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THERMODYNAMICAL ANALYSIS OF OPTIMAL RECOMBINATION CENTERS IN THYRISTORS

OLOF ENGSTRÖM and ANDERS ALM
ASEA AB, Electronics Division, Semiconductor Components Department, S-721 83 Västerås, Sweden

Abstract—The main criterion for an optimal recombination center in thyristors has been reformulated, starting from a basic thermodynamical level. From an extended grand canonical ensemble, statistical expressions for the thermal emission rates of an impurity atom are obtained in terms of changes in enthalpy, electronic and vibrational entropy. The ratio between lifetimes at high and low injection levels is evaluated for single and double level recombination centers and calculated for different enthalpy positions and entropy changes of the center and for different resistivities of the thyristor middle region. It is shown that the expected changes in entropy, when a charge carrier is emitted or captured by the center influences the optimal enthalpy position in silicon by as much as 0.1 eV. Also, a complete change in the influence of injection level on lifetime at standard resistivities and temperature for high power devices is noted. The optimization criterion is compared with experimental data pertinent to thyristor optimization. The paper demonstrates the necessity of making a profound thermodynamical analysis of the charge carrier traffic at a recombination center when using experimental data for deep impurities in the optimization of thyristor lifetime ratings.

NOTATION

- c_n thermal capture rate for electrons at recombination center, cm^3s^{-1}
- c_p thermal capture rate for holes at recombination center, cm^3s^{-1}
- e_n thermal emission rate for electrons at recombination center, s^{-1}
- e_p thermal emission rate for holes at recombination center, s^{-1}
- g_1, g_0 electronic degeneracies of energy levels
- h carrier injection level
- j identification index for an energy level in a set of levels
- k Boltzmann's constant, eV/K
- n free electron density, cm^{-3}
- n_0 equilibrium free electron density, cm^{-3}
- Δn excess free electron density, cm^{-3}
- n_i intrinsic electron density, cm^{-3}
- n_j equilibrium free electron density when the chemical potential coincides with the recombination level location, cm^{-3}
- n_T density of electrons trapped in a center, cm^{-3}
- p free hole density, cm^{-3}
- p_0 equilibrium free hole density, cm^{-3}
- Δp excess free hole density, cm^{-3}
- p_j equilibrium free hole density when the chemical potential coincides with the recombination level location, cm^{-3}
- p_T density of holes trapped in a center, cm^{-3}
- ΔG free enthalpy (Gibbs' free energy), eV
- ΔG_n free enthalpy needed to excite an electron from an impurity to the conduction band, eV
- ΔG_p free enthalpy needed to excite a hole from an impurity to the valence band, eV
- G_{Tj} free enthalpy of an energy level with j electrons, eV
- H_{ir} enthalpy levels of an impurity, eV
- ΔH enthalpy, eV
- ΔH_n enthalpy needed to excite an electron from an impurity to the conduction band, eV
- ΔH_p enthalpy needed to excite a hole from an impurity to the valence band, eV
- N number of particles
- N_c effective density of states at the conduction band edge, cm^{-3}
- N_v effective density of states at the valence band edge, cm^{-3}
- N_T density of recombination centers in the n-base, cm^{-3}
- P_1 probability to find a center which has captured one electron
- R_n recombination rate for electrons, $cm^{-3}s^{-1}$
- R_p recombination rate for holes, $cm^{-3}s^{-1}$
- ΔS_{cv} vibrational entropy change for excitation of an electron from the valence band to the conduction band, eV/K
- ΔS_{na} vibrational entropy change for a recombination center at electron excitation/deexcitation, eV/K
- ΔS_{ne} electronic entropy change for excitation/deexcitation at an impurity, eV/K
- ΔS_{pa} vibrational entropy change for a recombination center at hole excitation/deexcitation, eV/K
- ΔS_{pe} hole entropy change for excitation/deexcitation at an impurity, eV/K
- T absolute temperature, K
- X_n entropy factor for electrons
- X_p entropy factor for holes
- μ chemical potential for electrons, eV
- μ_i intrinsic chemical potential for electrons, eV
- Ω number of states
- Π partition function of the extended grand canonical ensemble
- τ charge carrier lifetime, s
- τ_{p0} hole lifetime in heavily doped n-type silicon, s
- τ_H high level lifetime, s
- τ_L low level lifetime, s
- ζ capture rate ratio parameter

1. INTRODUCTION

Charge carrier lifetime is an important parameter of thyristors, since it influences most of the electrical parameters characterizing the device, i.e. forward voltage drop, stored carrier charge, generation currents, turn-off and turn-on times and in an indirect way forward and reverse blocking capabilities. It would therefore be valuable to find recombination centers having optimal data combinations with respect to the electrical properties of the thyristor. Attempts in this direction were made recently[1, 2] and it was shown that the ratings of thyristors can be maximized by achieving a high ratio between high and low injection level lifetimes while simultaneously positioning the recombination energy level away from the center of the energy gap in order to obtain a low leakage current. These investigations,

however, suffer from the lack of a clear definition of the term "energy level" of the recombination center. The energy, being an integral part of Shockley–Read–Hall statistics[3] should be treated either as a free enthalpy (Gibbs' free energy) with a temperature dependence[4, 5] or as an enthalpy, in which case the entropy properties of the center should be taken into account[4, 5]. None of these cases was considered in Refs. [1] and [2]. In these treatments, therefore, problems will arise when experimental data from the literature are used for comparison with theoretically optimized values.

In this paper the main optimization criterion for a recombination center of thyristors will be reformulated against a thermodynamical background built on an "extended grand canonical ensemble", which has been shown to give a consistent description of deep impurities in semi-conductors[5].

The statistics will be written in terms of enthalpies, vibrational entropies and electronic degeneracies. It will be shown that the entropy and degeneracy of the center has a critical influence on its recombination properties at the temperatures (~400 K) and resistivities (~200 Ωcm) common in the use of high power thyristors. Furthermore, the lifetimes will be given for the case of coupled double energy levels, which is commonly assumed for deep impurities in silicon, and it will be shown when a single level approximation is possible.

2. THERMODYNAMICAL BACKGROUND

Considering an "extended grand canonical ensemble"[5] (i.e. a grand canonical ensemble with volume as an additional variable), we find the partition function Π of a subsystem with Ω states and N particles as

$$\Pi = \sum_{i=1}^{\Omega} \sum_{r=0}^{N} \exp\left(\frac{\mu r - H_{ir}}{kT}\right). \tag{1}$$

Here μ is the chemical potential and H_{ir} are the enthalpy levels of the subsystem. By applying this thermodynamical model on the system of a deep impurity in a semiconductor, it is easily shown that the thermal emission rates e_n for electrons and e_p for holes can be written alternatively in terms of free enthalpies ΔG or enthalpies ΔH in the following way:

$$e_n = c_n N_c \exp\left(-\frac{\Delta G_n}{kT}\right) = X_n c_n N_c \exp\left(-\frac{\Delta H_n}{kT}\right) \tag{2}$$

where

$$X_n = \frac{g_0}{g_1} \exp\left(\frac{\Delta S_{na}}{k}\right), \tag{3}$$

and

$$e_p = c_p N_v \exp\left(-\frac{\Delta G_p}{kT}\right) = X_p c_p N_v \exp\left(-\frac{\Delta H_p}{kT}\right) \tag{4}$$

where

$$X_p = \frac{g_1}{g_0} \exp\left(\frac{\Delta S_{pa}}{k}\right). \tag{5}$$

In the above equations, c_n and c_p are the thermal capture rates for electrons and holes respectively and N_c and N_v are the effective densities for the conduction and valence band respectively. ΔG_n and ΔG_p are the free enthalpy values needed to excite an electron from the impurity to the conduction band or a hole from the impurity to the valence band, respectively. ΔH_n and ΔH_p are the corresponding enthalpy values. The factors X_n and X_p originate from the change in entropy taking place when a charge carrier is excited from the impurity. This entropy change has two causes. Firstly, for a deep impurity where excited states can be neglected, the change in the number of electronic states is determined by the change in degeneracy. This is reflected in eqns (3) and (5) as the ratio between the degeneracies g_0 of an empty center, and g_1 of a center filled with one electron. Secondly, the emission or capture of an electron by the center changes the vibrational frequency of the center. The magnitude of the change depends on to what extent the electron state is bonding or anitbonding[6]. This leads to a change in vibrational entropy, represented by the exponents of $\Delta S_{na}/k$ and $\Delta S_{pa}/k$ in eqns (3) and (5). The two different ways of expressing eqns (2) and (4) depend on the fact that the free enthalpy $\Delta G_{n,p}$ and the enthalpy $\Delta H_{n,p}$ are related by

$$\Delta G_{n,p} = \Delta H_{n,p} - (\Delta S_{(n,p)e} + \Delta S_{(n,p)a})T \tag{6}$$

where

$$\Delta S_{ne} = k \cdot \ln(g_0/g_1) \tag{7}$$

$$\Delta S_{pe} = k \cdot \ln(g_1/g_0). \tag{8}$$

Therefore the statistics of an impurity center are to be treated in terms of free enthalpies, keeping in mind that these are temperature dependent quantities[4] or in terms of enthalpies, taking into account the entropy factors X_n and X_p.

3. CHARGE CARRIER LIFETIMES

For silicon, which is the only material hitherto used for the production of high power thyristors, most impurities give rise to multiple level recombination centers. In this section the charge carrier lifetime determined by a set of ν energy levels will be expressed analytically, with special interest focused on a double level center, which seems to be a common case in silicon. We will also demonstrate when a single level treatment is possible.

Consider a set $\{1, 2, \ldots, \nu\}$ of energy levels (Fig. 1), each with a concentration n_{Tj} of trapped electrons and p_{Tj} of trapped holes. The recombination rates R_{nj} for electrons and R_{pj} for holes are given by[7]

$$R_{nj} = c_{nj}(np_{Tj} - n_j n_{Tj}), \quad j = 1, 2, \ldots, \nu \tag{9}$$

$$R_{pj} = c_{pj}(pn_{Tj} - p_j p_{Tj}), \quad j = 1, 2, \ldots, \nu \tag{10}$$

where $n = n_0 + \Delta n$ and $p = p_0 + \Delta p$. The quantities n_0 and p_0 are the equilibrium free carrier concentrations of electrons and holes respectively, while Δn and Δp are the injected excess free carrier concentrations.

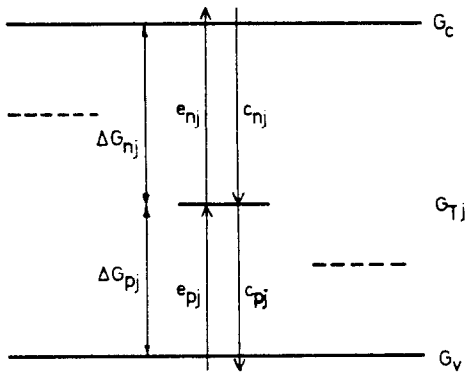

Fig. 1. Carrier generation and recombination via a set of energy levels with free enthalpy positions G_{Tj}, $j = 1, 2, 3, \ldots$.

The quantities n_j and p_j are defined by

$$n_j = N_c \exp\left(-\frac{\Delta G_{nj}}{kT}\right) \tag{11}$$

$$p_j = N_v \exp\left(-\frac{\Delta G_{pj}}{kT}\right). \tag{12}$$

At steady state the relation $R_{nj} = R_{pj}$ holds, and if we further look at the case $\Delta n, \Delta p \gg \sum_j n_{Tj}$ the charge neutrality condition can be formulated $\Delta n = \Delta p$, yielding a common lifetime τ for electrons and holes:

$$\tau^{-1} = \left(\sum_{j=1}^{\nu} R_{nj}\right)\Big/\Delta n = \left(\sum_{j=1}^{\nu} R_{pj}\right)\Big/\Delta p. \tag{13}$$

Combining eqns (9)–(12) for an n-type semiconductor, i.e. $n_0 \gg p_0$ (which is the usual case for the middle region of high power thyristors) and defining $h = \Delta n/n_0$, one finds

$$\tau^{-1} = \sum_{j=1}^{\nu} \frac{(1+h)c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}(1 + h + n_j/n_0) + c_{pj}(p_0/n_0 + h + p_j/n_0)}. \tag{14}$$

By letting $h \to \infty$ and $h \to 0$ the high and low injection lifetimes τ_H and τ_L are found for the general case of a set of ν energy levels

$$\tau_L^{-1} = \sum_{j=1}^{\nu} \frac{c_{nj}c_{pj}(n_{Tj} + p_{Tj})}{c_{nj}(1 + n_j/n_0) + c_{pj}p_j/n_0} \tag{15}$$

$$\tau_H^{-1} = \sum_{j=1}^{\nu} \frac{c_{nj}c_{pj}}{c_{nj} + c_{pj}}(n_{Tj} + p_{Tj}). \tag{16}$$

For the special case of a coupled double center the following relations between the total concentration N_T of centers and the trapped carrier concentrations are valid:

$$N_T = n_{T1} + n_{T2} + p_{T1} \tag{17}$$

$$p_{T2} = n_{T1}. \tag{18}$$

Here subscript 1 represents the energy level G_{T1} of a center which has captured only one electron and subscript 2 represents the energy level G_{T2} of a center which has captured two electrons. For an n-type semiconductor we may assume that $\mu - G_{T1} \gg kT$, which means that p_{T1} in eqn (17) approaches zero. This gives for the low injection lifetime τ_L the expression

$$\tau_L^{-1} = (K_1P_1 + K_2)N_T \tag{19}$$

where

$$K_j = \frac{c_{nj}c_{pj}}{c_{nj}(1 + n_j/n_0) + c_{pj}p_j/n_0}, \qquad j = 1, 2. \tag{20}$$

The quantity P_1 is the probability of finding a center which has captured only one electron. This probability, which can be found by using the partition function (1) and standard arguments of statistical mechanics[8] has the following form

$$P_1 = \left\{1 + \exp\left(-\frac{\mu - G_{T1}}{kT}\right) + \exp\left(\frac{\mu - G_{T2}}{kT}\right)\right\}^{-1} \tag{21}$$

The high injection lifetime τ_H can be found from eqns (16)–(18) as

$$\tau_H^{-1} = \frac{c_{n1}(c_{p1} + c_{n2})}{c_{n1}(1 + c_{n2}/c_{p2}) + c_{p1}} \cdot N_T. \tag{22}$$

It can be seen from eqns (19) and (22) that a single level approach is possible when $K_1P_1 \ll K_2$ and $c_{n1}, c_{p1} \ll c_{n2}, c_{p2}$. In that case the lifetime is completely determined by the two electron level G_{T2}. For a single level it is readily seen from eqns (15) and (16) that

$$\tau_L^{-1} = \frac{c_nc_p}{c_n(1 + n_1/n_0) + c_pp_1/n_0} \cdot N_T \tag{23}$$

$$\tau_H^{-1} = \frac{c_nc_p}{c_n + c_p} \cdot N_T. \tag{24}$$

4. THE SINGLE LEVEL APPROACH

Earlier treatments of optimal recombination centers have dealt only with single level statistics[1, 2]. In the above section it was shown that such a descripton is possible only under certain conditions. In this section we will use the single level approach in order to demonstrate the influence of entropy properties of the recombination center on the optimization criterion, which states that the ratio between high and low level lifetimes, τ_H/τ_L, should be maximized. This ratio can be evaluated in the following form from eqns (2)–(5), (11), (12), (23) and (24)

$$\frac{\tau_H}{\tau_L} = (1 + \zeta)\left[\frac{n_i^2}{N_vn_0}\frac{1}{X_p}\exp\left(\frac{\Delta H_p}{kT}\right) + \frac{N_v}{n_0}\zeta X_p \exp\left(-\frac{\Delta H_p}{kT}\right) + 1\right]^{-1} \tag{25}$$

where $\zeta = c_p/c_n$.

The entropy factor X_p contains the changes in electronic degeneracy and vibrational entropy (eqn (5)). In

order to demonstrate the influence of X_p it is necessary to estimate its possible range of variation. For a few centers, there exists optical measurements of the temperature dependences of the free enthalpy of the centers. An interpretation of these data[5] has yielded an estimate of the electronic degeneracy change g_0/g_1. The estimated range of variation for these centers is 0.25–0.5. In view of the lack of more detailed knowledge we use this range throughout the calculations of expression (25). The atomic entropy change ΔS_{pa} has the extremum values 0 and ΔS_{cv}, where ΔS_{cv} is the entropy change resulting from the excitation of an electron from the valence band to the conduction band. The enthalpy ΔH_p can be found experimentally from a measurement of thermal emission rates. A common temperature range for mid gap level measurements is 200–300 K. In this region $\Delta S_{cv} \simeq 2.5k$[9]. This means that the exponential in eqn (5) may vary between 1 and 12, so with the above estimate of g_1/g_0, X_p varies between 2 and 48 depending on the entropy properties of the impurity center. In Fig. 2 the calculated results of the ratio τ_H/τ_L are given as a function of enthalpy distance from the valence band for different values of ζ and for the extremum values of X_p. As can be seen, the optimal enthalpy position at which τ_H/τ_L has its maximum value is strongly influenced by X_p, the value of which must be known in order to find an optimal recombination center.

As is realized from eqn (25) the lifetime ratio is also influenced by the resistivity of the thyristor middle region. However, the magnitude of this resistivity dependence is also influenced by the values of X_p as shown in Fig. 3.

In order to demonstrate the influence of X_p on the

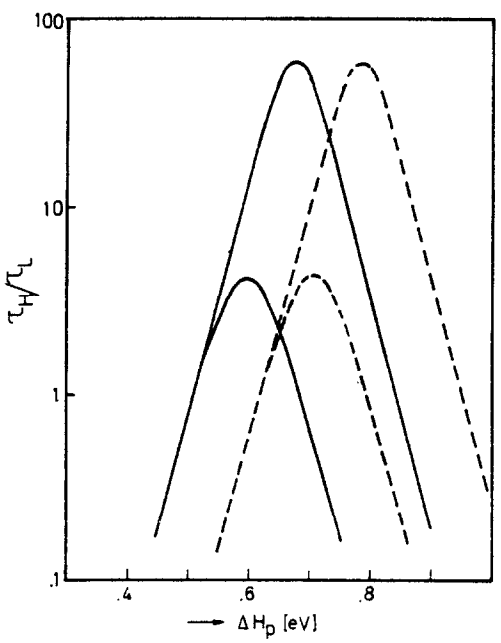

Fig. 2. High level to low level lifetime ratio of a single level center as a function of enthalpy distance from the valence band edge to the impurity at $T = 400$ K. Upper curves $\zeta = 1000$, lower curves $\zeta = 10$, solid curves $X_p = 2$, dashed curves $X_p = 48$.

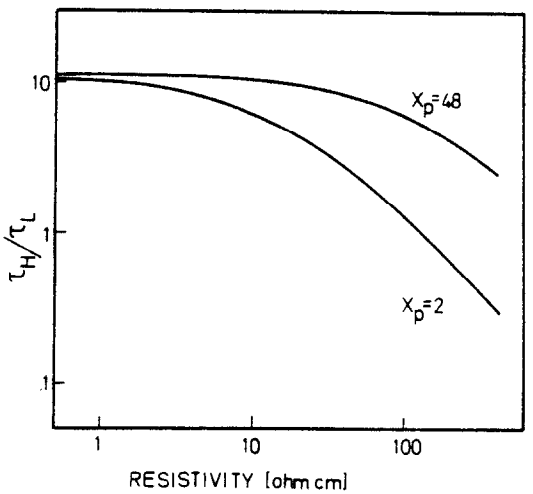

Fig. 3. High level to low level lifetime ratio of a single level center as a function of resistivity of the thyristor n-type middle region at different entropy factors and $T = 400$ K, $\Delta H_p = 0.70$ eV, $\zeta = 10$.

injection dependence of τ we derive the ratio τ/τ_{p0}, where $\tau_{p0} = 1/(N_T c_p)$, from eqn (23).

$$\frac{\tau}{\tau_{p0}} = 1 + \frac{1}{1+h}\left[\frac{n_i^2}{n_0 N_v}\frac{1}{X_p}\exp\left(\frac{\Delta H_p}{kT}\right) + \zeta\left(h + \frac{N_v}{n_0}X_p \exp\left(-\frac{\Delta H_p}{kT}\right)\right)\right]. \quad (26)$$

In Fig. 4 this ratio is plotted as a function of injection level h. As can be seen, a complete change in the injection dependence of lifetime is observed for the same enthalpy position of the center, when X_p is allowed to vary within a reasonable range. The curve with the negative slope is highly undesirable for the ratings of high power thyristors.

5. ANALYSIS OF THE GOLD CENTER IN SILICON

The most widely used recombination center for lifetimecontrol in silicon power devices is gold. The first electron captured by this center goes into a donor state with $\Delta G_{p1} = 0.35$ eV[10], which is pinned to the conduction band when the temperature is varied[11]. The second electron goes into an acceptor state with $\Delta G_{n2} = 0.55$ eV[10] which is also pinned to the conduction band[12]. Even though gold is one of the most thoroughly examined centers, large discrepancies for the capture rates are found in the literature. The values of the different capture rates used and their temperature dependences are taken from Refs[11, 13–17]. They are given in Table 1. The reason for using these particular values is that they give results in good agreement with the experimental values of τ_H/τ_L for gold in silicon, measured by Zimmermann[18] at room temperature.

Inserting these values into the expression for the low injection lifetime obtained in eqn (19), we find that $K_1 P_1 \ll K_2$ for resistivities around 200 Ωcm and temperatures of about 400 K, which are standard values in connection with high power thyristors. This means that the life time ratio τ_H/τ_L can be treated as the ratio

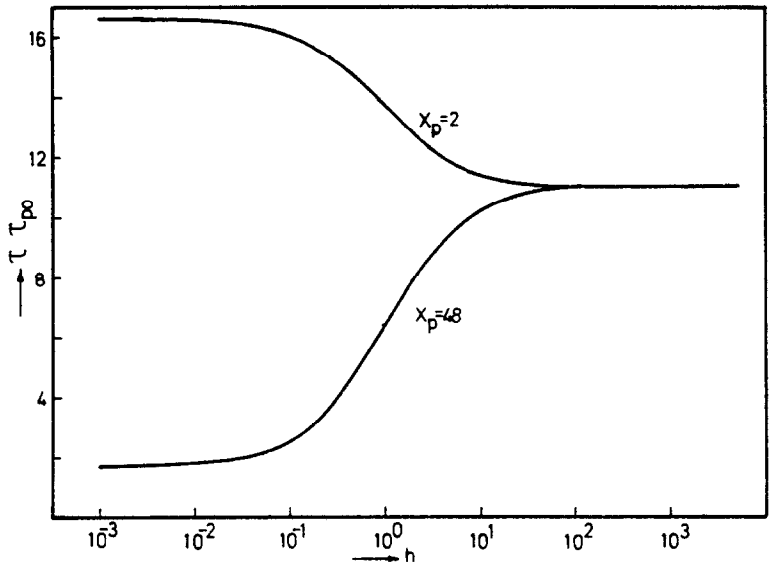

Fig. 4. Injection dependence of lifetime for a single level center for different entropy factors and $T = 400$ K $\Delta H_p = 0.70$ eV, $\zeta = 10$.

Table 1. The capture rates and their temperature dependence as used for the calculations of the curves in Fig. 5.

	c_{n1} (cm^3s^{-1})	c_{p1} (cm^3s^{-1})	c_{n2} (cm^3s^{-1})	c_{p2} (cm^3s^{-1})
Value at 300K	$4\cdot10^{-6}$ a)	$3\cdot10^{-8}$ b)	$2\cdot10^{-8}$ d,e)	10^{-7} d,e)
Temperature dependence	T^{-2} a)	$T^{0.7\pm0.8}$ c)	T^{0} a,d)	T^{-4} a,e)

a) ref. 13
b) ref. 14
c) ref. 11
d) ref. 15
e) ref. 16
f) ref. 17

between the high injection lifetime of a coupled double center (eqn (22)) and the low injection lifetime of a single level center, taken for the two electron acceptor level. This gives for the lifetime ratio of the gold center in silicon:

$$\frac{\tau_H}{\tau_L} = \frac{1+\zeta_2+\zeta_1\zeta_2}{\left(1+\frac{c_{p1}}{c_{n2}}\right)\left[1+\frac{n_i^2}{n_0N_v}\frac{1}{X_{p2}}\exp\left(\frac{\Delta H_{p2}}{kT}\right)+\zeta_2\frac{N_v}{n_0}X_{p2}\exp\left(-\frac{\Delta H_{p2}}{kT}\right)\right]} \tag{27}$$

where $\zeta_1 = c_{p1}/c_{n1}$ and $\zeta_2 = c_{p2}/c_{n2}$.

Since ΔG_{n2} of the gold acceptor is temperature independent, the total entropy change when exciting a hole from the acceptor to the valence band, ΔS_p, is equal to ΔS_{cv}. By using eqn (5) and the value of ΔS_{cv} taken from Ref. [9] one finds the values $X_p = 12$ at 300 K and $X_p = 24$ at 400 K. Inserting these values into eqn (27) together with the capture rates, the lifetime ratio τ_H/τ_L can be found for different enthalpy distances ΔH_{p2} of the gold acceptor as shown in Fig. 5. At 400 K the optimal enthalpy distance is found at a value which agrees well with the actual position of the gold acceptor. This has been pointed out earlier by considering the temperature dependence of the "location of the recombination level below the conduction band"[16] which in our language is the free enthalpy distance.

6. CONCLUSIONS

The difference between free enthalpies and enthalpies is very seldom pointed out in the literature. Often the satistical expressions are furnished with an "E", the meaning of which is not clearly mentioned. The use of free enthalpies or enthalpies is a question of with which

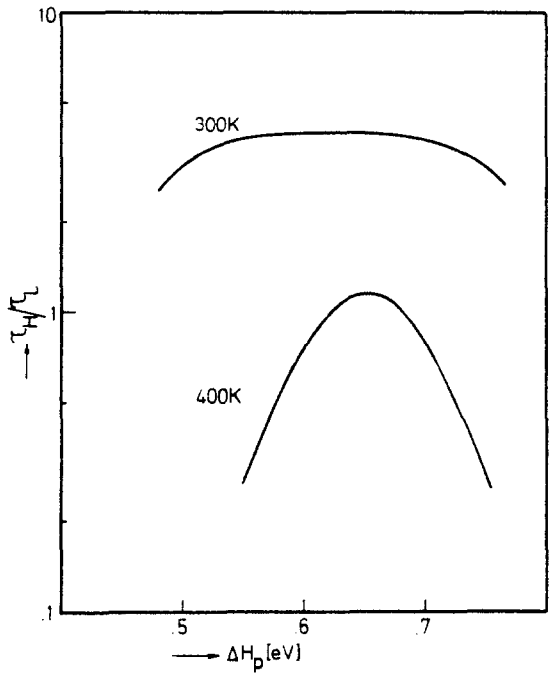

Fig. 5. High level to low level lifetime of a coupled double level center as a function of the enthalpy distance from the valence band to the two electron level. Parameter values for the capture rates and the one electron enthalpy position of the gold center in silicon have been used.

kind of experiments the theoretical results are compared. When energy levels are measured optically by the extrapolation of photoionization cross sections[19] the energy values obtained are free enthalpies[5]. Often the energy level values for deep impurities in silicon found in the literature are determined from thermal activation plots, giving the enthalpies[5]. It is therefore interesting to note that the difference in magnitude between the two quantities might be considerable. Regarding the optimal free enthalpy position G_T and the optimal enthalpy position H_T of a single level which can be found by maximizing the ratio τ_H/τ_L from eqns (23) and (24) one finds

$$G_T = \mu_i + \frac{kT}{2} \ln \zeta \tag{28}$$

and

$$H_T = \mu_i + \frac{kT}{2} \ln\left(\frac{X_p}{X_n}\zeta\right) \tag{29}$$

where μ_i is the intrinsic chemical potential for electrons. The difference $H_T - G_T$ is equal to $\frac{kT}{2}\ln(X_p/X_n)$, which for a reasonable value of $X_p/X_n = 20$ at 400 K approaches 0.1 eV.

Two points are left to emphasize in connection with thermal measurements. The first point is that also the enthalpy is temperature dependent[9] and related to the free enthalpy by

$$\Delta G = \Delta H + \frac{\partial \Delta G}{\partial T} \cdot T. \tag{30}$$

Experimental values of ΔH are therefore mean values of the linearly extrapolated values of ΔG to $T = 0$ K. The value of ΔH therefore depends on the temperature range in which the measurement is made.

The second point is that the slope in an activation plot of thermal emission rates is influenced by the temperature dependence of the capture rates[15]. For a thorough determination of optimal recombination centers these temperature dependences must be known. The number of different impurities in silicon for which all these optical and thermal parameters are experimentally determined is to the best of our knowledge limited to one, the gold center. In Table 2 of Ref. [2], "energy levels" and capture cross sections are given without specifying whether one has to deal with enthalpies or free enthalpies, and also without the temperature dependences of capture cross sections and the degeneracies. The use of this table might therefore lead to wrong conclusions when trying to find an optimal recombination center for high power thyristors. When searching for parameter values giving the optimal recombination center it is thus of importance whether the values are determined optically or from thermal activation plots. In the first case one needs the free enthalpy at a given temperature together with its temperature dependence and the capture rates and their temperature dependences. In the second case one needs the enthalpy together with the factors X_p and X_n the capture rates, and their temperature dependences. These two treatments are equivalent.

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