Dye Sensitization of Silicon

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ABSTRACT: *The direct current photoconductivity of the powdered silicon and photovoltaic effect in the monocrystallic silicon are investigated. It is shown that organic dyes on the semiconductor surface effectively increase the internal photo effect in the dye absorption band. The photoconductivity of dyed powdered samples in the absorption range of the dyes is higher than the photoconductivity of undyed silicon by more than an order of magnitude. The optimum concentration of dye molecules on the monocrystal surface for a sensitization is 3×10^{15} cm^{-2}, which corresponds to the dye film thickness of about 30 monolayers or 10-15 nanometers.*
Keywords: *DC Photoconductivity, Dye Sensitization, Photovoltaic Effect, Silicon.*

I. INTRODUCTION

Spectral dye sensitization of photovoltaic effect and photolysis in broad-band semiconductors (ZnO, AgHal, TiO$_2$, etc) is well known [1, 2]. In the conventional photography dye sensitization is the most effective method of varying the sensitivity level and spectrum of photographic materials based on silver halides [3], and dye-sensitized titanium dioxide solar cells were suggested as the alternative to silicon solar cells [4]. The main disadvantage of solar cells based on crystalline silicon is relatively low absorption coefficient in the band of indirect electron transitions [5, 6]. Therefore the thickness of photoelectric transducers produced on the basis of this semiconductor must be hundreds of microns [7]. Silicon CCD matrices are used as image sensors in modern electron photography systems [8], and light filters used for the color separation system lead to a loss of energy and valuable information [9]. The goal of this work was to study the photovoltaic effect in silicon and the influence on its effectiveness of the application of organic dyes to the semiconductor surface.

II. MATERIALS AND METHODS

Silicon powder 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 photoconductivity measurements were performed in special surface type cells for investigating the electro-physical properties of powder semiconductors [10], 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 platinum electrodes in the form of a solution; the distance between the electrodes was 0.1 mm, and the effective length of electrodes was 80 mm. The measurements were carried out in conditions of a constant sweeping electric field. The method used for the investigation of the monocrystal samples was the measurement of the condenser photo-EMF at the modulated irradiation [11]. To estimate the effectiveness of the photoeffect, the measured signals ΔI_{ph} and ΔU_{ph} were normalized to the same number of incident light quanta E.

III. RESULTS AND DISCUSSION

3.1 Powdered Silicon

Figures 1 and 2 show the photoconductivity spectra of the starting silicon sample and the samples with the dyes applied to the semiconductor surface [12, 13]. The results show that the photoconductivity of dyed samples in the absorption range of the dyes (curves 2 and 3, Fig. 1; curve 2, Fig. 2) is higher than the photoconductivity of undyed silicon by more than an order of magnitude (curves 1, Fig. 1 and 2).

The increase in photoconductivity in the absorption range of the dye cannot be associated 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.
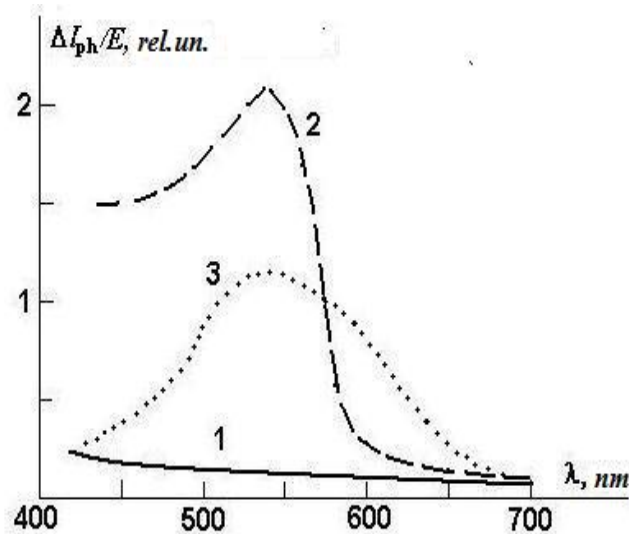
Figure 1: Photoconductivity spectra of undyed silicon (1) and samples dyed with erythrosine (2) and crystal violet (3).
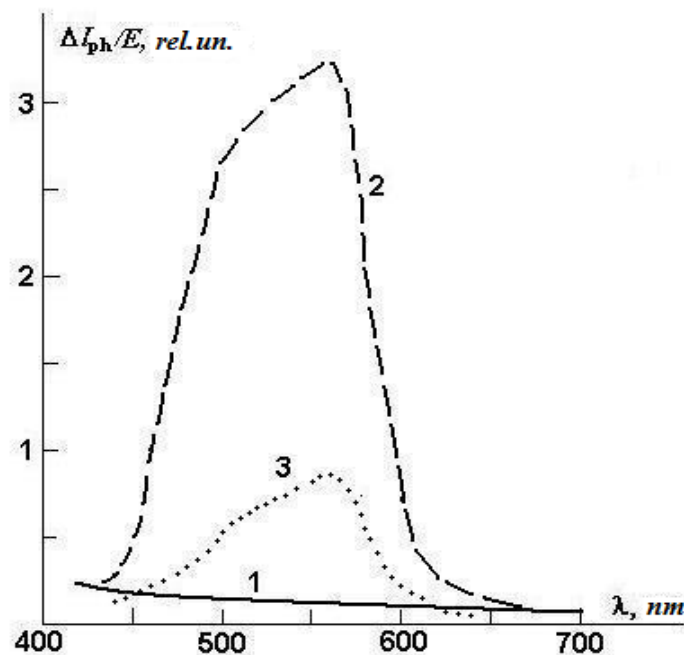

Figure 2: Photoconductivity spectra of undyed silicon (1) and samples dyed with rhodamine 6G with concentrations of 10^{-4} Mole/g of Si (2) and 2×10^{-4} Mole/g of Si (3).

3.2 Monocrystallic Silicon

In a range of condenser photo-EMF of monocrystal silicon the sensitization of photoeffect of the dyed samples in the absorption band of the dye (curve 2, Fig. 3) in comparison with undyed silicon is also observed (curve 1, Fig. 3) [14]. The magnitude of the sensitized photoeffect in silicon monocrystals is significantly smaller than in powder samples. This is a consequence of the fact that the specific surface area of finely divided powders is several orders of magnitude larger than in monocrystals. It should be noted that an increase in photoconductivity during light absorption by the dye happens because of a small extinction coefficient of silicon absorption and the carrier generation during a characteristic absorption happens rather deep in the crystal. We should also take into account the fact that the length of the efficient energy transfer radius during the dye sensitization is several nanometers [1], therefore the role of near-surface photoelectron generation increases. As the thickness of monocrystals is very considerable, the contribution of such near-surface processes is small in comparison with the volume carrier generation due to the characteristic absorption of the semiconductor.
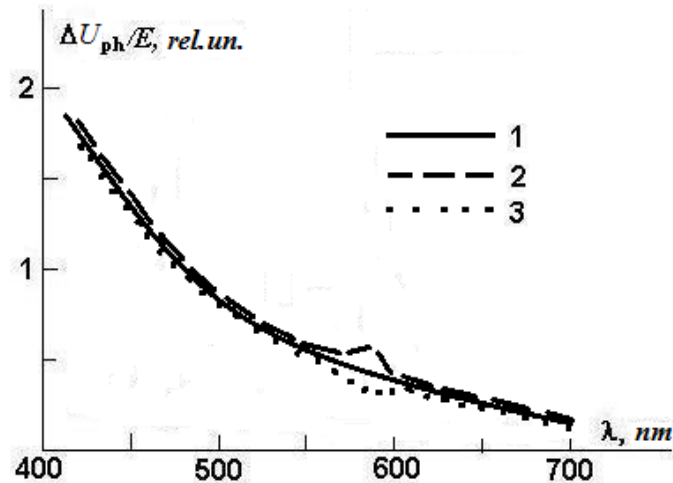
Figure 3: Photo-EMF spectra of undyed silicon monocrystals (1) and samples dyed with rhodamine 6G with dye molecule concentrations of 3×10^{15} cm^{-2} (2) and 6×10^{15} cm^{-2} (3).

3.3 Sensitization Mechinism

Let us consider the processes occurring in the dye-semiconductor system during light absorption by the dye. During the dye photoexcitation both non-radiative and radiative electron transitions can occur in the molecule. The rate of the internal energy degradation depends on the rigidity of the dye molecule skeleton, which determines the possibility of electron excitation energy exchange between the vibrational and rotational degrees of freedom. For the majority of dyes in the adsorbed state the molecular structure becomes more rigid and intramolecular conversion probability becomes insignificant. Therefore, the luminescent quantum yield of adsorbed dyes is measured in tens of percent on dielectrics [15], while 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 to the adsorbent [16].

During the light absorption by the dye the received photoexcitation energy can be transferred to the semiconductor, be observed as quantum luminescence and degrade within the molecule with the corresponding transition constants k_1, k_2 and k_3. Quantum efficiency of the electronic excitation transfer is determined by the ratio:

$$\Phi_{tr} = \frac{k_1}{k_1 + k_2 + k_3}. \tag{1}$$

For the majority of dyes the hardening of the molecule structure is observed in the adsorbed state. Therefore the intramolecular energy conversion rate on vibrational and rotational degrees of freedom k_3 becomes insignificant when compared to k_1 and k_2. As a result, luminescence becomes the main competing process with the effective sensitization of photophysical and photochemical processes in the semiconductor. The fluorescent state lifetimes of adsorbed dyes are 10^{-11}-10^{-10} s, and photoexcitation transfer rate constant k_1 in effectively sensitized semiconductors exceeds 10^{12} s^{-1}, so the effectiveness of the electronic excitation transfer Φ_{tr} approaches unity under such circumstances [1].

The efficacy 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:

$$\Phi_s = \Phi_a \cdot \Phi_{tr} \cdot \Phi_{ph}, \tag{2}$$

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

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 [17]. Local electronic states of the forbidden band play the role of the energy acceptors in broad-band semiconductor sensitization

One of the main reasons for the luminescence quenching in these systems is the existence of local electron states in the forbidden gap of the semiconductor capable of accepting energy from the dye. For the complete luminescence quenching a certain concentration of the surface state occupied by electrons, and an integrated density

10^9 -10^{10} cm^{-2} is sufficient [2, 16]. This is an essential requirement for the sensitization of broad-band semiconductors, in which surface states occupied by electrons are responsible for the weak absorption and photoconductivity in the impurity region. The dyes significantly increase the absorption in this region, thus providing spectral sensitization of the internal photoelectric effect.

In silicon this energy interval corresponds to electron transitions from the valence band to the conduction band; therefore, the density of states capable of accepting the photoexcitation energy of the dye is quite sufficient for the complete luminescence quenching. The significant increase in the efficiency of generating free carriers during the energy transfer from the dye compared with the intrinsic absorption of a light quantum by the semiconductor may be explained by the fact that this absorption is formed by indirect electronic transitions.

3.4 Dye Concentrations

The magnitude of the observed photocurrent sensitization effect depends on the amount of dye applied to the semiconductor surface: 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, hindering the transition of charge carriers among the semiconductor microcrystals.

When the dye concentration is increased on monocrystals the photoeffect at first increases and then decreases in an absorption band of the dye as well (curves 2 and 3, Fig. 3). The optimum concentration of dye molecules on the monocrystal surface for a sensitization is 3×10^{15} cm^{-2}. Taking into account that the area of dye molecules is 0.7-1.5 nm^2 [3], it corresponds to the dye film thickness of about 30 monolayers or 10-15 nanometers. As the efficient radius of energy transfer at the dye sensitization is 5-7 nanometers in length [1], part of the energy absorbed by the dye does not reach the semiconductor. Besides, with the increase in the film thickness during light absorption by the dye, the role of the intramolecular energy conversion rate on the vibrational and rotational degrees of freedom increases. All this as a result leads to a manifestation of the filter effect in an absorption band of the dye applied on the crystal surface, as it is observed in dye sensitization of aluminum hydride [18].

IV. CONCLUSION

In this work we have found the effective dye sensitization of the internal photoelectric effect in silicon which is described above. This sensitization can be used in semiconductor devices for converting the light energy into electric energy, such as solar panels or CCD matrices used as image sensors in modern electronic photography systems. CCD matrices used as image sensors in modern electron photography systems. In the latter case, the use of dye sensitization will allow the improvement of the color separation system during the recording of colored images by choosing appropriate dyes instead of light filters, which inevitably lead to a loss of energy and valuable information, to provide an effective increase in sensitivity in the required spectral range, as in traditional silver halide photography.

REFERENCES

[1]. I. A. Akimov, Yu. A. Cherkasov, and M. I. Cherkashin, Sensitized Photoeffect.(Moscow: Nauka, 1980).

[2]. M. Goryaev, Physical fundamentals of solid state photochemistry. Photolysis of inorganic solids (Saarbrucken: Lambert Acad. Publ., 2013).

[3]. T. H. James, The Theory of the Photographic Process (New York: Macmillan Publ. Company, 1977).

[4]. M. Gratzel, Dye-sensitized Solar Cells, Journal of Photochemistry and Photobiology C: Photochemistry Review, 4(2), 2003, 145-153.

[5]. Zh. I. Alferov, V. M. Andreev, and V. D. Rumyantsev, Solar Photovoltaics: Trends and Prospects, Semiconductors, 38(8), 2004, 899-908.

[6]. J. A. Duffie, W. A. Beckman, Solar Engineering of Thermal Processes (New York: John Wiley & Sons, Inc., 2013).

[7]. V. P. Afanasyev, E. I. Terukov, and A. A. Sherchenkov, Thin Film Solar Cells Based on Silicon (St. Petersburg: State Electrotech. Univ., 2011).

[8]. W. S. Boyle, Nobel Lecture: CCD—An extension of man's view, Review of Modern Physics, 82(3), 2010, 2305-2306.

[9]. M. A. Goryaev, and Yu. A. Dudnikov, Electronic and hybrid imaging systems, Zhurnal nauchnoi i prikladnoi fotografii i kinematografii, 35(5), 1990, 386-394.

[10]. T. I. Povkhan, K. B. Demidov, and I. A. Akimov, Cells for research of electrophysical properties of powdered semiconductors. Pribory and Tekhnika Eksperimenta, (3), 1974, 217-218.

[11]. I. A. Akimov, The internal photoeffect investigation in semiconductors by the condenser method. Soviet Journal of Optical Technology, 33(5), 1966, 248-257.

[12]. M. A. Goryaev, Dye sensitization of photoconductivity of polycrystalline silicon, Russian Journal of Physical Chemistry A, 89(12), 2015, 2320-2321.

[13]. M. A. Goryaev, Sensitized Photoconductivity in Silicon, Proc. 13th International scientific-technical Conf. on actual problems of electronic instrument engineering, Novosibirsk, 2016, 1(1), 24-26.

[14]. M. A. Goryaev, Dye sensitized photoeffect in silicon, Proc. VI International Conf. Photonics and Information Optics. Moscow, MEPHI, 2017, 68-69.

[15]. M. A. Goryaev, Quantum yield and luminescence spectra of dyes in the adsorbed state. Optics and Spectroscopy, 51(6), 1981, 562-564.

[16]. I. A. Akimov, and M. A. Goryaev, Photoprocesses in semiconductors with adsorbed dye, Zhurnal fizicheskoi khimii, 58(5), 1984, 1104-1107.

[17]. V. L. Ermolaev, E. N. Bodunov, and E. B. Sveshnikova, Inductive-resonant mechanism of nonradiative transitions in ions and moleculec in condensed phase. Uspehi Fizicheskih. Nauk, 166(3), 1996, 279-302.

[18]. M. A. Goryaev, Photoprocesses in aluminum hydride with an adsorbed dye, Optics and Spectroscopy, 49(6), 1980, 625-627.