve 3). It should be noted that the kinetic curve of the photovoltaic effect is non-monotonic at a relatively high concentration of the dye (Fig. 3b, curve 3). This behavior may be explained by the fact that the generation of additional carriers due to the transfer of photoexcitation energy from the dye molecule to the semiconductor begins later than carriers appear after direct absorption of light during interband transition in silicon.

The investigation of DC photoconductivity revealed spectral sensitization of powdered silicon samples with both electron and hole conductivity (Fig. 4).

The photoconductivity of n-type semiconductors without dye (Fig. 4a, curve 1) is slightly higher than photoconductivity of p-type samples (Fig. 4b, curve 1), and the photoelectric effect, when a dye is applied, is almost two orders of magnitude higher than the photoconductivity of the original samples (Fig. 4, curves 2). This is due to the fact that both electrons and holes generated when the transfer of photoexcitation energy occurs from the dye to the semiconductor lead to an increase in photoconductivity, and the high efficiency of sensitization is due to the fact that the specific surface area of powdered silicon is several orders of magnitude larger than the specific surface area of monocrystal samples.

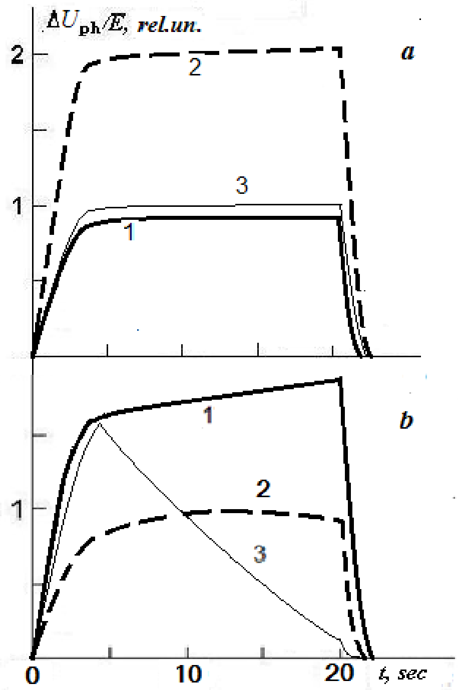

Fig. 3. Kinetics of the photovoltaic effect in silicon without dye (1) and in samples dyed with rhodamine 6G with dye molecule concentrations of 40 nm^{-2} (2) and 70 nm^{-2} (3); a — n-type semiconductor, b — p-type semiconductor

Conclusion

The adsorption of an organic dye on the surface of silicon monocrystals provides a sensitizing effect in the dye absorption band on the photovoltaic Dember effect in samples with n-type conductivity and a desensitizing effect in p-type samples. In silicon powder samples, efficient sensitization of DC photoconductivity is observed for semiconductors with both n-type and p-type conductivity. Spectral sensitization with dyes can be used to increase the efficiency of silicon systems for converting light energy into electrical energy, and the identified sensitizing and desensitizing actions of the dye on the photovoltaic effect in silicon with different types of conductivity must be taken into account when complex systems with heterojunctions are created for such semiconductor devices.

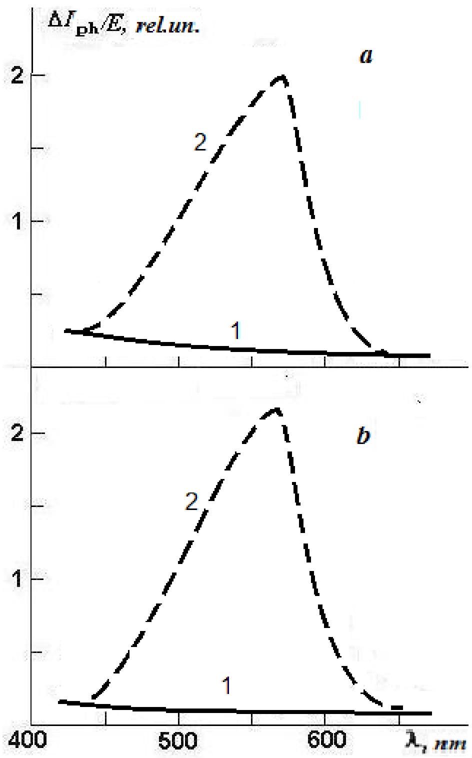

Fig. 4. Photoconductivity spectra of silicon without dye (1) and samples dyed with rhodamine 6G with a dye molecule concentration of 10^{-4} mol/gSi (2); a — n-type semiconductor, b — p-type semiconductor

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

The authors have made equal contributions to the paper.

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