Spectral Computing of the Dependence of the Photocurrent and the Photochemical Decomposition Velocity of Heavy Metal Azides

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Abstract – The stationary equation of diffusion for holes is computationally solved with account of multiple reflection. Spectral dependences of the photocurrent and the photochemical decomposition velocity of heavy metal azides have been calculated.

Photoconductivity and photochemical decomposition of heavy metal azides (HMA) were studied in [1–8]. Spectral characteristics of the photocurrent and photolysis depend on a mutual direction of the vector of the electric field E and the wave vector $\vec{k}$ of optical radiation. A photochemical reaction of HMA decomposition to form the nitrogen molecules occurs at the surface of crystals, the quantum yield $\eta \ll 1$. Nuclei of metals are formed mainly at the surface of an alternating-sign face. At $\vec{E} \perp \vec{k}$ the following spectral regularities are observed: 1) spectral dependences of photocurrents in HMA are mainly represented by curves with a strongly pronounced maximum; 2) in the field of weak absorption and at low photocurrent efficiency in the field of strong absorption, the photocurrent grows linearly with increasing in efficiency $i \sim I$; 3) in the field of strong absorption of the photon, the photocurrent is $i \sim \sqrt{I}$; 4) the rate of a photochemical reaction with energy increase in the photon quanta monotonously grows.

To account for spectral regularities, let us assume that electrons and holes decay at the surface not only as a result of recombination, but also as a result of their participation in a photochemical reaction. HMA are photoconductors of p-type conductivity. Let us write the stationary equation of the diffusion for holes with account of multiply reflection of photon [9]

$$D \frac{\partial^2 p}{\partial x^2} - \frac{p}{\tau} + \frac{\alpha(1-R)I \exp(-\alpha x)}{1 - R^2 \exp(-2\alpha d)} \times$$
$$\times [1 + R \exp(-2\alpha d) \exp(2\alpha x)] = 0 \qquad (1)$$

and nonlinear boundary conditions at the surfaces at $x = 0$ and $x = d$

$$-D \frac{dp_{0,d}}{dx} = \mp s_1 p_{0,d} \mp s_2 p_{0,d}^2, \qquad (2)$$

where τ is the lifetime of the holes in the bulk of a crystal; s_1 – the constant of linear recombination of holes; s_2 – an effective constant of holes' decay in a bimolecular reactions to form nitrogen molecules; R – the reflectivity coefficient; α – the absorption coefficient.

The given model holds true before nuclei of metals begin to form at a crystalline surface. It is accounted for by the fact that the growth of nuclei of metals re-

sults in topochemical autocatalysis of the decomposition velocity and the heterojunction potential difference between metallic nuclei and azide. Owing to this, the activation energy of the photolysis velocity changes. For example, in the case of lead azide $Ea = E_{a1} + 2\Delta W \approx 1{,}2 eV$, which agrees with the experiment [7]. Here $\Delta W = 0{,}6$ eV is the difference in work functions of lead azide and lead, $E_{a1} \approx 0{,}03$ eV – the activation energy of the photolysis velocity at the initial stage.

Equation (1) has the following solution

$$p(x) = C_1 \exp(-x/l_d) + C_2 \exp(x/l_d) + $$
$$+ B_1 \exp(-\alpha x) + B_2 \exp(\alpha x), \qquad (3)$$

where l_d is the diffusion length of holes; C_1, C_2 – the constants determined from the boundary condition (2), and the constants

$$B_1 = \frac{\alpha I(1-R)}{1 - R^2 \exp(-2\alpha d)} \times \frac{\tau}{1 - \alpha^2 l_d^2},$$
$$B_2 = B_1 R \exp(-2\alpha d).$$

The algebraic equations to define C_1 and C_2 are very bulky. Therefore, to find-out some qualitative regularities for the solution (3), let us assume that α^{-1}, $l_d \ll 1$. In this approximation the boundary condition (2) and the solution (3) have the following form

$$D \, dp_0/dx = s_1 p_0^2 + s_2 p_0^2, \quad p_d = 0, \qquad (4)$$
$$p(x) = C \exp(-x/l_d) - B \exp(-\alpha x), \qquad (5)$$

where $B = \dfrac{\alpha \tau I(1-R)}{\alpha^2 l_d^2 - 1}$. According to (4) and (5)

$$C = B - \frac{D}{2 l_d s_2} - \frac{s_1}{2 s_2} + $$
$$+ \sqrt{\frac{\alpha \tau D(1-R)I}{s_2 l_d (1 + \alpha l_d)} + \left(\frac{D}{2 l_d s_2} + \frac{s_1}{2 s_2} \right)^2}. \qquad (6)$$

The concentration of the holes at $x = 0$ is as follows

$$p_0 = -\frac{D}{2 l_d s_2} - \frac{s_1}{2 s_2} + $$
$$+ \sqrt{\frac{\alpha \tau D(1-R)I}{s_2 l_d (1 + \alpha l_d)} + \left(\frac{D}{2 l_d s_2} + \frac{s_1}{2 s_2} \right)^2}. \qquad (7)$$

The integral concentration of the holes defining conductivity of a crystal is equal to

$$P = C \int_0^\infty \exp(-x/l_d) dx - B \int_0^\infty \exp(-\alpha x) dx = l_d C - B/\alpha.$$

After integrating, we obtain

$$P = \frac{\tau I(1-R)}{1+\alpha l_d} - \frac{D}{2s_2} - \frac{s_1 l_d}{2s_2} +$$

$$+ l_d \sqrt{\frac{\alpha l_d I(1-R)}{s_2(1+\alpha l_d)} + \left(\frac{D}{2l_d s_2} + \frac{s_1}{2s_2}\right)^2} . \quad (8)$$

Let us carry out the qualitative analysis of expressions (7) and (8) relative to the absorption strength and the absorption coefficient. Let us consider two polar cases.

a) The generation velocity of holes is small:

$$\frac{\alpha l_d(1-R)I}{s_2(1+\alpha l_d)} << \left(\frac{D}{2l_d s_2} + \frac{s_1}{2s_2}\right)^2 .$$

Using the given inequality, let us transform the right terms of (7) and (8) to the following form

$$\sqrt{\frac{\alpha l_d(1-R)I}{s_2(1+\alpha l_d)} + \left(\frac{D}{2l_d s_2} + \frac{s_1}{2s_2}\right)^2} \approx$$

$$\approx \frac{D}{2l_d s_2} + \frac{s_1}{2s_2} + \frac{\alpha l_d(1-R)I}{(1+\alpha l_d)(D/l_d + s_1)} . \quad (9)$$

Equations (7) and (8) at smaller generation velocities with account of (9) may then be rewritten as

$$p_0 = \frac{\alpha \tau(1-R)I}{(1+\alpha l_d)(1+s_1 l_d/D)} ,$$

$$P = \frac{\tau(1-R)I}{(1+\alpha l_d)} \left[1 + \frac{\alpha l_d}{1+s_1 l_d/D}\right] . \quad (10)$$

From equations (10) at smaller photon efficiencies or a very low absorption coefficient it is seen that:

1) The concentration of holes is defined by their lifetime in the bulk of a crystal;

2) The photocurrent is directly proportional to the photon efficiency $i \sim I$;

3) The rate of a photochemical reaction is $v \sim I^2$. These conclusions qualitatively agree with the experimental data in [3, 4, 8, 10].

b) The generation velocity of holes is high:

$$\frac{\alpha l_d(1-R)I}{s_2(1+\alpha l_d)} >> \left(\frac{D}{2l_d s_2} + \frac{s_1}{2s_2}\right)^2 .$$

Following the given inequality, (7), (8) may be rewritten as

$$p_0 \approx \sqrt{\frac{\alpha \tau D(1-R)I}{s_2 l_d(1+\alpha l_d)}} , \quad (11)$$

$$P = \frac{\tau I(1-R)}{1+\alpha l_d} + l_d \sqrt{\frac{\alpha l_d(1-R)I}{s_2(1+\alpha l_d)}} . \quad (12)$$

At $\alpha \to \infty$ equations (11) and (12) are simplified to:

$$p_0 \approx \sqrt{\frac{I(1-R)}{s_2}} , \quad P = l_d \sqrt{\frac{I(1-R)}{s_2}} . \quad (13)$$

From equations (11) – (13) it follows that:

1) At higher photon efficiencies and moderate α values, the concentration of holes is defined by both the lifetime of holes in the bulk of a crystal and the

bimolecular decay constant of holes during a photo-chemical reaction;

2) The photocurrent is directly proportional to the photon efficiency $i \sim I$;

3) The rate of a photochemical reaction is $v \sim I$ and with increasing α, it increases as $\sqrt{\alpha}$; 4) at $\alpha \to \infty$ the photocurrent is $i \sim \sqrt{I}$, the photolytic decomposition velocity – $v \sim I$, and their spectral dependences no longer depend on the quantum energy of the photon flux. These conclusions qualitatively agree with the experimental data in [6, 8] relative to the photocurrent in silver azide vs. the photon efficiency (Fig. 1) and the energy (Fig. 2).
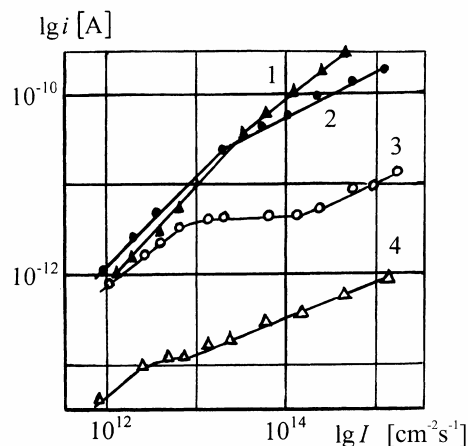
Fig. 1. Dependence of the photocurrent from the photon efficiency for various wavelengths: 1 – 400 nm, 2 – 390 nm, 3 – 380 nm, 4 – 370 nm [8].

Equation (1) with the boundary conditions (2) was solved numerically both for one separate crystal and for a pile of crystals with account of the transmittance factor

$$A = \frac{(1-R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} .$$

A pile of crystals was used as a model for a polycrystalline tablet. A few calculations at the photon efficiency $I = 10^{14}$ cm^{-2}·s^{-1} and $K = 0,2$ are given in Fig. 3 and Fig. 4.
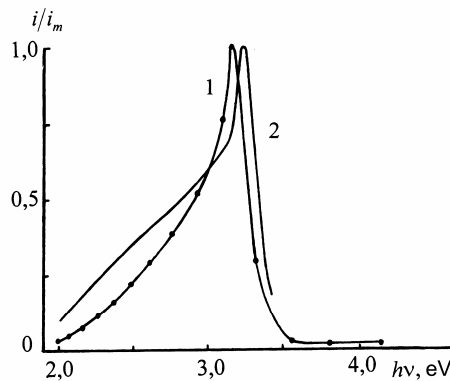
Fig. 2. Spectral dependence of the silver azide photocurrent from the exposure efficiency 10^{14} cm^{-2}·s^{-1}: 1 – the experiment [6], 2 – alculations
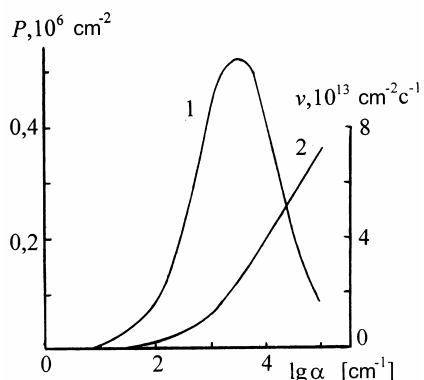
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Fig. 3. Dependence of the integrated concentration of the holes (1) and the photolysis velocity (2) from the absorption coefficient ($D=1$ cm^2/s, $\tau=10^{-8}$ s, $d=10^{-3}$ cm, $s_1=10^3$ cm/s, $s_2=10^{-2}$ cm^4/s,)

It follows that the spectral maximum of a photocurrent depends on crystal dispersity. The photocurrent and the photochemical decomposition velocity of "tablets" in the extrinsic absorption region are higher than those for separate crystals, the decomposition velocity of MC in the region of strong absorption at $d{\sim}\alpha^{-1}$ being insignificantly dependent from α (Fig. 4). The calculated spectral curves of the photocurrent and the photochemical decomposition of the crystal at $d=10^{-3}$ cm (Fig. 3) qualitatively agree with the results of the experiment relative to spectral dependence of photoconductivity and the photodecomposition velocity of lead azide [5].
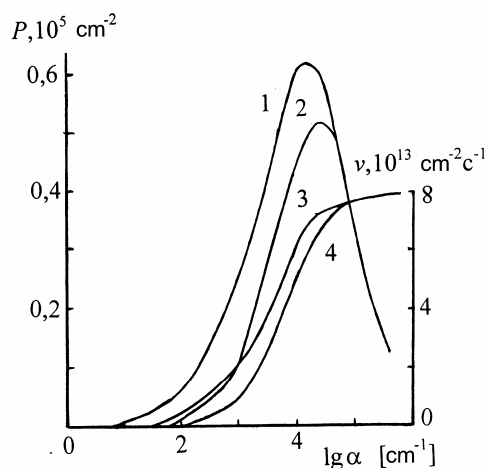

Fig. 4. Dependence of the integrated concentration of the holes (1, 2) and the photolysis velocity (3, 4) from the absorption coefficient: curves 1, 3 – "tablet", curves 2, 4 – a small crystal ($D=1$ cm^2/s, $\tau=10^{-8}$ s, $d=10^{-4}$ cm, $s_1=10^3$ cm/s, $s_2=10^{-2}$ cm^4/s)

Spectral dependence of the photocurrent in a single crystal of silver azide was calculated in terms of equation (1). The calculations were made for the following parameters: $D=1$ cm^2/s, $\tau=10^{-6}$ s, $d=0,3$ cm, $s_1=10^3$ cm/s and $s_2=1$ cm^4/s using the experimental spectral dependences for α and R from [6]. Changes of parameters s_1, s_2 and τ by several orders of magnitude

almost do not influence the spectral position of the maximum of the photocurrent. The position of the maximum of the photocurrent is appreciablly influenced by the crystal thickness. From Fig. 2 it is seen that the experimental and calculated parts of the curves in the region of intrinsic absorption are qualitatively similar, but shifted relative to each other approximately by $\Delta E_g{\approx}0,1$ eV. What is the reason for this?

The shift of the maximum of the photocurrent in the area of smaller energies during the treatment of the surface is observed in many semiconductors. The change of the surface recombination velocity does not account for the shift of the photocurrent spectrum [11]. According to [11] this effect is caused by the change of the band bending and is due to Franz-Keldysh's effect when the carriers are excited in the area of the volume charge [12, 13]. Hence, one of the reasons of the spectral shift of the calculated and experimental curves can be Franz-Keldysh's effect. However, this requires the generation of electrically active defects during a heterogeneous photochemical reaction.

The kinetic treatment of the relaxation of the photocurrent after the maximum has been achieved, confirms the above hypothesis. As seen from Fig. 5, the decay of the photocurrent obeys the law
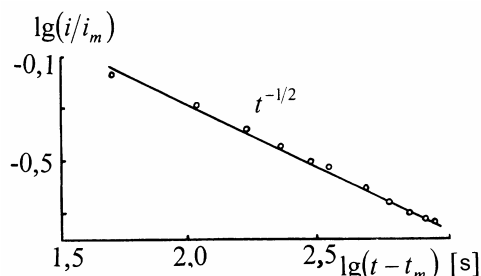
$$i \sim t^{-1/2}. \qquad (14)$$

Fig. 5. Kinetics of the photocurrent decrease (decay) in silver azide at $I=10^{14}$ cm^{-2}s^{-1} and $\lambda = 380$ nm [8] after the achievement of the maximum

The concentration of the holes, and, hence, and the photocurrent, are proportional to the lifetime of the holes τ. The lifetime τ is inversely proportional to the concentration of the recombination centers $\tau{\sim}1/n_r$. Hence, the concentration of newly formed recombination centers is $n_r{\sim}t^{1/2}$. Kinetics (14) corresponds to the kinetics of the diffusion of particles into the semi-bounded body from the constant source located in the plane $x=0$ [14]. At $t<d^2/D_C$ the average concentration of defects diffusing in the bulk is

$$n_r = \frac{2c_0}{d}\sqrt{\frac{D_c t}{\pi}},$$

where c_0 is the concentration of the particles in the plane $x=0$, D_C – diffusion coefficient of the particles.

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Let us estimate the intension of the electric field E arising in silver azide on photolysis relative to the shift ΔE_g. According to [13], the change α in the electric field is

$$\alpha(\omega, E) = \alpha(\omega, 0)\exp\left(\frac{\sigma\Delta E_g}{k_B T}\right),$$

where $\alpha(\omega, 0)$ – the absorption coefficient of the photon in the absence of the electric field; σ – the Urbakh constant. The shift is

$$\Delta E_g = \frac{\hbar^2 \sigma^2 q^2 E^2}{24\mu(k_B T)^2}. \qquad (15)$$

Here

$$\mu^{-1} = \left(m_n^*\right)^{-1} + \left(m_p^*\right)^{-1}$$

is the reduced effective mass of the electron-hole pair formed during optical transition. To define the electric field it is necessary to know σ. The Urbakh constant can be defined from $\Delta\ln\alpha/\Delta h\nu = \sigma/k_B T$ [13]. By means of exponential dependence of the absorption coefficient from the quantum energy [6] we estimate the slope of the absorption edge of silver azide $\Delta\ln\alpha/\Delta h\nu = 57{,}5$ eV^{-1}. Whence $\sigma \approx 1{,}5$ at $T = 293$ K. At m_n^* and m_p^* equal to the mass of a vacant electron, according to (15), we obtain

$$E = \frac{2k_B T}{\hbar\sigma q}\sqrt{6\mu\Delta E_g} \approx 7\cdot10^5 \text{ V/cm}.$$

So, a spectral shift of the photocurrent maximum in silver azide can be accounted for by Franz-Keldysh's effect caused by forming the electrically active defects due to a heterogeneous photochemical reaction.

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