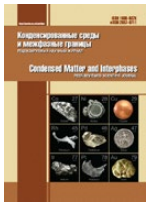

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Refined formula for the calculation of the coefficient of efficiency of an electrochemical generator

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Abstract

Objective: Analytical calculations and preliminary assessment of the efficiency of electrochemical generators (chemicurrent generators) are important for the analysis of the mechanisms of conversion of chemical energy into electrical energy. This process is based on the transformation of the energy of a heterogeneous chemical reaction of hydrogen molecule formation into the electronic excitation energy on the surface of a semiconductor catalyst. When calculating the probability of excitation of hot electrons (high-energy electrons in the conduction band of the semiconductor), earlier studies did not take into account the phonon channel of chemical energy accommodation. This is acceptable, if we neglect the interaction between the excited electron and the lattice. However, the scattering of the chemical reaction energy causes an inevitable shift in the equilibrium positions of oscillators, resulting in the emission and absorption of phonons. Therefore, the calculation method should take into account both electron and phonon accommodation channels. The purpose of the study was to derive a theoretical formula for the efficiency coefficient of an electrochemical generator taking into account thermally stimulated excitation of electrons to the conduction band and analyze particular cases of its application.

Theoretical analysis: We performed a theoretical analysis of the effect of local thermal vibrations initiated by the chemical reaction energy of formation of a hydrogen molecule on the catalyst surface on the rate of generation of high-energy electrons. The derived formulas for the calculation of the efficiency coefficient of electrochemical generators specify the corresponding formulas suggested in earlier studies. The study demonstrated a significant impact of thermally stimulated excitation of electrons to the conduction band of the semiconductor at room temperatures.

Conclusions: The obtained results can be used for qualitative analysis of chemical energy accommodation with regard to the conversion of chemical energy into electrical one.

Keywords: Catalyst surface, Accommodation, Phonon channel, Franck-Condon energy, Schottky barrier, Efficiency coefficient of electrochemical generators

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1. Introduction

Direct conversion of chemical energy into electrical energy can be performed by means of electrochemical generators [1], which are semiconductor heterostructures with various electronic parameters. Semiconductors with pronounced catalytic properties are considered promising materials [2]. Catalytic properties of semiconductors are largely accounted for by surface defects (shallow and deep impurities), which serve as traps for atoms and molecules of gaseous media [3–8]. The surface functions as a catalyst (K) for the formation (decay) of hydrogen molecules and helps to reduce the energy barrier (activation energy) as compared to the gaseous medium. Energy from the heterogeneous exothermic reaction H + K → HK, HK + H → H_2 + K is used to excite (form) high-energy electrons, which, affected by the electrical double layer, easily overcome the potential barrier at the heterointerface [1, 9]. Chemical energy accommodation can proceed along two channels: electron and phonon. In the first case, the energy of the exothermic reaction is transferred by impulse directly to the bound electron generating a high-energy electron. In the second case, the excessive energy is used for the excitation of high-energy phonons, which actively interact with valence electrons causing them to oscillate in accordance with the vibrations of the crystal lattice [10–13]. The adsorbed H_2 molecules oscillate at frequencies significantly higher than the Debye frequency. Therefore, the decay of local vibrations of hydrogen molecules is hindered, and the electron channel can become dominant over the phonon channel [14]. However, at high temperatures close to critical values, for instance the melting point, thermal fluctuations increase dramatically [15], and there is a possibility of thermally stimulated excitation of the valence electron to the conduction band. In this case, the phonon channel can be compatible with the electron channel. Thermally stimulated excitation of the valence electron to the conduction band is also possible at lower temperatures as a result of electron-phonon interaction [16]. For semiconductors with strong electron-phonon couplings, both accommodation channels should be taken into account. In this case, the probability of an elementary relaxation act [1] can be described as:

$$P(E_g,T)=\int_{E_g}^{\infty} w(E,T)f(E)dE, \quad (1)$$

E_g is the bandgap of the semiconductor, $w(E,T)$ is the probability of thermally stimulated excitation of the valence electron to the conduction band, $f(E)=(1/\Theta_{char})\exp(-E/\Theta_{char})$ is the experimentally established probability of generation of high-energy electrons [1, 2], Θ_{char} is the characteristic energy of the exothermic reaction forming the H_2 molecule (about 0.2 eV) on the catalyst surface, which generates an electron-hole $(e^- - p^+)$ pair [2].

Hot electrons in the conduction band are nonequilibrium charge carriers. Therefore, the function $f(E)$ characterizes the probability of the formation of a $(e^- - p^+)$ pair in the tail of the Maxwellian distribution function in the vicinity of energy Θ_{char} [1] does not take into account the phonon channel of energy accommodation $w(E,T)$. This is acceptable in the case of direct electron transitions in direct bandgap semiconductors. However, in the case of indirect-gap semiconductors it is necessary to take into account intermediate phonon states to preserve the quasi momentum of the hot electron. The existing formulas for calculating the efficiency coefficient of electrochemical generators [1, 14, 17] are probably a specific (limited) case of a more general (in terms of theory) formula.

The results presented in [1, 14, 17] do not take into account the shift of the adiabatic term during the transition of the hydrogen molecule back to the ground state: $H_2^* \rightarrow H_2 + Q$. The released energy Q can cause vibrations of the hydrogen molecule. When its own vibrations $\omega \propto 1/\sqrt{m_{H_2}}$ are within the band gap of the matrix, the H_2 molecule demonstrates local vibrations. The results presented in [1, 14, 17] correspond to the situation, when the natural frequency $\omega \propto 1/\sqrt{m_{H_2}}$ is within the band gap of the matrix. Besides, the position of the minimum of the configuration coordinate of the term $^1\Sigma_g^+$ shifts, which also requires energy, since the Franck–Condon principle is only partially met. It is obvious that the energy released by a locally vibrating center (in the case of resonance)

initiates thermally stimulated excitation of the electron to the conduction band of the semiconductor. Therefore, when generating the chemicurrent, both accommodation channels should be taken into account.

The purpose of the study was to derive a theoretical formula for the efficiency coefficient of an electrochemical generator taking into account thermally stimulated excitation of electrons to the conduction band and analyze particular cases of its application [1, 14, 17]. The deriving of the formula was based on the assumption that the generation of hot electrons requires the outer (peripheral) electron to be excited by high-energy phonons in order to break the bonds with neighboring atoms, since each outer electron forms electron-pair bonds between the atoms. In this case, contrary to [1], for Θ_{char}, some of the thermal energy Q of reaction $H + H \rightarrow H_2 + Q\uparrow$ is used for the excitation of the electron and the other for the direct (impact) excitation of the outer electron.

2. Calculation of the efficiency coefficient and discussion

According to the classical description of multi-phonon transitions valid for $k_B T >> \hbar\omega_0$ ($\hbar\omega_0$ is the energy of the quantum of matrix vibrations) [16]:

$$w(E,T) = \exp\left(-\frac{\mu(E)}{k_B T}\right), \mu(E) = \frac{\left(E_{opt} - E\right)^2}{4 E_{FC}}, \quad (2)$$

where E_{opt} is the optical transition energy associated with the thermal energy of excitation: $E_{opt} = E_T + E_{FC}$, E_{FC} is the Franck-Condon energy characterizing the *e-ph* interaction force. Substitution of (2) in (1) taking into account $f(E) = (1/\Theta_{char})\exp(-E/\Theta_{char})$ gives the following result:

$$P(E \geq E_g) = \frac{1}{\Theta_{char}} \int_{E_g}^{\infty} \exp\left(-\frac{E}{\Theta_{char}}\right) \exp\left[-\frac{\left(E_{opt} - E\right)^2}{4 E_{FC} k_B T}\right] dE. \quad (3)$$

A Gauss-type function $\exp\left[-\frac{\left(E_{opt} - E\right)^2}{4 E_{FC} k_B T}\right]$ characterizes local vibrations of the adiabatic term with the electron near the point of energy release of the chemical reaction (Fig. 1). These vibrations are loosely coupled with natural vibrations of the crystal lattice. The valence electron of the matrix near the heat release center Q (of the H_2 molecule) is associated with the *DX* center on the catalyst surface. Calculating the integral (3) we obtain the following expression:

$$P(E \geq E_g) = \frac{\sqrt{\pi}}{2} \exp\left(\frac{E_{FC} k_B T - \Theta_{char} E_{opt}}{\Theta_{char}^2}\right) \times \left[1 - \Phi\left(\frac{E_g - E_{opt}}{2\sqrt{E_{FC} k_B T}} + \frac{\sqrt{E_{FC} k_B T}}{\Theta_{char}}\right)\right]. \quad (4)$$

$\Phi(x)$ – is the error function; the electric current occurrence condition $E_{opt} \geq E_g + \varphi$ (φ is the potential barrier) (Fig. 1):

$$P(E \geq E_g) = \frac{\sqrt{\pi}}{2} \exp\left(\frac{E_{FC} k_B T}{\Theta_{char}^2} - \frac{E_g + \varphi}{\Theta_{char}}\right) \times \left[1 - \Phi\left(\frac{\sqrt{E_{FC} k_B T}}{\Theta_{char}} - \frac{\varphi}{2\sqrt{E_{FC} k_B T}}\right)\right]. \quad (5)$$

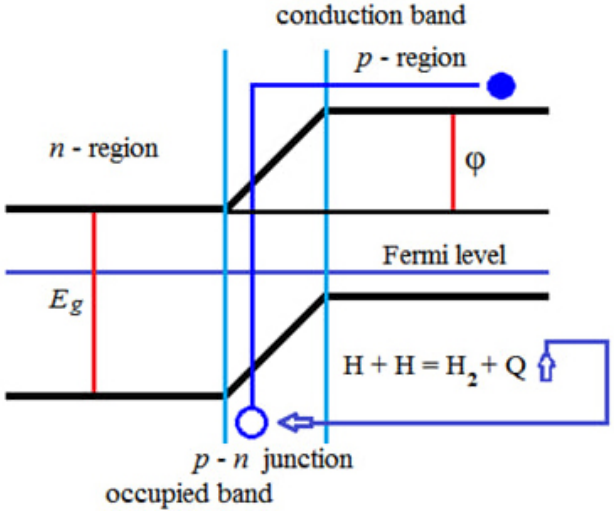

Fig. 1. Generation of mobile carriers under effect of chemical reaction energy. In the electric field of the depletion layer high-excited electrons accelerates and throws into conduction band *p*-type semiconductor, formating the external current. Semiconductor-catalyst *p*-type sufficiently thin so that the condition $\exp(-d/l) \approx 1$ was complianced, where d – its thickness, l – diffusion length path of high-energy electron into width of catalyst, which, for example, in high-quality monocrystalline silicon can be constitute of hundreds and thousands of micrometers

Provided that $2E_{FC}k_BT \cong \varphi\Theta_{char}$ (which demonstrates that the spread of the electron transition energy near $E = E_{opt}$ is limited by local heat release), from (5) follows:

$$P(E \geq E_g) = \frac{\sqrt{\pi}}{2}\exp\left(-\frac{\varphi}{2\Theta_{char}}\right)\exp\left(-\frac{E_g}{\Theta_{char}}\right). \quad (6)$$

We should note that condition $2E_{FC}k_BT \cong \varphi\Theta_{char}$ does not impair the criterion of local vibrations. Indeed, at high temperatures ($k_BT \gg \hbar\omega_0$) $E_{FC} \approx \hbar\omega N_{ph} \approx (\omega/\omega_0)k_BT, 2(\omega/\omega_0)(k_BT)^2 \approx \varphi\Theta_{char}$. Here ω is the frequency of quasi-local vibrations, N_{ph} is the average number of acoustic phonons. For instance, the calculation for germanium at room temperature and $\Theta_{char} \leq E_g$ [1] results in $\omega/\omega_0 \leq \varphi E_g/2(k_BT)^2 \approx 100$. It shows that some of the heat is used for the excitation of local phonons. Therefore, it is necessary to take into account the phonon accommodation channel, along with the electron channel, to accurately calculate the efficiency coefficient of an electrochemical generator. The condition $2E_{FC}k_BT \cong \varphi\Theta_{char}$ is satisfied, for instance, by the following values: $E_{FC} \approx 1.1$ eV, $k_BT \approx 0.027$ eV, $\Theta_{char} = 0.2$ eV, φ = 0.3 eV for GaAlAs [1,18]. Other optimal values can also be found. If $E_g = 0$ (similar to narrow band semiconductors and metals), then:

$$P(0) = \frac{\sqrt{\pi}}{2}\exp\left(-\frac{\varphi}{2\Theta_{char}}\right), \quad (7)$$

which specifies the corresponding formula for the excitation of high-energy electrons, whose energy is equal to or higher than the Schottky barrier φ in Pd/n-Si, Pt/GaAs, Pd/GaP diodes (Fig. 1) [17]. Taking into account formula (6) and the results presented in [1] the efficiency coefficient of an electrochemical generator can be calculated using the formula ($\Theta_{char} \leq Q$):

$$\eta = \frac{\sqrt{\pi}}{2}\exp\left(-\frac{\varphi}{2\Theta_{char}}\right)\frac{mE_g}{Q}\exp\left(-\frac{E_g}{\Theta_{char}}\right), \quad (8)$$

m is the average number of possible transitions along the electron channel of accommodation [1]. The efficiency coefficient of an electrochemical generator based on the Schottky diodes is calculated using the following formula [19, 20]:

$$\eta = \frac{\sqrt{\pi}}{2}\frac{\varphi}{Q}\exp\left(-\frac{\varphi}{2\Theta_{char}}\right). \quad (9)$$

According to formula (8) the efficiency coefficient is about 40% of the efficiency coefficient obtained when only the electron channel is considered [1], and according to formula (9) the efficiency coefficient is practically 90%. Thus, the effect of thermally stimulated excitation of electrons on the rate of chemicurrent generation is more prominent in non-degenerate semiconductors than in metals. Thus, for *n*-type wide-band semiconductors (φ = 0) using formula (5) we obtain the following:

$$P(E \geq E_g) = \frac{\sqrt{\pi}}{2}\exp\left(\frac{E_{FC}k_BT}{\Theta_{char}^2}\right)\times \times\left[1-\Phi\left(\frac{\sqrt{E_{FC}k_BT}}{\Theta_{char}}\right)\right]\exp\left(-\frac{E_g}{\Theta_{char}}\right). \quad (10)$$

We can assume that $\sqrt{E_{FC}k_BT} \cong \Theta_{char}$. Then the efficiency coefficient calculated using formula (10) is about 40% of the efficiency coefficient obtained, when only the electron channel is considered [1]. At high temperatures

$$P(E \geq E_g) \approx \frac{\Theta_{char}}{2\sqrt{E_{FC}k_BT}}\exp\left(-\frac{E_g}{\Theta_{char}}\right), \quad (\sqrt{E_{FC}k_BT} > \Theta_{char}). \quad (11)$$

The efficiency coefficient is respectively

$$\eta \approx \frac{\Theta_{char}}{2\sqrt{E_{FC}k_BT}}\frac{mE_g}{Q}\exp\left(-\frac{E_g}{\Theta_{char}}\right), \quad (T > 400\ \text{K}). \quad (12)$$

At temperatures of about 500 K, the efficiency coefficient calculated using formula (12) is about 45% of the efficiency coefficient obtained, when only the electron channel is considered [1]. We can see that in all the cases, when thermally stimulated excitation of electron was considered, the efficiency coefficient reduced on average by 60% and by 10%, when the barrier (φ = 0) was not considered (using formula (8)). This case is the closest to the results presented in [1].

3. Conclusions

As a result of the study, we derived formulas (8), (9), and (12). We also analyzed the effect of local thermal vibrations on the generation of hot electrons in semiconductors and metals. The study demonstrated a significant

contribution of the phonon channel of chemical energy accommodation at room and higher temperatures in non-degenerate semiconductors. The derived formulas can be used for the modelling of electrochemical generators and their optimization, when considering the problem of conversion of chemical energy into electrical energy.

Conflict of interests

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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