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ELECTRONIC PROCESSES ON THE SURFACE OF WIDE-GAP SEMICONDUCTORS VIA EXCITATION BY THERMAL ENERGY ATOMS AND ULTRA-VIOLET LIGHT

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The electronic channel of energy accommodation of chemical reactions by atomic particles of thermal energy (H, O) on the surface of wide-gap semiconductors Zn₂SiO₄-Mn, ZnS, CdS-Ag, ZnS-Tm, ZnS-Cu, Al are surveyed. The kinetic mechanism of radical-recombination luminescence excitation of semiconductors, for which phenomenon – high-efficiency electronic heterogeneous accommodation (HEHA) is found out are determined. The mathematical model is written. The effective involvement of electronic states in energy accommodation of heterogeneous plasmochemical reactions is demonstrated. Usage of a phenomenon HEHA for definition of the electronic traps energy depth are surveyed.

Key words: electronic trap, accommodation of energy, heterogeneous plasmochemical reactions, luminescence.

The chemical reactions proceeding on a surface of semiconductors in process for example of epitaxial growth, plasma etching, adsorption or recombinations of atomic particles, in some cases are accompanied by considerable liberation of energy (up to several eV for the elementary act). This energy at the first moment is concentrated on the reformed chemical bond and has the form of high-excited vibrational movement of nucleus of reaction product. Then the molecule relaxes due to transfer of energy to the semiconductor (the process of accommodation). The basic channel of energy accommodation of plasmochemical interactions on semiconductors and dielectrics is the phonon one. Molecules, which formed on a surface (H₂L, O₂L and others) in case of participation of light particles (H, O and others) in reaction, have the vibration frequencies laying outside of a crystal phonon spectrum, and energy of vibrational quanta is much greater than optical phonons energy in the semiconductor. Therefore process of relaxation is a multiphonon or proceeding with a rather small speed. It enables to participate of electronic states of the semiconductor in an accommodation of energy of heterogeneous plasmochemical reactions.

The whole series of the non-equilibrium chemoeffects connected to generation of electron-hole pairs in semiconductors was found out in the 70s. That is a chemomagnitoelectrical effect on Ge [1] (analogue of Kikoin-Noskov photomagnitoelectric effect), valve chemoeffect on p-n transition in Ge at excitation by

H atoms [2], abnormal chemovoltaic effect on CdTe [3]. Non-equilibrium chemoconductivity raised due to energy of atoms recombination was discovered in [4] (system: atoms H – CdS), and non-equilibrium adsorbconductivity (H – ZnO) was discovered in [5]. The electronic accommodation is exhibited in excitation of luminescence of a wide-gap semiconductors and dielectrics (radical-recombination luminescence (RRL) and adsorboluminescence (AL)) in visible area at processing of heterogeneous chemical reactions [6] and electrons and ions chemoemission from a surface [7]. In other words the chemical reactions on the semiconductor surface reduce to forming of the non-equilibrium electronic effects similar to effects at photoexcitation. The luminescence and the other electronic chemoeffects are the product of the chemical reaction on the surface and consequently carry the information about the semiconductor surface, physical and chemical processes on it and the gas environment.

The probability of wide-gap semiconductors electronic excitation to the act of chemical interaction is not too large ($\leq 10^{-2}$) as distinct from the photoexcitation, and consequently the electronic channel of energy accommodation was neglected. The new non-equilibrium phenomenon – high-efficiency electronic heterogeneous accommodation of energy of chemical reaction on the surfaces of electron-excited wide-gap semiconductors was revealed in [8]. That phenomenon consists in increase in some times of the heterogeneous reaction speed at excitation of samples by ultra-violet (UV) light owing to a relaxation of energy of the vibrational-excited molecules along the electronic channel and in increase on some orders of electrons generation speed in a conductivity band (or holes in a valence band) due to reaction energy in comparison with the unexcited semiconductors by UV-light. The HEHA allows approaching to the explanation of catalytic action of surface and photostimulated growth of semiconductors in a new way and allows operating with the speed and selectivity of reaction. Owing to superficial character of radical-recombination excitation the HEHA may be used for diagnostics of electronic conditions on the surface of luminescing semiconductors.

Measurements of RRL were carried out on a high-vacuum setup with the realized method of an atomic probe [9]. For RRL excitation was used hydrogen or oxygen atoms, which were generated of non-electrode HF discharge or pyrolysis source (for creation of the pulse atomic stream normalized in intensity). A mercury lamp was used to photoexcite of the sample. An UV quantum stream onto surface was changed with the help of diaphragm. FEU-97 or FEU-118, calibrated in absolute units, registered the luminophore radiation. The oil-free pump-down by magnetic-dischargeable pump NMD-016 was used.

Powdery semiconductors Zn_2SiO_4 -Mn; ZnS,CdS-Ag ($\lambda_{max} = 520$ nm); ZnS,CdS-Cu,Al (540 nm); ZnS-Tm (478 nm) and self-activated monocrystals ZnS (480 nm) were used as samples. The stream density of excitation light was $\leq 10^{15}$ cm²s⁻¹. Preliminary irradiated sample in a reactionary cell was probed with the pulse stream of H (O)-atoms ($j \sim 10^{14}$ sm⁻²s⁻¹), which was normed in intensity, from the atomic pyrolysis source. The pulse stream was switched on for 2s during the process of de-excitation of the accumulated light sum by the semiconductor. The intensity flash of RRL at the moment of probing by atomic stream and also intensity of afterglow I_A were registered. The low density and short time of atomic probing stream did not change the surface condition and the character of de-excitation of the accumulated light sum. It has been found the magnitude of RRL intensity flash I_{RRL}^e at the probing moment was proportional to the concentration of electrons on traps at current moment and exceeded almost on two

orders of the RRL intensity, which was excited by the same atomic stream on the unexcited surface by UV light (fig. 1). The value of concentration of electrons on traps was determined by the afterglow intensity magnitude of the sample.

The dependence of flash magnitude I_{RRL}^e in experiments was directly proportional to the concentration of the filled electronic traps n_e . That specifies participation of the excited electronic conditions in the accommodation of energy of the heterogeneous reaction. The increase of RRL intensity at pulse switching on of an atomic stream on the ZnS,CdS-Ag sample is explained with the electron transfer from the electronic trap to the crystal conductivity band by the vibrational energy of molecule formed in the recombination reaction, and the subsequent recombination of this electron with a hole, located on the center of a luminescence (the ionization mechanism of excitation of heterogeneous chemiluminescence [10]). The dependence of I_{RRL}^e on concentration of electron traps on ZnS-Tm sample (for which the intercenter mechanism of RRL excitation is characteristic [11]) testifies to it. Therefore I_{RRL}^e of ZnS-Tm sample should not depend on the concentration of excited electronic conditions, as it was observed in experiment.

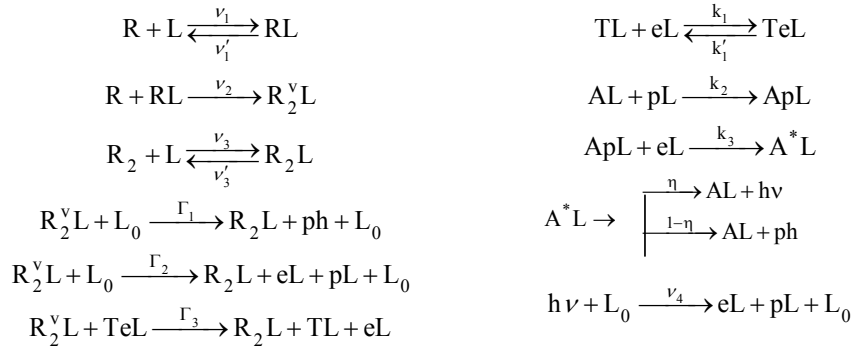
The dependence of I_{RRL}^e of ZnS,CdS-Ag sample from intensity of a crystal phosphorous photoluminescence (I_{PL}) excited by a stationary UV light stream, at pulse probing by H-atoms stream is represented on fig. 2. The values of n_e and I_{PL} at small UV light Φ streams are proportional to Φ , and the given technique enabled to investigate the dependence of I_{RRL}^e from n_e . The I_{RRL}^e is proportional to Φ at $\Phi < 10^{12}$ quantum/(cm²s), and it grew approximately by 5 orders of magnitude at $\Phi = 6 \cdot 10^{11}$ quantum/(cm²s) in comparison with I_{PPJ}^e of the unexcited sample by light [12]. The increase of I_{RRL}^e was more than 3 orders of magnitude for ZnS,CdS-Ag. The I_{RRL}^e of ZnS,CdS-Ag and monocrystal ZnS at $\Phi > 10^{12}$ quantum/(cm²s) and $T = 295$ K almost did not achieve the maximal value and varied at the further increase of electronic excitation level by UV light. The increase of T resulted to decreasing of I_{RRL}^e at constant values of the light stream and atomic stream density with activation energy of 0,17 and 0,62 eV for ZnS,CdS-Cu,Al; 0,17 eV for ZnS,CdS-Ag; 0,17 and 1,16 eV for self-activated ZnS, that coincided with energy depth of electronic traps in researched samples [9]. In its turn, the UV light illumination of ZnS-Tm sample with the direct mechanism of RRL excitation did not influence to the I_{RRL}^e .

The obtained dependence of RRL intensity at pulse probing of sample by atoms on the level of semiconductor electronic excitation (concentration of the filled electronic traps), and also high efficiency of the excitation of irradiated sample with UV light (increase on 3 – 5 orders of the value) due to energy of heterogeneous reaction enable to use HEHA as sensitive and practically inertialless tool for semiconductors research usage. Owing to surface character of radical-recombination excitation HEHA may be used for studying actually surfaces, in particular for diagnostics of surface electronic

conditions in luminescent semiconductors (an optical method of heterogeneous surface spectroscopy).

The semiconductor band model that contains one type of electronic traps (TL) and the luminescence centers (AL) is represented on fig. 3. Electronic traps (TeL) filling and ionization of luminescence centers (ApL) (transitions 1 and 2, accordingly) happens during the preliminary photoexcitation of the semiconductor. At switching on of atomic stream (for example the stream of hydrogen H) to the surface there is an adsorption and recombination of atoms, resulting in to formation of a vibrational-excited molecule $H_2^V L$. Due to anharmonicity of vibrational bond in $H_2^V L$ transitions through some vibrational levels at once (fig. 3, transition 3) are possible already in the first order of decomposition of quadruple moment of molecule on internuclear distance [13]. Due to interaction of quadruple ($H_2^V L$) – dipole (electron in the electronic trap) the direct switchover of energy (which one was liberated in acts of $H_2^V L$ vibrational relaxation) to the excitation energy of electron on the electronic trap is possible. Then transfer of the electron into conduction band (transition 4) is possible [10]. The delocalization of electron from an electronic trap is also possible as a result of thermal excitation (transition 5). Electrons from a conductivity band are grasped by the empty electronic traps (transition 6) or recombined with the holes located on the ApL luminescence centers (transition 7) with emission of luminescence quantum.

The kinetic mechanism of RRL excitation of semiconductors, for which HEHA is found out, includes the following basic stages: adsorption, desorption of R atoms and R_2 molecules on a surface centers L, recombination of atoms from a gas phase with atoms on a surface (the Rideal-Eley mechanism of recombination), ionization of traps and generation of electron-hole pairs due to reaction and light irradiation.



Here ph – heating of a sample – phonons; ν_i , ν'_i , k'_i are probabilities of appropriate processes referred to a unit time; Γ_i ($i = 1 \approx 3$), k_j ($j = 1 \approx 3$) are constants of appropriate stages speeds; η is a probability of radiating relaxation of the luminescence center. We shall enter designations for concentration of the surface and volume centers in the moment t: $[L] \rightarrow N(t)$, $[RL] \rightarrow N_1(t)$, $[R_2 L] \rightarrow N_2(t)$, $[R_2^V L] \rightarrow N_2^V(t)$, $[TL] \rightarrow n(t)$, $[TeL] \rightarrow n_e(t)$, $[AL] \rightarrow m(t)$, $[ApL] \rightarrow m_p(t)$, $[eL] \rightarrow n_{eL}(t)$, $[pL] \rightarrow n_{pL}(t)$. The following system of the kinetic equations corresponds to the given model:

$$\begin{cases}
 \dot{N}_1 = v_1 N - v'_1 N_1 - v_2 N_1, \\
 \dot{N}_2 = v_3 N - v'_3 N_2 + (\Gamma_1 N_0 + \Gamma_2 N_0 + \Gamma_3 n_e) N_2^v, \\
 \dot{N}_2^v = v_2 N_1 - (\Gamma_1 N_0 + \Gamma_2 N_0 + \Gamma_3 n_e) N_2^v, \\
 \dot{n}_e = k_1 n_{eL} n - (\Gamma_3 N_2^v + k'_1) n_e, \\
 \dot{m}_p = k_2 n_{pL} m - k_3 n_{eL} m_p, \\
 \dot{n}_{eL} = (\Gamma_2 N_0 + \Gamma_3 n_e) N_2^v + k'_1 n_e + v_4 N_0 - k_1 n_{eL} n - k_3 n_{eL} m_p, \\
 \dot{n}_{pL} = \Gamma_2 N_0 N_2^v - k_2 n_{pL} m + v_4 N_0.
 \end{cases} \quad (1)$$

As time of the excited conditions life is small the quasi-equilibrium $\dot{N}_2^v = 0$, $\dot{n}_{eL} = \dot{n}_{pL} = 0$ takes place, and then $\dot{n}_e = \dot{m}_p$. It allows to simplify system (1) and to reduce it to the following kind:

$$\begin{cases}
 \dot{N}_1 = v_1 N - v'_1 N_1 - v_2 N_1, \\
 \dot{N}_2 = v_3 N - v'_3 N_2 + v_2 N_1, \\
 \dot{n}_e = (\Gamma_2 N_0 N_2^v + v_4 N_0) \frac{k_1 n}{k_1 n + k_3 m_p} - (\Gamma_3 n_e N_2^v + k'_1 n_e) \frac{k_3 m_p}{k_1 n + k_3 m_p}.
 \end{cases} \quad (2)$$

Here the next designation is supposed: $N_2^v = \frac{v_2 N_1}{\Gamma_1 N_0 + \Gamma_2 N_0 + \Gamma_3 n_e}$.

The HCL intensity is equal to

$$I = \eta \frac{k_3 m_p}{k_1 n + k_3 m_p} (\Gamma_2 N_0 N_2^v + \Gamma_3 n_e N_2^v + k'_1 n_e + v_4 N_0). \quad (3)$$

At that the condition of a constancy of full number adsorption places N_0 on surface $N + N_1 + N_2 = N_0$ and the charge conservation law $n_e = m_p$ are fulfilled.

The decision of the received equations system (2) with expression for luminescence intensity (3) together allows to determine the dependence of stationary RRL intensity on temperature, density of atoms and molecules streams and also to describe kinetics of RRL inflaming at switching-on of atoms above the clean surface; enables to describe the non-equilibrium ionization of traps, the changing of RRL intensity at modulation of atomic stream density and dependences of RRL intensity on time at switching-on of atoms after "dark" pauses.

The intensity of the luminescence arising at "switching-on" of atomic stream on the semiconductor surface in a metastable condition is equal $I = I_{RRL} + I_{RRL}^e + I_A$.

Here I_{RRL} is an intensity of radical-recombination luminescence; I_{RRL}^e is the contribution to the luminescence intensity, caused by excitation of electrons on electronic traps by vibrational-excited molecules energy; I_A is an intensity of the sample afterglow. At absence of exciting atomic stream and Φ switching off we have for afterglow intensity from (3):

$$I_A = \eta \frac{k_3 m_p}{k_1 n + k_3 m_p} k'_1 n_e \quad (4)$$

At switching-on of pulse atoms stream j of small density ($t < 2$ s) in process of de-excitation of the accumulated light sum, as it follows from (3), I_{RRL}^e will be equal

$$I_{RRL}^e = \eta \frac{k_3 m_p}{k_1 n + k_3 m_p} \Gamma_3 n_e N_2^v \quad (5)$$

Here considered that owing to HEHA $\Gamma_3 n_e N_2^v \ll \Gamma_2 N_0 N_2^v$. Due to (4) expression (5) will be written as $I_{RRL}^e = N_2^v \frac{\Gamma_3}{k_1'} I_A$, that is I_{RRL}^e is directly proportional to I_A , as it also was observed in experiments (fig. 1). We shall estimate the relative increase Δ of intensity of the chemiluminescence due to HEHA:

$$\Delta = I_{RRL}^e / I_{RRL} = \Gamma_3 I_A / (\eta \Gamma_2 N_0 k_1')$$

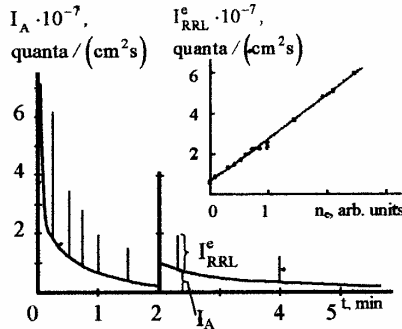


Fig. 1. Dependence of afterglow intensity and RRL excited by hydrogen atomic probe at the moment t_i of ZnS, CdS-Ag sample on time after UV excitation switching off. On an insert – the I_{RRL}^e dependence on electrons concentration on traps, $T=295$ K

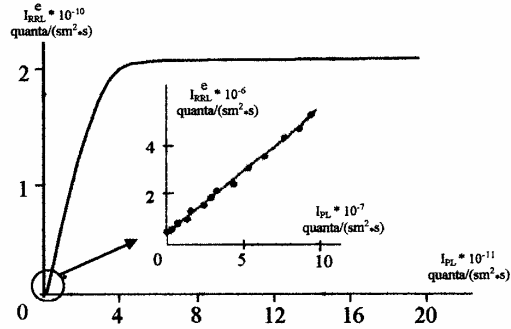


Fig. 2. Dependence of RRL intensity at pulse switching-on of a hydrogen atomic stream on Zn_2SiO_4 -Mn surface on the sample photoluminescence intensity, $T=300$ K

Since $k_1' = k_{10}' \cdot \exp(-E/kT)$ (where k_{10}' is the frequency factor of an electronic trap thermal relaxation; E is an electronic trap depth; T is the semiconductor temperature) the expression (6) will become: $\Delta = \frac{\Gamma_3 I_A}{\eta \Gamma_2 N_0 k_{10}'} \exp\left(\frac{E}{kT}\right)$.

$$\text{From here } E = \frac{k(\ln(\Delta_1) - \ln(\Delta_2))}{1/T_1 - 1/T_2}$$

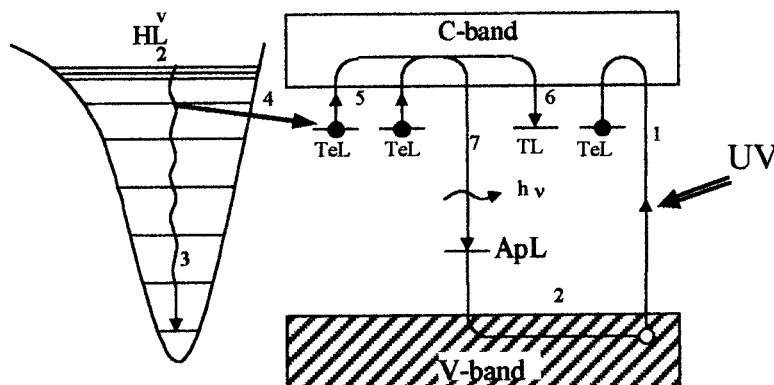


Fig. 3. Electronic processes on the surface of semiconductor

Here Δ_1 and Δ_2 are the relative increase of chemiluminescence intensity due to HEHA at two various valuations of semiconductor temperatures T_1 and T_2 . For ZnS,CdS-Cu,Al sample the following values of depth of electronic traps occurrence are received: 0,17 eV, 0,68 and 0,72 eV. For ZnS, CdS-Ag the basic were fine traps with $E = 0,20$ eV, and besides them for ZnS monocrystal in the high concentration were the traps with depth of 1,11 eV. Electronic conditions of semiconductors, obtained with the help of the given method, coincide with the data received by method of curve of thermostimulated luminescence (TSL) and on dependence of photoluminescence attenuation speed after preliminary UV excitation switching off from the sample temperature.

The reviewed results testify that for a series of electronic-excited semiconductors a main channel of energy accommodation of heterogeneous reaction is electronic instead of phonon one. Designed HCL-based method of definition of electronic states energetic places in semiconductors can be applied for a broad spectrum of luminescent semiconductors and dielectrics. The given method can be realized for study of electronic states of surfaces purely. HEHA allows managing of epitaxial growth speed of semiconductors and films. There is a possibility of control by cross-section, speed and selectivity of reaction that is relevant in chemical physics, plasmochimistry, and adsorptive isotope separation.

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**ЕЛЕКТРОННІ ПРОЦЕСИ НА ПОВЕРХНІ ШИРОКОЗОННИХ
НАПІВПРОВІДНИКІВ У ЗБУДЖЕННІ АТОМАМИ ТЕПЛОВОЇ ЕНЕРГІЇ ТА
УЛЬТРАФІОЛЕТОВИМ СВІТЛОМ**

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Розглянуто електронний канал акомодатії енергії хімічної реакції атомних часток теплової енергії (H, O) на поверхні широкозонних напівпровідників Zn_2SiO_4-Mn , ZnS, CdS-Ag, ZnS-Tm, ZnS-Cu, Al. Визначено кінетичний механізм збудження радикалорекомбінаційної люмінесценції напівпровідників, для яких винайдено явище високоефективної гетерогенної акомодатії (ВЕГА). Побудовано математичну модель.

Продемонстрована ефективна участь електронних станів у акомодатії енергії плазмохімічних реакцій. Розглянуто використання ВЕГА для визначення енергії глибини залягання електронних пасток.

Ключові слова: електронні пастки, акомодатія енергії, гетерогенні плазмохімічні реакції, люмінесценція.

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