



UDC 538.9 + 535.3

EDN TNBLEU

<https://www.doi.org/10.33910/2687-153X-2026-7-3-106-110>

Influence of the concentration value of sensitizing dyes on the photovoltaic effect in monocrystalline n-type silicon in the optical region

M. A. Goryaev^{✉1}, A. P. Smirnov¹

¹ Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia

Authors

Mikhail A. Goryaev, ORCID: [0000-0002-2182-6763](https://orcid.org/0000-0002-2182-6763), e-mail: mgoryaev@mail.ru

Alexander P. Smirnov, ORCID: [0000-0003-2463-2056](https://orcid.org/0000-0003-2463-2056), e-mail: veter8808@mail.ru

For citation: Goryaev, M. A., Smirnov, A. P. (2026) Influence of the concentration value of sensitizing dyes on the photovoltaic effect in monocrystalline n-type silicon in the optical region. *Physics of Complex Systems*, 7 (3), 106–110. <https://www.doi.org/10.33910/2687-153X-2026-7-3-106-110> EDN TNBLEU

Received 5 May 2026; reviewed 8 June 2026; accepted 15 June 2026.

Funding: The study did not receive any external funding.

Copyright: © M. A. Goryaev, A. P. Smirnov (2026). Published by Herzen State Pedagogical University of Russia. Open access under [CC BY License 4.0](https://creativecommons.org/licenses/by/4.0/).

Abstract. This paper investigates the impact of sensitizing organic dyes located on the surface of monocrystalline n-type silicon on the character of the photovoltaic effect. It studies the sensitized photovoltaic effect with erythrosine and methylene blue dyes used as sensitizers at different concentrations. The findings are discussed from the point of view of the mechanism of nonradiative inductive-resonant transfer of energy absorbed by the sensitizing dye to the surface of silicon crystal.

Keywords: monocrystalline n-type silicon, erythrosine and methylene blue dyes, sensitized photovoltaic effect, concentration of sensitizing dyes, absorption spectra of the sensitizing dyes

Introduction

The relatively low extinction coefficient of silicon in the region of indirect transitions predetermines a serious limitation of solar cells based on this type of semiconductors; therefore, converters of light energy into electrical energy manufactured on its basis must have a comparatively large thickness (Alferov et al. 2004). In turn, spectral sensitization by dyes with an absorption band in the visible and near infrared region of the spectrum of organic dyes provides effective control over the spectrum and level of photosensitivity of classical silver halide photographic materials (James 1977). Moreover, this sensitization is widely used to increase the efficiency of photophysical and photochemical processes in various wide-band gap semiconductors (Akimov et al. 1980; Goryaev, Pimenov 1975; 1980). Photoelectrochemical cells based on titanium dioxide particles with sensitizing dyes are proposed as an alternative to silicon solar cells (Gratzel 2003). The efficiency of organic dye application is primarily determined by the high extinction coefficient in the absorption band. Spectral sensitization by dyes was observed for DC photoconductivity in powdered silicon (Goryaev 2015) and for photo-EMF in a monocrystalline semiconductor (Goryaev 2019). The paper (Goryaev, Smirnov 2025) shows that sensitization of photo-EMF is observed only in silicon with electron conductivity, and in samples with hole conductivity desensitization of the photoelectric effect occurs. Effective sensitization of photoconductivity at direct current is manifested in samples with any type of conductivity for powdered silicon (Goryaev, Smirnov 2025). This paper delves into the photovoltaic effect in n-type silicon samples and the influence of organic dyes

with absorption bands in the region of indirect electron transitions in silicon on its spectra, which are located on the surface of the semiconductor.

Experiment

This work focused on monocrystalline n-type silicon samples doped with phosphorus. The sample area was approximately 1 cm^2 , with the thickness of $360\text{--}450 \text{ }\mu\text{m}$. The photo-EMF spectra were measured using a capacitor method (Akimov 1966; Goryaev, Smirnov 2025). Adsorption of dye molecules on the surface of the samples was carried out by dosed application of an ethanol solution of a certain concentration of this dye to the sample under study. After the adsorption, the sample was dried for 1–2 days. Erythrosine and methylene blue were used as organic dyes. The samples were irradiated with modulated light, and the absorption spectra of ethanol solutions of the dyes measured using an SF-26 spectrophotometer. To adequately assess the degree of expression of the internal photoelectric effect in different regions of the spectrum, the photo-EMF signals ΔU_{ph} were normalized to the number of light quanta E incident on the sample at a corresponding wavelength.

Results and discussion

Fig. 1 shows the spectrum of the photovoltaic effect in silicon without a dye. The magnitude of photo-EMF decreases monotonically with an increasing wavelength. This behavior of spectral dependence is associated with the fact that the considered range corresponds to the region of indirect transitions in silicon. These transitions occur in a semiconductor at an energy of absorbed light quanta from 2.5 eV (the vertical gap between the valence and conduction bands of silicon) to 1.08 eV (the thermal gap between the bands at 300 K) and are characterized by a monotonic decline in absorption with decreasing energy in the specified range (Bonch-Bruevich, Kalashnikov 1977; Wert, Thomson 1969).

Erythrosine and methylene blue dyes are effective sensitizers in the visible and near infrared spectral regions (Akimov et al. 1980; Goryaev 2015). Fig. 2 shows the absorption spectra of these dyes in an ethanol solution.

The efficiency of spectral sensitization of the photovoltaic effect in a semiconductor by a dye is characterized by the value $(\Delta U/\Delta U_0)-1$, where ΔU and ΔU_0 are the measured photo-EMF signals of the dyed and undyed samples, respectively. This value shows the proportion of the sensitized photoelectric effect value to the intrinsic photoelectric effect value, and its dependence on the wavelength represents the differential spectrum of the sensitized photoelectric effect.

Fig. 3 shows the differential spectra of the sensitized photoelectric effect of silicon dyed with erythrosine (a) and methylene blue (b).

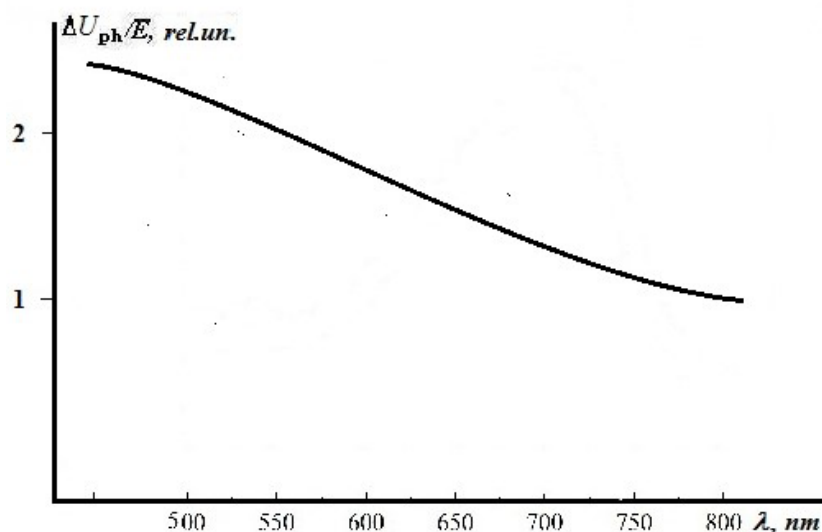


Fig. 1. Photo-EMF spectrum of silicon without a dye

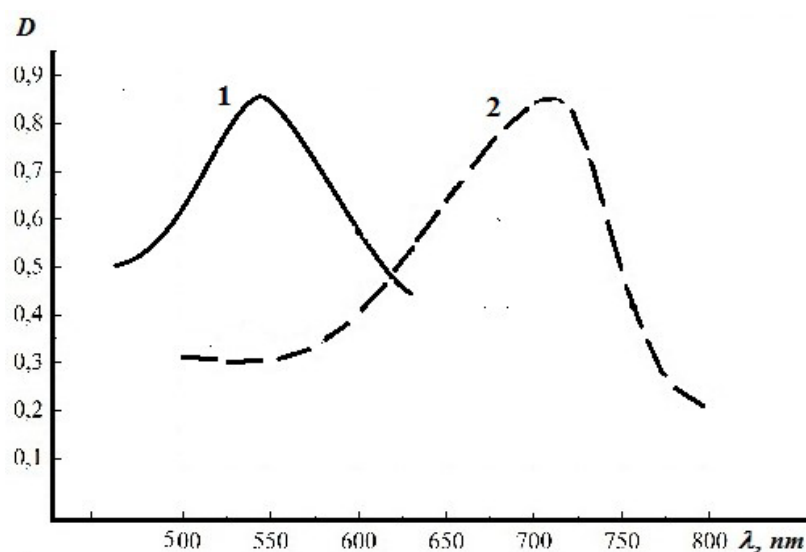


Fig. 2. Absorption spectra of erythrosine (1) and methylene blue (2) in ethanol with a dye concentration of $2 \cdot 10^{-4}$ M/L

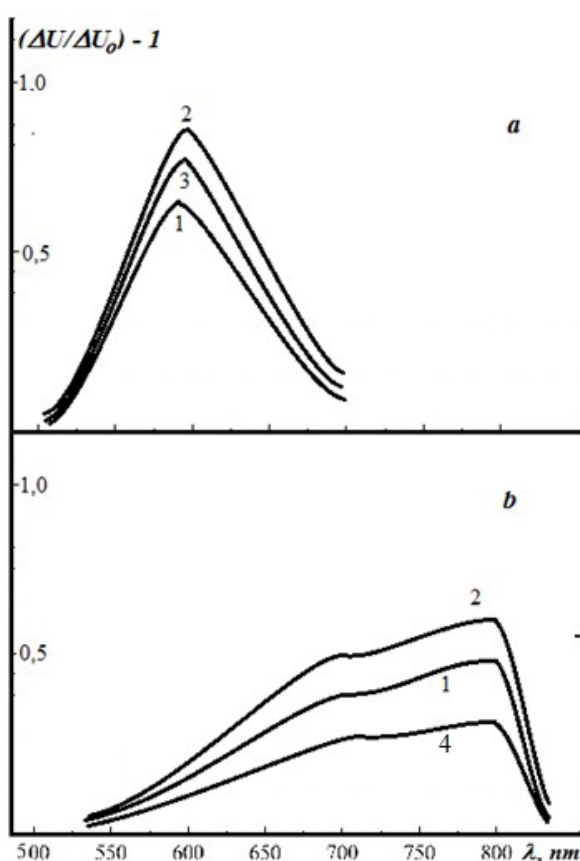


Fig. 3. Differential spectra of the sensitized photoelectric effect in dyed silicon samples with dye molecule concentrations of 40 nm^{-2} (1), 70 nm^{-2} (2), 110 nm^{-2} (3), and 210 nm^{-2} (4). a — semiconductor with an adsorbed erythrosine dye; b — semiconductor with an adsorbed methylene blue dye

When the dye concentration increases, the magnitude of the sensitized photoelectric effect rises to certain limits, reaching 80% for erythrosine and 60% for methylene blue relative to photo-EMF in an undyed sample (Fig. 3, curves 1 and 2). It should be noted that the efficiency of sensitization in the infrared region can be augmented using supersensitizers, as done in silver halide photography (Goryaev,

Shapiro 1997). A comparison between the sensitization spectra of the photoelectric effect and the absorption spectra of the dyes shows that the sensitization maxima are shifted to the longer wavelength region relative to the maxima of the absorption bands (Figs. 2 and 3). This is probably due to the interaction of the dyes with the semiconductor surface during adsorption (Akimov et al. 1980; Goryaev, Pimenov 1980). Also playing a role in this shift is the fact that the first phase of the sensitization process is the nonradiative transfer of energy absorbed by the dye to the semiconductor. According to theory, the efficiency of inductive-resonant non-radiative 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 spectral density of the donor luminescence radiation, $\varepsilon_a(\nu)$ is the molar 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, as confirmed by a more intensive quenching of the luminescence of dyes in the long-wavelength region of the spectrum when energy is transferred to a solid (Goryaev, Akimov 1979). Therefore, the spectra of the sensitized photoelectric effect are shifted relative to the absorption spectra of the dye to the long-wave region.

The maximum efficiency of sensitization is observed at a dye concentration of 70 nm^{-2} on the semiconductor surface. If the concentration continues to rise, the photo-EMF value decreases (Fig. 3, curves 3 and 4). This is due to the fact that an increase in the dye layer thickness amplifies the role of intramolecular processes of non-radiative disappearance of absorbed energy. Furthermore, a great part of the light energy does not hit the silicon crystal, and a filter effect exists in the dye absorption band (Goryaev 1980; 2015; 2019). In turn, a low concentration of the dye on the surface of silicon crystal leads to an insufficient influence of this dye on the photovoltaic effect.

Conclusion

Organic dyes on the surface of silicon monocrystals with electronic conductivity have a sensitizing action on the photovoltaic effect in the absorption band of the dye in the region of indirect electronic transitions of the semiconductor. The optimal concentrations of the dyes have been determined for the case when the sensitized photo-EMF almost reaches the value of its own photoelectric effect. A higher amount of dye applied to the semiconductor is associated with a filter effect and a significant reduction in the photovoltaic effect.

Conflict of Interest

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

Author Contributions

Authors' contributions to the paper are equal.

Acknowledgements

The authors are grateful to V. G. Kossov and V. A. Ivanov for providing the silicon samples.

References

- Akimov, I. A. (1966) Investigation of the internal photoelectric effect in semiconductors using the capacitor method. *Optiko-Mekhanicheskaya Promyshlennost'*, 33 (5), 248–255. (In Russian)
- Akimov, I. A., Cherkasov, U. A., Cherkashin, M. I. (1980) *Sensitized photoeffect*. Moscow: Nauka Publ., 384 p. (In Russian)
- Alferov, J. I., Andreev, V. M., Rumyantsev, V. D. (2004) Solar photovoltaics: Trends and prospects. *Semiconductors*, 38 (8), 899–908. <https://doi.org/10.1134/1.1787110> (In English)
- Bonch-Bruевич, V. L., Kalashnikov, S. G. (1977) *Physics of Semiconductors*. Moscow: Nauka Publ., 672 p. (In Russian)

- Ermolaev, V. L., Sveshnikova, E. B., Bodunov, E. N. (1996) Inductive-resonant mechanism of nonradiative transitions in ions and molecules in condensed phase. *Physics-Uspеhi*, 39 (3), 261–282. <https://doi.org/10.1070/PU1996v039n03ABEH000137> (In English)
- Goryaev, M. A. (1980) Photoprocesses in aluminum hydride with adsorbed dye. *Optics and Spectroscopy*, 49 (6), 625–627. (In English)
- Goryaev, M. A. (2015) Dye sensitization of photoconductivity of polycrystalline silicon. *Russian Journal of Physical Chemistry A*, 89 (12), 2320–2321. (In English)
- Goryaev, M. A. (2019) Spectral sensitization of Photo-EMF in monocrystalline silicon. *Optics and Spectroscopy*, 127 (1), 167–169. (In English)
- Goryaev, M. A., Akimov, I. A. (1979) Luminescence of dyes adsorbed on aluminum hydride and its variation during photolysis of the adsorbent. *Optics and Spectroscopy*, 47 (2), 229–230. (In English)
- Goryaev, M. A., Pimenov, Yu. D. (1975) Effect of an electric field on photochemical processes in aluminum hydride. *Optiko-Mekhanicheskaya Promyshlennost'*, 42 (9), 50–54. (In Russian)
- Goryaev, M. A., Pimenov, Yu. D. (1980) Managing the processes of image formation in inorganic materials. *Uspekhi nauchnoj fotografii*, 20, 96–105. (In Russian)
- Goryaev, M. A., Shapiro, B. I. (1997) Sensitization of silver heat-developable materials to the near-IR range. *Zhurnal nauchnoj i prikladnoj fotografii*, 42 (2), 65–67. (In Russian)
- Goryaev, M. A., Smirnov, A. P. (2025) Spectra and kinetics of dye-sensitized photovoltaic effect in silicon. *Physics of Complex Systems*, 6 (3), 134–138. <https://doi.org/10.33910/2687-153X-2025-6-3-134-138> (In English)
- Gratzel, M. (2003) Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C-photochemistry Reviews*, 4 (2), 145–153. (In English)
- James, T. H. (1977) *The theory of the photographic process*. New York: Macmillan Publ., 562 p. (In English)
- Wert, Ch., Thomson, R. (1969) *Physics of solids*. Moscow: MIR Publ., 558 p. (In Russian)