

Conference Paper

Conditions for the Dye Sensitization of Photoprocesses in Semiconductors

M. A. Goryaev

Herzen Russian State Pedagogical University, Saint Petersburg, Russia

Abstract

The necessary requirements for the photoeffect sensitization are the existence of electron states in the semiconductors capable of accepting energy from the dye and subsurface band bending. Methods for control of the sensitization efficiency are discussed.

Keywords: Internal Photo Effect, Semiconductors, Dye Sensitization.

Corresponding Author:

M. A. Goryaev
mgoryaev@mail.ru

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1. INTRODUCTION

Spectral dye sensitization of photoelectric and photochemical sensitivity in visible and infrared spectral regions is well known for broad-band semiconductors (ZnO, AgHal, TiO₂, etc). 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 [1-4]. Photoelectrochemical cells based on the dye-sensitized titanium dioxide provide an alternative to silicon solar batteries [5]. The main disadvantage of solar cells based on crystalline silicon is relatively low absorption coefficient in the band of indirect electron transitions, which necessitates the thickness of photoelectric transducers produced on the basis of this semiconductor to be hundreds of micrometers [6-8]. Silicon CCD matrices are used as image sensors in modern electron photography systems, and light filters used for the color separation system lead to a loss of energy and valuable information [9, 10]. The dye sensitization of the photoconductivity in powdered silicon and photovoltaic effect in the monocrystalline silicon were found in works [11, 12]. In the present study we consider the photoelectric sensitivity formation processes in semiconductors with dyes applied on the surface and the possibilities to control this processes.

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2. Materials and methods

Semiconductor powder samples with micrometer-sized microcrystals and flat monocrystals of 1-2 cm² 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 photoconductivity measurements were performed in special surface type cells for investigating the electro-physical properties of powder semiconductors [13], in which the sample in the pellet form was pressed to a quartz plate under constant pressure (approx. 10 kg/cm²). 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 [14]. The method used for the investigation of the monocrystal samples was the measurement of the condenser photo-EMF at the modulated irradiation [15]. 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 .

3. RESULTS AND DISCUSSION

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, 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 [2-4, 16].

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 [2-4]. 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. Figure 1 shows the photoconductivity spectra of the starting silicon sample and the samples with the dyes applied to the semiconductor surface. The results show that the photoconductivity of dyed samples in the absorption range of the dyes (curves 2 and 3, Fig. 1) is higher than the photoconductivity of undyed silicon by more than an order of magnitude (curves 1, Fig. 1). The increase in photoconductivity in the absorption range of the dye cannot be attributed 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, where the photoconductivity is absent altogether.

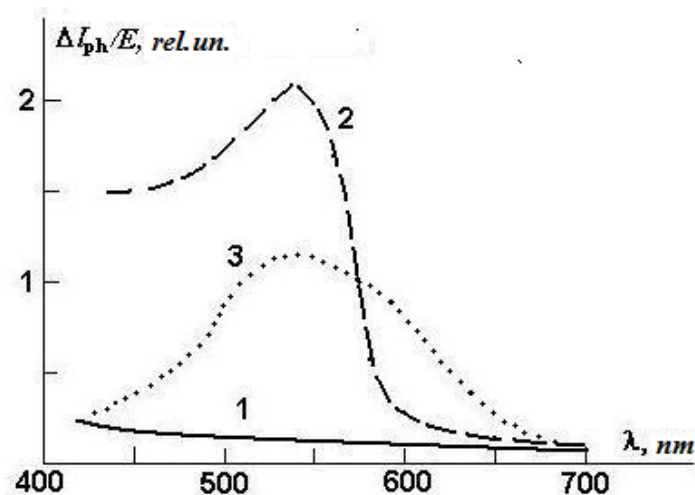


Figure 1: Photoconductivity spectra of undyed silicon (1) and samples dyed with erythrosine (2) and crystal violet (3).

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. 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 [2].

In a spectrum 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. 2) in comparison with undyed silicon (curve 1, Fig. 2) is also observed.

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. 2). The optimum concentration of dye molecules on the monocrystal surface for a sensitization is $3 \times 10^{15} \text{ cm}^{-2}$. Taking into account that the area of dye molecules is 0.7-1.5 nm²[1], 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 [2], 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 results in 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 [4, 17].

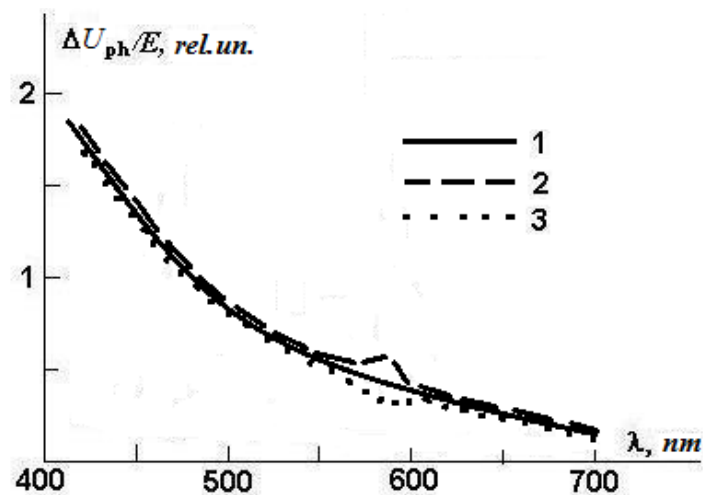


Figure 2: Photo-EMF spectra of undyed silicon monocrystals (1) and samples dyed with rhodamine 6G with dye molecule concentrations of $3 \times 10^{15} \text{ cm}^{-2}$ (2) and $6 \times 10^{15} \text{ cm}^{-2}$ (3).

The adsorbed dye has a filtering effect on the photoconductivity spectrum of AlH_3 in the doped region (curves 1' and 1, Fig. 3), i.e. the energy absorbed by dye converts inside the molecule, part of the incident light does not reach semiconductor and the failure in the photoconductivity spectrum is observed in the absorption band of the dye.

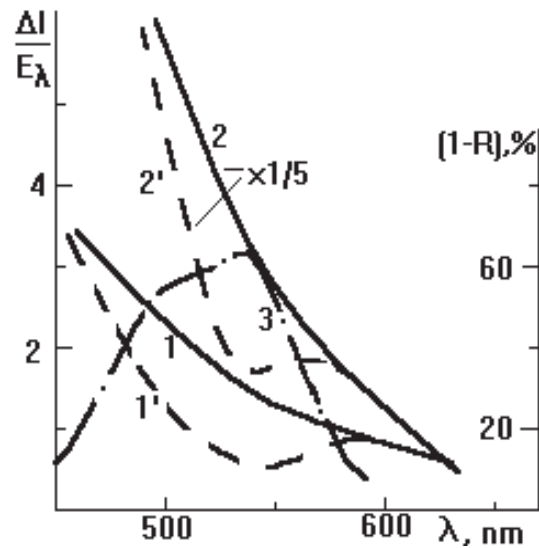


Figure 3: Photoconductivity spectra of undyed (1,2) and dyed with rhodamine 6G (1',2') AlH_3 . 1,1' - initial; 2,2' - exposed by UF light sample; 3 - absorption spectrum of adsorbed dye.

During aluminium hydride photolysis the considerable luminescence quenching of the adsorbed dye is observed due to the emergence of new defects, accepting the energy [4, 18] and photoconductivity strongly increases in the doped region (Fig. 3). However, luminescence quenching is not accompanied by the emergence of a sensitized photocurrent in the semiconductor and a filtering effect of adsorbed dye is observed for the exposed aluminium hydride as well (curves 2' and 2, Fig. 3). Thus, the energy from the dye transferred to the semiconductor centers that do not provide sensibility of the photoelectric effect.

The magnitude of the sensitized photoeffect in silicon monocrystals is significantly smaller than in powder samples. This is not only a consequence of the fact that the specific surface area of finely divided powders is several orders of magnitude larger than in monocrystals. 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 [15]. 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 [19]. The subsurface band bending in semiconductors can be controlled by an external electric field or an additional illumination [15], as well as the adsorption of the electron-acceptor and electron-donor molecules on the semiconductor surface [20].

Shallow local centres take part in the formation of band bending. Full luminescence quenching of dyes adsorbed on zinc and cadmium sulphides also does not always guarantee the sensitized photoelectric effect in these semiconductors and the weak filter effect caused by partial internal energy degradation in the dye is only observed in the impurity photoconductivity spectrum [3]. The absence of a sensitized photoelectric effect in these cases is due to the fact that energy from the dye transferred to the centers, which are ineffective for photoconductivity due to small life time of generated free carriers (fast recombination).

The introduction of shallow local centres (adhesion levels) can change the tempo of the carriers recombination in semiconductors. In the original aluminum hydride and zinc sulfide integrated surface concentration of levels is 10^9 - 10^{10} cm^{-2} [2-4] that is clearly insufficient to create subsurface electric fields, significantly changing the surface carriers recombination. In good sensitized AgI and ZnO the concentration of adhesion levels is more than 10^{12} cm^{-2} [2, 4]. After the introduction of chlorine ions in the ZnS lattice, concentration of shallow donor levels in the semiconductor reaches 10^{14} cm^{-2} [21] and such processing of sulphides of zinc and cadmium can turn them from nonsensitized to good sensitized photoconductors [2]. Aluminium quazimetallic particles appearing as a result of photolysis can be the centers accepting the photoexcitation energy from an dye in aluminum hydride, and the energy transferred from the dye is quickly dissipated on these centres – the products of photolysis. At the same time the secondary photochemical processes develop in the semiconductor and ultimately an effective dye sensitization of the integral photochemical sensitivity of aluminium hydride has been observed [17, 22].

4. Conclusions

Methods of creating conditions for the dye sensitization of photoprocesses in semiconductors considered here enable us to control the efficiency of spectral sensitization. The sensitization of the internal photoelectric effect in silicon after creating appropriate conditions discovered here can be used in such semiconductor devices for converting the light energy into electric energy, as solar panels or CCD matrices used as image sensors in modern electronic photography systems. In the first case, the conversion efficiency can be increased and the thickness of silicon cells can be decreased. In the second case, the use of dye sensitization will allow an improvement in the color separation system during the recording of colored images by choosing appropriate

dyes instead of light filters to provide an effective increase in sensitivity in the required spectral range, similar to the traditional silver halide photography.

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