Photoprocess in Heterogeneous Lead Azide – Semiconductor (CdTe, Cu$_2$O) Systems[1]

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Abstract – It is established, that creation of contacts lead azide with cadmium telluride (CdTe) and copper oxide (Cu$_2$O) alongside with reduction of rate of photolysis and a photocurrent in own area of absorption of lead results in expansion of area of spectral sensitivity PbN$_6$ (Am). It is shown, that in fields of an intensive irradiation (I > 1 10^{14} quantum × sm^{-2} × s^{-1}·) on kinetic curves of rate of photolysis heterogeneous PbN$_6$ – the semiconductor systems are observed characteristic for individual lead azide sites: non – stationary, stationary, increases, saturation, postgas evolutions. As a result of measurements of a contact potential difference, current – voltage characteristics and photo – emf it is established, that character of influence of semiconductors on photosensivity of lead azide is determined by a condition of a surface of contacting partners. The model of photolysis of heterogeneous PbN$_6$ – the semiconductor systems, including generation, recombination, redistribution in a contact field nonequilibrium electron – hole pairs, formation microheterogeneous "azide – metal (a product of photolysis)" systems and formation of end – products of photolysis – nitrogen and lead is offered.

1. Introduction

Investigation into the origin and mechanism of processes in heterogeneous lead azide – semiconductor systems (one component of which undergoes irreversible transformation) is of interest in physics and chemistry of solids in connection with the possibility of producing materials with controllable photosensitivity on the basis of these structures [1 – 7].

In the present work results of researches of influence of additives of semiconductors on kinetic and spectral laws photolysis of lead azide in vacuum (P=1 × 10^{-5}Pa) are submitted. As semiconductors have been chosen CdTe and Cu$_2$O as they differ with width of the forbidden zone, type of conductivity, thermoionic works functions and a condition of a surface.

2. Experimental

Lead azide of Am trademark was synthesized by slow double – jet crystallization: 0.2 N of twice recrystallized commercial sodium azide was drop – by – drop added (at a rate of 2 drops per min) to a 0.2 N solution of ("kh.ch.") grade lead nitrate at pH 3 and T = 293 K

during 60 min. Test samples were prepared by the intimate mixing of corresponding weighed samples of PbN$_6$ (Am) and semiconductors (CdTe and Cu$_2$O) in the solid state or in ethanol followed by drying and compacting into pellets to 1 cm in diameter under a pressure of 4×10^3 kg/cm^2. Another mode of preparation of test samples involved the deposition of CdTe and Cu$_2$O onto the illuminated surfase of PbN$_6$ (Am) pellets by the thermal evaporation in a vacuum (1·× 10^{-3} Pa) using a VUP – 5M universal vacuum station. In the comparison of results obtained, the light transmission of CdTe and Cu$_2$O was accounted for.

The photolysis rate V$_{ph}$, photocurrent i$_{ph}$, and photoemf Uph were measured in a high vacuum (1 × 10^{-5}Pa) using experimental facilities. Mercury – vapor (DRT – 250) and xenon (DKsSh – 1000) lamps were used as light sources. The desired spectral region was isolated using an MSD – 1 monochromator and a set of filters. Actinometry of the light sources was carried out using an RT – 0589 radiometer thermal element. V$_{ph}$ was measured using an IPDO – 1 omegatron type mass – spectrometer with an RMO – 4S detector placed on the detection of nitrogen. I$_{ph}$ and U$_{ph}$ were measured using a V7 – 30 electrometric voltmeter or a TR – 1501 electrometer.

Diffuse reflection (DR) spectra were measured at a pressure of 101,3 kPa using a Specord M40 spectrophotometer with an 8^{0}d reflection attachment and in a vacuum (1 × 10^{-4} Pa) using the facility [1]. The contact potential difference (CPD) between PbN$_6$(Am), CdTe, Cu$_2$O and a platinum reference electrode was measured by the modified Kelvin method [8].

3. Results and discussion

As a result of comparison of kinetic curves of rate of photolysis (V$_{ph}$), measured for PbN$_6$ (Am) and heterogeneous "PbN$_6$ (Am) – semiconductor" systems, it is established, that alongside with change by semiconductors V$_{ph}$ on different portions of kinetic curves samples show the general kinetic laws. In fields of an intensive irradiation (I > 1 ×10^{14} quantum·cm^{-2} s^{-1}) on kinetic curves V$_{ph}$ heterogeneous "PbN$_6$ (Am) – semiconductor" systems are shown characteristic for individual lead azide segments: I – non – stationary, II – stationary, III – increases, IV – saturation, V – gas postliberation [9]. Decrease in intensity of falling light (I < 1 quantum·× cm^{-2} × s^{-1}) results in reduction V$_{ph}$,

and also to increase in duration of portions of kinetic curves V_{ph}. At the big concentration of additives (more than 30 %) take place blackout (shielding) a part of a surface of lead azide.

Rate of photolysis substantially depends on conditions and a storage time, preliminary thermal and light processings of samples (Fig. 1).
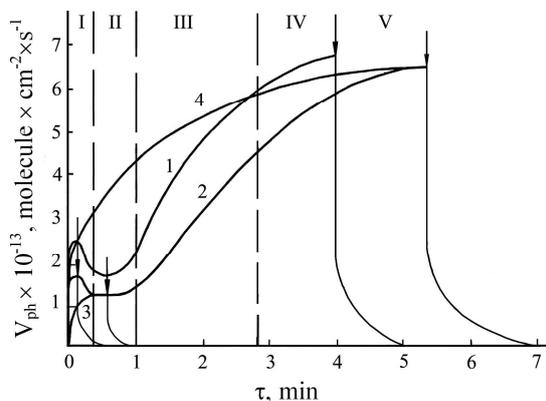

Fig. 1. Kinetic curves for the photolysis rate in (1) PbN_6 (Am) and (2) PbN_6 (Am) – CdTe (2) heterogeneous systems at $\lambda = 380$ nm and an incident light intensity of $I = 2 \times 10^{15}$ quantum $\times$ cm$^{-2} \times$ s^{-1} and also in PbN_6 (Am) – CdTe systems after removal of sample illumination in regions (3) II and (4) IV. Arrows mark moments at which the light was switched off

The repeated irradiation of samples (after interruption of light on II segments and I) does not result in appreciable change of values V_{ph} on II, III and IV segments of kinetic curves V_{ph}. Thus V_{ph} on segment I decreases. After preliminary light processing samples up to segment IV of kinetic curves V_{ph} monotonously grows up to constant value and corresponds to values V_{ph} on a segment I of samples not processed by light.

The subsequent processing pre – exposed heterogeneous systems in the oxidizing environment, in "atmospheric" conditions and in vacuum (P = 1 × 10^{-3} Pa) within one month results storage in partial restoration of the form of kinetic curves V_{ph}.

On values V_{ph} on a stationary segment II, curves of spectral distribution of photolysis rate have been received (Fig. 2).

By consideration of curves of spectral distribution and kinetic curves V_{ph} it is established, that creation heterogeneous systems lead azide with semiconductors (Cu$_2$O, CdTe) alongside with reduction of rate of photolysis and a photocurrent in the field of own absorption of lead azide, results in occurrence of new long – wave areas of photosensivity (in which PbN_6 practically does not absorb light), corresponding to areas of absorption and photochemical sensitivity of semiconductors.

The long – wave edge of diffuse reflection spectra of PbN_6 (Am) – CdTe (Cu$_2$O) systems ($\lambda \approx 410$nm)

coincides with that for PbN_6(Am). The formation of PbN_6(Am) – CdTe (Cu$_2$O) systems and their exposure to light at $\lambda = 380$ nm are accompanied by a decrease in the intensity of diffuse reflection from PbN_6(Am) in the region $410 - 850$ nm. With exposures as short as regions I and II in kinetic curves of V_{ph}, the diffuse reflection spectra not only decrease in intensity in the region (Cu$_2$O) $\lambda = 410–850$ nm but also exhibit broad peaks at $\lambda = 470$ and 600 nm. The increase of the exposure time to region IV is accompanied by further broadening of the peaks and their shift toward the long – wave region of the spectrum.
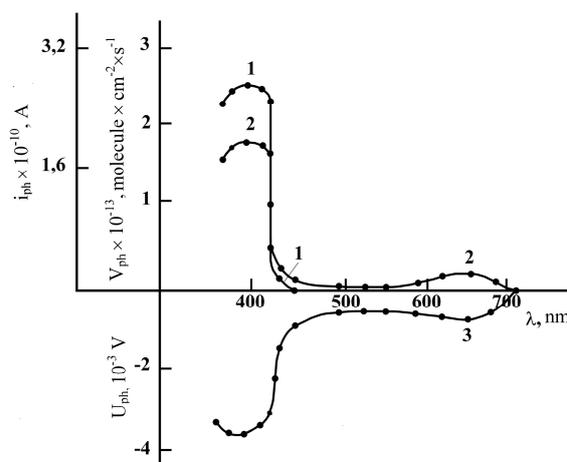

Fig. 2. Spectral distributions of photolysis rate (1,2), photocurrent (1,2), photo – emf (3) in PbN_6(Am) (1) and PbN_6(Am)–Cu$_2$O (2,3) heterogeneous systems; $I = 3,17 \times 10^{15}$ quantum $\times$cm$^{-2} \times$ s^{-1}

From the kinetic curves of V_{ph} at different intensities of the incident light, we calculated time dependences of the amount of photolysis – produced metal and correlated them with variations in areas under diffuse reflection curves of PbN_6(Am)–CdTe (Cu$_2$O) systems measured in the course of their irradiation. The good correlation between the dependences indicate that the changes observed in diffuse reflection curves of PbN_6(Am)–CdTe (Cu$_2$O) systems in the course of their irradiation are due to the formation of lead by photolysis of lead azide. In this case, the observed maximums are due to the formation of lead particles of certain size. The solid – phase (lead) and gaseous (nitrogen) photolysis products are in the stoichiometric ratio and formed largely on the sample surface.

In order to elucidate the energy band structure of contacts the PbN_6(Am) – CdTe and PbN_6(Am) – Cu$_2$O and the reason for the observed changes in V_{ph} of lead azide in different spectral regions, the complex of electrophysical researches (measurement photo – emf, current–voltage characteristics (CVCs), a contact potential difference (CPD)) has been undertaken.

According to ratio of thermoionic works functions (Table 1) [8] it was necessary to expect a various sign photo – emf for systems with CdTe and Cu_2O, and also effects of straightening on current–voltage characteristics (CVCs). However, on experimental CVC the effect of straightening is absent, and a sign photo – emf negative from the lead azide side, both for systems with Cu_2O, and for systems with CdTe. Thus kinetic curves of rate of photolysis, a photocurrent and photo – emf correlate. These facts, and also measurements of contact potential difference, testify that during redistribution of nonequilibrium carriers of a charge in darkness and at illumination a significant role own superface electronic eigenstates (SEEs – Ts^+, Ts^-) of lead azide and play superficial surfase electronic states junctions of contact azide with the semiconductor (SESjs – Sj^+, Sj^-). As a result of the analysis of measurements diagrams of power zones heterogeneous systems with which attraction, the model of photolysis lead azide in contact to semiconductors is offered are constructed.

At influence on heterogeneous PbN_6 (Am) – CdTe (Cu_2O) systems light from range of fundamental absorption lead azide takes place intensive generation electron – hole pairs in lead azide and semiconductors (Fig. 3, transitions 1, 2).

$$N_3^- \rightarrow p + e \qquad (1)$$

As the quantum yield of photolysis of heterogeneous PbN_6 (Am) – semiconductor systems at exposition $\tau \geq$ of 1 mines varies from 0,002 – 0,010, a part of photoinduced carriers of a charge recombine (Fig. 3, transitions 3 и 3'):

$$R^+ + e = R^0 \qquad (2)$$
$$R^0 + p = R^+, \qquad (3)$$

where R^+ is a recombination center

Pair of charge carriers generated in the in the space – charge region (SCR) of lead azide and semiconductors of are redistributed in a contact field which is caused by discrepancy of thermoionic works functions of contacting partners, by presence SEEs and SESjs. Nonequilibrium holes from a valent zone of lead azide and nonequilibrium electrons from a zone of conductivity of semiconductors pass to levels SEEs and SESjs.

$$T_S^- + p = T_S^0, \qquad (4)$$
$$S_J^- + p = S_J^0, \qquad (5)$$
$$T_S^+ + e = T_S^0, \qquad (6)$$
$$S_J^+ + e = S_J^0. \qquad (7)$$
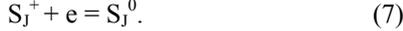
Settled at levels SESjs electrons and holes can recombine or to exchange with nearby zones of the semiconductor and lead azide.

$$S_J^0 + e = S_J^- \qquad (8)$$
$$S_J^0 + p = S_J^+ \qquad (9)$$

At exposure heterogeneuos PbN_6 (Am) – CdTe (Cu_2O) systems light from absorption band of semiconductors intensive generation electrone – hole pairs in semiconductors takes place. Generated in SCR semi-

conductors nonequilibrium carriers of a charge are redistributed in a contact field with transition electrons from a zone of conductivity of semiconductors on levels SEEs and SESjs. Sold sign U_{ph} from the lead azide side for heterougeneuos PbN_6(Am) – CdTe (Cu_2O) testifies to an opportunity of realization of considered transitions. Simultaneously with the marked transitions, which result in formation U_{ph} and to displacement of power levels at contacting partners) streams of equilibrium carriers of a charge take place. In a result, concentration holes in SCR of lead azide (in contact to semiconductors) will change in comparison with their concentration in individual lead azide.
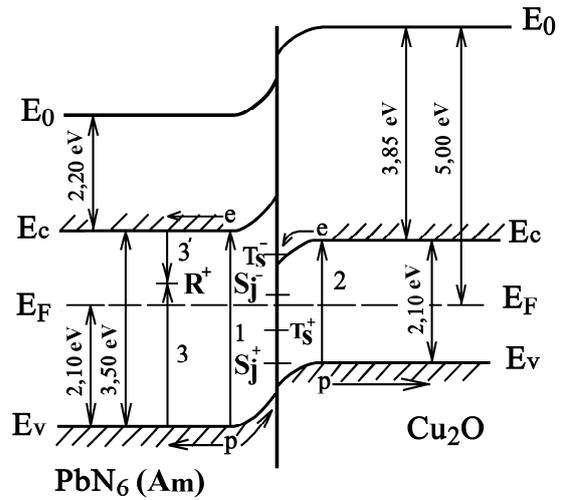

Fig. 3. Energy – band diagram for the PbN_6 (Am) – Cu_2O heterogeneous system; E_V is the valence band top, E_C is the conduction band bottom, E_F is the Fermi level, E_0 is the vacuum level, and R^+ is the recombination center

Resulting change of holes concentration in SCR of lead azide will lead to to corresponding downturn i_{ph} and V_{ph} in own absorption area of lead azide and to occurrence i_{ph} and photolysis in the long – wave areas of a spectrum adequate to areas of absorption and photo – electric sensitivity of semiconductors contacting with azide on accepted for photolysis of heavy metals azides (HMA) to reactions of formation of nitrogen:

$$p + V_K^- = V_K^0, \qquad (10)$$
$$p + V_K^0 = V_K^+, \qquad (11)$$
$$V_K^+ = 3 N_2 + 2 V_A^+ + V_K^-, \qquad (12)$$
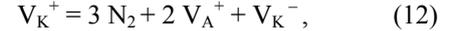
where V_K^- and V_A^+ – cationic and anionic vacancies.

We believe, that SEEs of lead azide and SESjs are the centers of formation photolytic metal:

$$T_S^0 + Me^+ \leftrightarrow (T_S Me)^+ + e \leftrightarrow \dots$$
$$\leftrightarrow (T_S Me_m)^+, \qquad (13)$$
$$S_J^0 + Me^+ \leftrightarrow (S_J Me)^+ + e \leftrightarrow \dots$$
$$\leftrightarrow (S_J Me_m)^+. \qquad (14)$$

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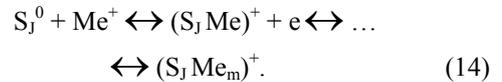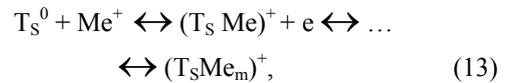
Observable reduction V_{ph} by an initial segment (I) in process and after preliminary exhibiting samples confirms the irreversible charge of the superficial centers. During growth of particles photolytic metal microheterogeneous systems "azide – metal (a product of photolysis)" are formed. Generated in SCR of lead azide pair carriers are redistributed in the contact field generated because of discrepancy between thermionic works functions of lead azide and photolytic lead, with transition non – equilibrium holes from valent zone PbN_6 (Am) in lead.

$$(T_S Me_m)^- + p \longrightarrow (T_S Me_m)^0. \qquad (15)$$
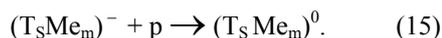
Simultaneously takes place photoemission electrons from lead in a conductivity zone of lead azide. These processes can stimulate diffusion of ions to growing particles:

$$(T_S Me_m)^0 + Me^+ \longrightarrow (T_S Me_{m+1})^+ \qquad (16)$$
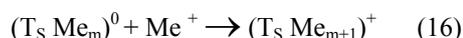
In process of photolysis the border undressed contacts "lead azide – semiconductor" becomes covered by a layer photolytic metal and at the big degrees of transformation photochemical processes in heterogeneuos "lead azide – the semiconductor" systems will be substantially will be determined by photo – electric processes on border "azide – metal (a product photolysis) – the semiconductor". On kinetic curve rate of photolysis the constant of rate of postprocesses is designed. In table 2 constants of rate of process responsible for gas postliberation are resulted.

Table 1. Contact potential differences (B) between PbN_6(Am), CdTe, Cu_2O and a platinum reference electrode

Sample	CPD (T =293 K)	
	10^5 Pa	10^{-5} Pa
PbN_6 (Am)	+ 0,28	+ 0,46
CdTe	+ 0,64	+ 0,64
Cu_2O	+ 0,31	+ 0,20

Table 2. Rate constants of gas postliberation ($k \times 10^2$, s^{-1}) calculated from kinetic curves measured after removal of sample illumination in regions I, II, and IV

Sample	I	II	IV
PbN_6 (Am)	(4,32± 0,16)	(3,10 ± 0,15)	(0,24 ± 0,12)
PbN_6 (Am) – CdTe	(4,20 ± 0,08)	(3,95 ± 0,05)	(0,23 ± 0,05)
PbN_6 (Am) – Cu_2O	(4,40 ± 0,05)	(4,20 ± 0,02)	(0,24 ± 0,02)

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