Additional Opportunities in Spectral Sensitization of Photothermographic Systems

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Introduction

The main method of regulation of sensitivity spectrum of photothermographic systems with inorganic light sensitive component is, as well as in conventional photographic materials, their dye sensitization[1,2]. The modern theories of spectral sensitization basically consider two alternate mechanisms: electron or energy transfer from dye to a wideband semiconductor[3-5]. However sensitization of photothermographic systems has features and for their explanation in papers[6,7] were offered additional sensitization mechanisms: lightguide and sensitization of the photochemical image amplification. In the present paper the contributions of these sensitization channels in efficient increasing of cumulative process are appreciated on the basis of the elementary photophysical and photochemical processes analysis in a heterogeneous system dye-semiconductor on a example of materials "dry silver" and aluminium hydride.

Efficiency of Lightguide Mechanism

The spectral sensitization efficiency of primary photochemical products formation in solids after light absorption by adsorbed dye is determined by a ratio:

$$F_s = F_a \cdot F_{tr} \cdot F_{ph}, \qquad (1)$$

where F_a - absorption efficiency, determined by a dye extinction factor and its concentration in lightsensitive layer; F_{tr} - efficiency of the electronic excitation transfer (energy or electron) from a dye to a semiconductor; F_{ph} - efficiency of the primary photochemical products formation in a solid as a result of the electronic excitation transfer from a dye.

The occurrence of an electron in a conductivity band as the first stage of the photochemical process is result of the electron transfer from a excited dye level or the energy transfer to local electronic levels in a forbidden band with an electron transition to a conductivity band. After light absorption by a dye the received energy can be transferred to a semiconductor, be highlighted in a kind of a luminescence quantum and be degraded inside of a molecule according to constants of the transitions k_1, k_2 and k_3. The quantum efficiency of the electronic excitation transfer is determined by a ratio:

$$F_{tr} = k_1/(k_1+k_2+k_3), \qquad (2)$$

For the majority of adsorbed dye is observed the strengthening of a molecule structure and the constant of internal conversion of energy to oscillations and rotations k_3 becomes immaterial in a comparison with k_1 and k_2. As a result the luminescence becomes main competitive process for the effective sensitization of photophysical and photochemical processes in a semiconductor. The fluorescent lifetimes of adsorbed dyes have values of 10^{-11}-10^{-10} s [8,9], and constant k_1 in well sensitizing semiconductors exceeds value 10^{12} s^{-1} [4,5], therefore in such conditions the efficiency of the electronic excitation transfer F_{tr} comes nearer to unit.

It should note, that in such complex systems as real photolayers it is necessary to consider not only dye molecules directly adsorbed on a light sensitive component. In silver photothermographic materials according to offered in the work[6] lightguide mechanism of spectral sensitization in sensitization process dye molecules adsorbed on a silver stearate - dielectrics participate also, and dielectrics concentrates a part of the dye luminescence light on a sensitive silver halide of the composition. Then the common electronic excitation transfer efficiency of all dye molecules to a semiconductor will be determined by a ratio:

$$F_{tr}=k_1[(c_1+c_2q_2k'_2/(k'_2+k'_3)]/(c_1+c_2)(k_1+k_2+k_3), \qquad (3)$$

where c_1 and c_2 - concentrations of dyes adsorbed accordingly on a silver halide and stearate; q_2 - concentrating efficiency of luminescence light of dye adsorbed on a silver stearate to a silver halide; k'_2 and k'_3 - constants accordingly radiative and nonradiative recombination in dye molecules adsorbed on a silver stearate.

The concentrating efficiency of luminescence light q_2 according to lightguide mechanism on depends on a ratio between refractive parameters of the silver stearate n and environment n_0. In our conditions n > 1,6 and n_0 = 1,485 light at corners of fall more than 65-70° has the complete internal reflection on the internal surface of a silver stearate particle[6]. In this connection the value q_2 is appreciably less unit. However, quantity of dye molecules adsorbed on a silver stearate in several ten times exceeds number of molecules adsorbed on a silver halide, i.e. $c_2 \gg c_1$[6]. Therefore the contribution of molecules adsorbed on a non light sensitive silver organic salts can be essential. For determination of this contribution the experimental researches of the photolayer spectral sensitivity and the

adsorbed dye absorption were made and it has been shown, that the contributions of dyes adsorbed on a silver halide and dyes adsorbed on a silver stearate in common spectral sensitization process are about identical.

Obviously, the quantum efficiency of the electronic excitation transfer determined under the formula (3), always less value according to the formula (2), since here is taken into account only light absorbed by dye. If to consider light dropping on photolayer (namely it is important from positions of photographic sensitivity increasing), the spectral sensitization efficiency of a photothermographic material on the formula (1) will be higher, as far as common dye concentration in a layer, and, hence, an absorption efficiency F_a in such system will be more, than in conventional silver halide emulsion. Indeed, the photographic sensitization efficiency of real thermally processed compositions is appreciably higher, than similar conventional silver halide emulsions[11].

Efficiency of Photochemical Image Amplification

At the subsequent stages of process the efficiency sensitization is determined by an electron life in a conductivity band of a semiconductor. This electron still there can remain free a sufficient time, stipulating sensitizated photoconductivity, or recombinate rapidly. Sensitizated photoconductivity is the first stage of photochemical process[3,4] and the free carriers determine a formation of primary photochemical products with the constant k_4. Recombination of carriers in a semiconductor may occur as nonradiatively as with highligating of the sensitizated luminescence quantum with appropriate constants k_5 and k_6. In the latter case transformed by a similar way energy absorbed by dye will be unused in the relation of the sensitizated photochemical sensitivity.

The surface bend of bands, which is determined by local donor centres and surface acceptor states can change the recombination rate of carriers in a semiconductor[4,12,13]. In well sensitizating photoconductors the concentration of donor levels should exceed 10^{12} cm^{-2} [4] and under these conditions the constant k_4 can prevail over k_5 and k_6. In case of the aluminium hydride the concentration of donor levels is small and the filter effect of absorbed dye is only observed in a photoconductivity spectrum[6] even after photochemical modification, when the electronic excitation energy is effectively transmitted to a semiconductor and a dye luminescence decreases[12-14], i.e. here occurs fast nonradiative recombination of carriers with dissipation of energy in a semiconductor.

However, if the recombination centres are centres of the secondary photochemical processes, it is observed the effective sensitization of such processes by dyes and as a result it occurs a spectral sensitization of the photochemical image amplification in the aluminium hydride[6]. In general case the efficiency of a photochemical product formation in a solid at an electronic excitation transfer is determined by the formula:

$$F_{ph} = (k_4 + q_5 k_5)/(k_4 + k_5 + k_6),\qquad(4)$$

where q_5 - efficiency of the photochemical image amplification.

The valuation of the photochemical image amplification efficiency in the aluminium hydride can be received after the consideration of electronic excitation energy dissipation processes in a solid. As a result of occurring thus nonradiative transitions new intrinsic defects can be generated pursuant to the theory of statistical interaction between electrons and defects in semiconductors[15]. Within the framework of this theory at temperatures above zero after the introduction superfluous electron in a crystal a formation of intrinsic lattice defect, on which is located such electron, is more energetically suitably than formation of an electron at the bottom of a conductivity band or polaron. Thus the temperature threshold (T_{min}) of a defect formation is determined by a ratio[15]:

$$T_{min} > (W+E_p-E_a)/k \ln(N^2 V/N_c),\qquad(5)$$

where W - energy of defect formation; E_p - energy of a polaron state; E_a - depth of a trap level; N - density of units of a lattice; N_c - density of states in a conductivity band; V - a crystal volume.

Under the formula (5) the realization opportunity of the electronic excitation energy dissipation channel with new defect formation can be appreciated at photochemical image amplification in the aluminium hydride. In papers[16,17] complete local state spectra in pure AlH_3, which naturally to attribute to intrinsic lattice defects, were determined using Kroger classification[18].

The most probably at the electronic excitation energy dissipation in AlH_3 there is the occurrence of intrinsic defects in a kind of hydrogen vacancies $V_H{}^x$. The hydrogen vacancy formation occurs at gap two bridge bonds of a hydrogen in a crystal[19]. In conditions, when the spectral sensitization of the photochemical image amplification is observed, i.e. on a border of section primary quasimetallic centre - aluminium hydride, the energy of one bridge bond gap will be 0,67 eV[19], i.e. W=1,34 eV. Volume of AlH_3 microcrystals used in work[6,16,17] lies within the limits of 10^{-9} cm^3. The depth of a trap level E_a on the work[16] for $V_H{}^x$ will be 0,95 eV. In view of that usually significances E_p=0,2 eV; the effective significances N=3·10^{23} cm^{-3} and N_c=10^{18} cm^{-3} [15], the threshold temperature of a defect formation for the aluminium hydride in secondary photochemical processes will be 150 K. Thus, at photoexcitation in AlH_3 the formation of new vacancies near to a primary centre of the image with participation free electrons begins at reasonably low temperatures.

Within the framework of the theory of statistical interaction between electrons and defects in semiconductors[15] concentration of vacancies formed in such conditions in the aluminium hydride N_v can be appreciated. Using parameters for the aluminium hydride, we receive at room temperature for concentration of electrons in a conductivity band 10^{15} cm^{-3} the significance N_v=10^{15}-10^{17} cm^{-3}. Thus, recombination of one nonequilibrum carrier can

stimulate formation up to 100 new vacancies, i.e. effective amplification of defect formation is provided reasonably.

Occurrence of high concentration of lattice defects due to thermal formation of defects with participation redundant electrons, excited in a conductivity band by light, results in downturn of photoelectrons concentration, i.e. named photoconductivity self-compensation[15] is displayed so. By it, in particular, absence of the sensitizated photoconductivity and supervision of filter effect in a dye absorption spectrum can be explained at availability effective sensitization of the cumulative photochemical image amplification process in AlH_3 by dyes[6].

The formation of vacancies near to a primary image centre on a offered mechanism provides observable photochemical image amplification due to increasing of this centre at the expense of the aluminium in boundary units lattices. The vacancies can associate, stipulating occurrence of microemptiness at the decomposition AlH_3, which are well identified on spectra of photochemically induced absorption[20].

In silver photothermographic materials is also observed photochemical image amplification[21], and consequently and it is here necessary to consider the probable electronic excitation energy dissipation with new defects formation and development of the image centres formation.

In summary it should note, that the processes considered in the given work do not cover all set of the factors, of determining efficiency of spectral sensitization, and take into account only main photophysical and photochemical processes, which will be realized in particular photothermographic systems. But at creation new and perfection of existing photomaterials it is expediently to use offered opportunities of increase of efficiency spectral sensitization for the account of a lightguide mechanism and a photochemical image amplification by regulation of constants of appropriate transitions.

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