CONDITIONS FOR THE TEMPERATURE STABILIZATION OF THE THERMOELECTROMOTIVE FORCE IN SEMICONDUCTIVE MATERIALS

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The possibility of the stabilization of the common thermoelectromotive force versus the temperature is observed for materials with the standard band structure of one-type charge carriers and for those, having the complex construction of the valent band or)and) the conduction band (two-band model). It is shown, that the stabilization of the common thermoelectromotive force α is possible for the energy spectrum of the charge carriers corresponding to the two-band model if the width of the forbidden band ΔE is more than the value of the energy gap $\Delta\varepsilon$ between subbands.

The practical value of the semiconductive substance, which is applied in various thermal converters is determined firstly by the average value of the dimensionless parameter *ZT*, in which at the given temperature *T* the value of the thermal efficiency *Z*, according to the A.F. Ioffe criterion, is equal to:

$$Z = \frac{\alpha^2\sigma}{\chi_{com}} \sim \frac{u}{\chi_{cat}} \qquad (1)$$

where α, σ, χ_{com} are the common thermoelectromotive force, electroconductivity and heat conductivity, respectively, *u* is the mobility of the charge carries, χ_{lat} is the lattice heat conductivity.

The maximum of *Z* (Z_{max}) at the given temperature *T* [1] depends on: 1) the reduced Fermi level μ^*; 2) the dimensionless coefficient:

$$\beta = \frac{2(2\pi)^{3/2}}{h^3 e}(\kappa o)^{7/2}\frac{u}{\chi_p}\left(\frac{m^*}{m_o}\right)^{3/2} T^{5/2} \qquad (2)$$

and 3) the parameter of the charge carriers scattering *r*, where h is the Planck's constant, *e* is the electron charge, k_0 is the Boltzmann's constant, $\left(\frac{m^*}{m_o}\right)$ is the effective mass, *T* is the temperature.

The dependence of *Z T* on the reduced Fermi level μ^* has maximum, the sharpness and value of which depend on β [1] and respective thermoelectromotive force α and electroconductivity are optimal - α_{opt} and σ_{opt}.

The stabilization of the reduced Fermi level μ^* in the determined temperature interval corresponding to the value α_{opt} leads to the considerable growth of the parameter $Z_{ave}\ \Delta\ T$ and, consequently, to the maximal temperature gradient ΔT_{max}, the maximal cooling coefficient K_{max} and maximal efficiency ζ_{max}, in this interval, what has a great value for the development and practical use of the applied material in various cooling and generator devices.

The term "stabilization" means not the expression $\alpha(T)$ and $\alpha(n)$; $\alpha(p)=const$, but the change of the value α in determined limits, usually ±5-7% from the value of α_{opt}. At present time in the applied thermal material of *n* and *p*-type the value of the thermoelectromotive force α corresponds to the case of weak electrons and holes degeneration and its value versus the Fermi level μ^* is determined as:

$$\alpha = \frac{\kappa_o}{e}\left[\frac{(2r+5)F_{r+3/2}(\mu^*)}{(2r+3)F_{r+1/2}(\mu^*)} - \mu^*\right] \qquad (3)$$

where $F_r = \int_0^\infty \chi^r\left[exp(x-\mu^*)+1\right]dx$ is the Fermi integral, the value of which is tabulated in [2], *r*-is the scattering parameter.

The reduced Fermi level μ^* is connected with the charge carriers concentration *p(n)*, the effective mass of the state density m^*/m_0 (electrons and holes) and the temperature *T* through the Fermi integral as:

$$F_{1/2}(\mu^*) = \frac{p(n)\sqrt{\pi}h^3}{4(2\pi k_0 T m^*/m_o)^{3/2}} \qquad (4)$$

It is seen from the formula (2) that at conditions $m^*/m_0(T)=const$, $r=const$, $p(n)\sim T^{3/2}$ the Fermi integral $F_{1/2}(\mu^*)$, and consequently μ^* and α, for substances with the standard parabolic band and one-type charge carriers, do not depend on the temperature, i.e. they are stabilized.

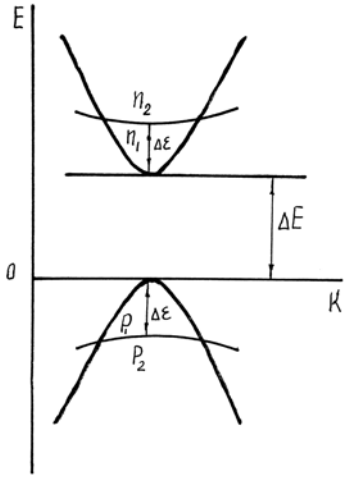

Fig. 1. Schematic picture of the energy bands of the complex structure.

For known semiconductive materials the theory of the transfer phenomena gives much stronger dependence *n(T)* and *p(T)*, and therefore the stabilization of the thermoelectromotive force *α(T)* is impossible in them. For substance with the complex band structure, to which Bi_2Te_3 of *p* and *n*-type, Sb_2Te_3 of *p*-type and etc. refer, it is possible to suppose the possibility of the condition fulfillment $F_{1/2}(\mu^*)\approx const$ at the stability of the common charge carriers concentration in the subzone $(p_{com}(T)=const)$ (fig.1).

At such condition the common thermoelectromotive force is:

$$\alpha_{com} = \frac{\alpha_1\sigma_1 + \alpha_2\sigma_2}{\sigma} \qquad (5)$$

the common electroconductivity is:

$$\sigma = \sigma_1 + \sigma_2$$

the common charge carriers concentration is:

$$p = p_1 + p_2 \qquad (6)$$

$$n = n_1 + n_2 \qquad (7)$$

where indices 1,2 refer to the first and second subzone of the valent band or the conduction band.

At the primary carriers scattering at the acoustic oscillation of the lattice (*r=-1/2*), the partial thermoelectromotive force, electroconductivity and the carriers concentration in the subbands have the form:

$$\alpha_1 = \frac{\kappa_0}{e}\left|\frac{2F_1(\mu^*)}{F_0(\mu^*)} - \mu^*\right| \qquad (8)$$

$$\alpha_2 = \frac{\kappa_0}{e}\left|\frac{2F_1(\mu^* - \Delta\varepsilon)}{F_0(\mu^* - \Delta\varepsilon)} - (\mu^* - \Delta)\right| \qquad (9)$$

$$\sigma_1 = 2e\frac{(2\pi m_0 k_0 T)^{3/2}}{h^2} F_0(\mu^*) u_{01}\left(\frac{m_1^*}{m_0}\right)^{3/2} \qquad (10)$$

$$\sigma_{21} = 2e\frac{(2\pi m_0 k_0 T)^{3/2}}{h^2} F_0(\mu^* - \Delta) u_{021}\left(\frac{m_2^*}{m_0}\right)^{3/2} \qquad (11)$$

$$p_1(n_1) = 4(2\pi\, m^*/m_0 k_0 T)^{3/2} F_{1/2}(\mu^*) \qquad (12)$$

$$p_2(n_2) = 4(2\pi\, m_2^*/m_0 k_0 T)^{3/2} F_{1/2}(\mu^* - \Delta) \qquad (13)$$

where u_{01}, u_{02} are the mobility of non-degenerated carriers in the first and second subbands, respectively.

For the analysis of the thermal and concentration dependence of the common thermoelectromotive force α_{com}, the ratio of the effective mass of the state density in the subbands $\left(\frac{m_2^*}{m_1^*}\right)$, the charge carriers mobility $\left(\frac{u_1}{u_2}\right)$, and also the value of the energy gap $\Delta\varepsilon$, and the width of the forbidden band ΔE are usually accepted as constant values, subbands are parabolic, and the mechanism of the charge carriers scattering is equal. At low temperatures ($kT \ll \Delta\varepsilon$) the charge carriers of the first subband mainly take part in the conduction process, the second subzone is almost empty and therefore (formulae 5-7)

$$\sigma \approx \sigma_1;\ p \approx p_1;\ \alpha \approx \alpha_1$$

by this

$$\frac{p_1}{p_2} \gg 1,\ \sigma_1 \gg \sigma_2,\ \alpha_1 \ll \alpha_2$$

and the common thermoelectromotive force α_{com} grows in a linear fashion with the temperature increase (part 1; fig. 2).

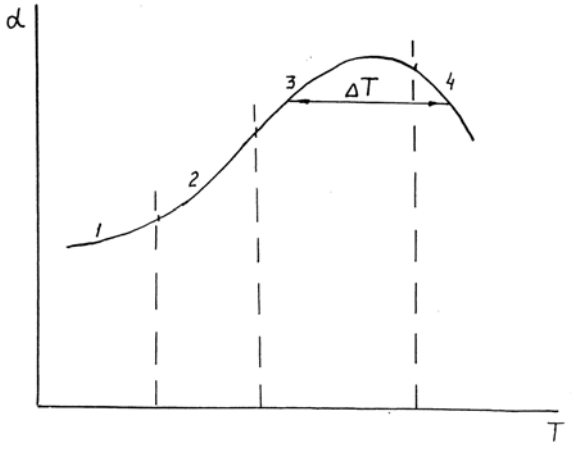

Fig.2. The temperature dependence of the thermoelectromotive force for n/n materials of *p*-type and with $\Delta E > \Delta\varepsilon$.

The redistribution of the charge carriers between subbands occurs with the further temperature growth, the behavior of the thermoelectomotive force α_{com} and electroconductivity σ_{com} will depend on the relation between the thermal activation energy of the charge carriers ΔE_T and the width of the energy gap $\Delta\varepsilon$ between subbands. Two cases are possible by this: 1) $\Delta\varepsilon < \Delta E$ and 2) $\Delta\varepsilon = \Delta E$.

1. In the first case the reduction of the carriers concentration in the low subzone $p_1(n_1)$ and its growth in the second $p_2(n_2)$ lead to the increase of the thermoelectromotive force α_1 and electroconductivity σ_2, the reduction of the elctroconductivity σ and thermoelectromotive force α_2.

By the temperature growth the reduced Fermi level μ^* approaches the top of the "heavy" holes subbands; the contribution of its carriers in the transfer process increases and at the determined *T* (depending on subbands parameters $\Delta\varepsilon$, ΔE, $\left(\frac{m_T^*}{m_{JI}^*}\right)$ and etc.) the product $\alpha_2\,\sigma_2$ becomes more than $\alpha_1\,\sigma_2$ and the common thermoelectromotive force α_{com} grows according to much stronger law, it follows from the theory for substances with one-type carriers in the degenerated state

$T \approx \left(\frac{\Delta\varepsilon}{K_0}\right)$, the primary contribution of the second subband carriers is shown in the conduction process

$$\alpha_{com} \approx \alpha_2, \sigma_{com} \approx \sigma_2, p_{com} \approx p_2$$

The further increase of the charge carriers concentration in the second subzone leads to the reduction of the thermoelecromotive force α_2 (the formula Pissarencko) and in spite of the growth of σ_2(T) the product $\alpha_2\ \sigma_2$ reduces and the common thermoelectromotive force α_{com}, passing through the maximum, reduces (the formula 5) part 4.

The common electroconductivity σ_{com} falls by this, both in the consuquence of the carriers number growth with the high effective mass of the state density $\left(\frac{m_2^*}{m_0}\right)$ and the low mobility u_2, and the dependence of u_2 on the temperature, the exponent «K» in the expression $\sigma_{com} \approx T^k$ as it is more than 3/2 by this (at the charge carriers scattering in the second subzone on the acoustic oscillation of the lattice r = - ½).

Therefore, in the observed case the temperature dependence $\alpha_{com}(T)$ differs a bit from the value α_{max} and they might be concerned stabilized to a required precision. The interval value ΔT (its length) depends on the relation $\Delta\varepsilon$ and ΔE.

2. $\Delta\varepsilon = \Delta E$. In this case the contribution in the common thermoelectromotive force α_{com} and electrons electroconductivity σ_{com} of the conduction band α_n and σ_m occurs at determined temperatures, respectively, formulae (5)-(6) have the form:

$$\alpha_{экс} = \frac{\alpha_1\sigma_1 + \alpha_2\sigma_2 - \alpha_n\sigma_n}{\sigma_1 + \sigma_2 + \sigma_n} \qquad (14)$$

Creating solid solutions on the base of the matrix (basic) materials, it is possible to obtain optimal values ($\Delta\varepsilon < \Delta E$) at ($\Delta\varepsilon = \Delta E$) the common electroconductivity σ_{com} will increase - it is seen from the formula (13) at the whole temperature interval.

From applied in the present time in the thermal converters materials of the complex energy spectrum of the charge carriers, allowing to explain the behavior of kinetic parameters α_{com}, σ_{com}, R_x versus the temperature and concentration, have mainly tellurides GeTe, SnTe, PbTe [3,4'; $SbTe_3$, Bi_2Te [5,6]. In all indicated tellurides the value of the energy gap $\Delta\varepsilon$ is lesser than the width of the forbidden band ΔE, i.e they meet the first case and it is possible by means of the solid solution creation on their base to achieve the stabilization of the common thermoelectromotive force α_{com} in the respective temperature interval.

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YARIMKEÇİRİCİ MADDƏLƏRDƏ TERMO-ELEKTRİK HƏRƏKƏT QÜVVƏSİNİN TEMPERATURDAN ASILI OLARAQ STABİLLƏŞDİRMƏ ŞƏRTLƏRİ

Məqalədə mürəkkəb quruluşlu keçirici və valent zonaya malik olan və bir növ yükdaşıyıcı, standart zolaqlı maddələr üçün temperaturdan asılı olaraq ümumi T.E.h.q-nin stabilləşməsi halı araşdırılmışdır. Göstərilmişdir ki, ΔE qadağan olunmuş zolağın eni $\Delta\varepsilon$ - energetik məsafənin qiymətindən böyük olduqda yükdaşıyıcılarının energetik spektri iki zolaqlı modula uyğun gələn maddələr üçün T.E.h.q-nin stabilləşdirilməsi mümkündür.

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УСЛОВИЯ ТЕМПЕРАТУРНОЙ СТАБИЛИЗАЦИИ ТЕРМОЭДС В ПОЛУПРОВОДНИКОВЫХ МАТЕРИАЛАХ

Рассмотрена возможность стабилизации общей термоэдс в зависимости от температуры для материалов со стандартной зонной структурой с одним сортом носителей заряда или обладающими сложным строением валентной зоны и, или зоны проводимости (двухзонная модель). Показано, что для веществ с энергетическим спектром носителей заряда, соответствующих двух-зонной модели, возможна стабилизация общей термоэдс α, если ширина запрещенной зоны ΔE больше величины энергетического зазора $\Delta\varepsilon$ между подзонами.

Received: 04.12.02