

STUDY OF SOME ADDITIONAL POSSIBILITIES AND OF THE EVALUATION LIMITS OF THE DARK CURRENT SPECTROSCOPY (DCS) METHOD

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Abstract. *The basic goal of this work is to explore the possibilities and limits of the computational approach of the dark current spectroscopy method (DCS) to characterize the traps and impurities from the pixels of Charge Coupled Devices. In this aim, the experimentally measured dark current and their associated standard deviations for 8 temperatures and 20 randomly chosen pixels were studied starting from the rigorous quantum theoretical model of Shockley-Read-Hall. Besides the modulus $|E_t - E_i|$ of the difference of the trap and intrinsic Fermi level energies, the polarization degree (pdg) of the capture cross-sections of free electrons and holes, respectively, was defined by this work and used as a second uniqueness parameter intended to the traps identification. The proposed assignments of the $|E_t - E_i|$ and pdg numerical results to certain traps and impurities are based on the specialty literature data and on some special properties of the manganese complexes, particularly.*

Keywords: Charge Coupled Devices, Diffusion and Depletion Dark Current, Intrinsic Fermi level, Deep Traps Energies in Silicon, Capture Cross-Sections of electrons and holes

1. Introduction

As it is well-known, the main goal of the Dark Current Spectroscopy (DCS) is to characterize the impurities and/or defects present in the crystalline lattices of some semiconductor devices, as the Charge-Coupled Devices (CCDs) [1], [2], the semiconductor solar cells [3] etc., starting from the temperature dependence of their dark current. Taking into account the complex character of semi-conductors, they are described by a huge number of uniqueness parameters. In fact, the existing non-negligible measurement errors allow accurate evaluations only for few dominant uniqueness parameters, specific to the physical processes characteristic to a certain experimental method. For this reason, the achievement of some sufficiently complete physical characterizations of the impurities and/or defects of a semi-conductor lattice requires the use of two or more complementary measurement methods.

Or, the systematic study of the implications of the measurement errors on the characterization possibilities of impurities and/or defects of each experimental method, hence of its limits, is unfortunately practically completely missing.

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Given being the above findings, the main goals of the present work are to study systematically the: *a)* implications of the measurement errors referring to the: *(i)* number of uniqueness parameters which can be accurately evaluated by the DCS method, and to point out: *(ii)* the corresponding dominant uniqueness parameters, *(iii)* the additional characterization possibilities and the limits of this experimental method, *b)* other existing main characterization methods, in order to identify the procedures which can be complementary to the DCS method.

2. Theoretical Part (the Main Sources of Dark Current)

The most important sources of dark current in semiconductors are [1], pp. 605-648, [2], pp. 37-45: *a)* the field-free regions (diffusion and substrate¹) dark current, *b)* the depletion (or bulk) dark current generated in the depletion region, and: *c)* the surface dark current generated at the Si-SiO₂ interface. If the CCD is operated in a multi-pinned phase (MPP) mode, then the interface is completely inverted with a high hole carrier concentration, hence the surface dark current from the Si-SiO₂ interface will be almost completely suppressed. The analysis of the field-free regions (diffusion and substrate) and depletion dark current, respectively was achieved in the frame of various books on semiconductors, the more important being those of Grove [4] and Sze [5].

2.1. The field-free regions (diffusion and substrate) dark current

Starting from the basic works [4], [5], the problem of the temperature dependence of the diffusion dark current was examined thoroughly in the frame of works [6], being derived the expression:

$$De_{diff}^{-}(T) = De_{0,diff}^{-} \cdot T^3 \exp\left(-\frac{E_g}{kT}\right) \quad (1)$$

where the field-free regions pre-exponential factor is given by the relation:

$$D_{0,ffr}^{-} = \frac{D_{eff} \cdot A_{pix} \cdot c_n^2}{x_{eff} \cdot N_A} \quad (2)$$

The parameters implied in the above expression (2) have the following physical meanings: D_{eff} and x_{eff} are the effective (taking into account both effects of diffusion and Auger re-combination) the diffusion coefficient and characteristic length, respectively, N_A is the concentration of the acceptor impurities, A_{pix} is the area of a pixel, while:

$$c_n = 2 \left(\frac{2\pi k}{h^2} \right)^{3/2} \cdot m_e^{3/4} \cdot m_h^{3/4} \quad (3)$$

¹Dominant for very heavily doped ($\geq 10^{17}$ cm⁻³) semiconductors.

2.2. The depletion dark current

According to the rigorous theoretical model [7], the contribution of the depletion processes to the dark current is given by the expression:

$$De_{SRH}^- = -\frac{x_{dep} \cdot n_i^2 \cdot A_{pix}}{U}, \quad (4)$$

where the net generation-recombination rate U corresponding to the impurities and/or imperfections of the semiconductor lattice is described by the relation¹

$$U = \frac{\sigma_p \sigma_n V_{th} (n \cdot p - n_i^2) N_t}{\sigma_n \left[n + n_i \exp\left(\frac{E_t - E_i}{kT}\right) \right] + \sigma_p \left[n + n_i \exp\left(\frac{E_i - E_t}{kT}\right) \right]} \quad (5)$$

In the above expression, σ_p, σ_n are the capture cross-sections for holes and electrons, respectively, V_{th} is the thermal velocity, E_i is the intrinsic Fermi energy level, N_t is the concentration of traps, i.e. of bulk generation-recombination centers at the energy level E_t , while n, p , and n_i are the electrons, the holes and the intrinsic carrier concentration, respectively, given by the expressions:

$$n = 2 \left(\frac{2\pi \cdot m_n kT}{h^2} \right)^{3/2} \exp \frac{\mu - E_c}{kT}, \quad p = 2 \left(\frac{2\pi \cdot m_p kT}{h^2} \right)^{3/2} \exp \frac{E_v - \mu}{kT} \quad (6)$$

$$n_i = 2 \left(\frac{2\pi \sqrt{m_n m_p} \cdot kT}{h^2} \right)^{3/2} \cdot \exp \left(-\frac{E_g}{2kT} \right) = c_n(T) \cdot T^{3/2} \cdot \exp \left(-\frac{E_g}{2kT} \right) \quad (6')$$

where m_n, m_p are the effective masses of the free electrons and holes, respectively, E_c, E_v, μ , and E_g are the lower/higher threshold of the conduction/valence band, respectively, the electrochemical potential and the energy gap of the considered semiconductor, respectively, which are also temperature dependent. One finds that the expression (5) is symmetrical relative to the permutation $n, \sigma_n, E_t - E_i \leftrightarrow p, \sigma_p, E_i - E_t$, which leads to the DCS possibility to evaluate $|E_t - E_i|, |\ln \sigma_n / \sigma_p|$, etc, but not of the absolute values $E_t - E_i, \sigma_n, \sigma_p$ etc. without additional elements given by other experimental methods.

¹At thermal equilibrium: $n \cdot p = n_i^2$, hence $U_{dep} = 0$ (the recombination and generation rates being then equal).

3. Numerical Modeling

From relations (1)-(6'), it results that the numerical description of the temperature dependence of the dark current in CCDs requires a huge number of uniqueness parameters: $D_n, x_c, A_{pix}, N_A, m_e, m_h, E_g, x_{dep}, n_i, \sigma_p, \sigma_n, V_{th}, N_t, n, p, |E_t - E_i|$ etc, many of them [e.g. n, p, n_i , etc, as it results from relations (7), (7')] being also temperature dependent, hence introducing some additional uniqueness parameters [as μ, E_c, E_v etc. which are also temperature dependent, implying other uniqueness parameters, and so on]. We have to underline that it is necessary to use also some additional relations expressing e.g.: *a)* the effective diffusion coefficient D_{eff} and the characteristic length x_{eff} in terms of the parameters of the diffusion and Auger processes, respectively; *b)* the temperature dependence of the energy gap E_g by means of the rather intricate expression: $E_g = E_{g0} - \alpha T^2 / (T + \beta)$, with still discussed values of the parameters E_{g0}, α, β even for the pure Si:

$$E_{g0} \cong 1.17 \text{ eV}, \alpha \cong 4.73 \cdot 10^{-4} \text{ K}^{-2}, \beta \cong 636 \text{ K} \quad [5], \quad (7)$$

$$E_{g0} \cong 1.1557 \text{ eV}, \alpha \cong 7.021 \cdot 10^{-4} \text{ K}^{-2}, \beta \cong 1108 \text{ K} \quad [8]. \quad (7')$$

One finds so that the description of the temperature dependence of the dark current in CCDs requires also: *(i)* some simplifications of the rigorous quantum mechanics Shockley-Read-Hall model, *(ii)* some numerical descriptions of the temperature dependence of some uniqueness parameters (as the energy gap E_g), *(iii)* an ordering of the uniqueness parameters upon their influence on the dark current values and a convenient choice of a limited number of uniqueness parameters, which can describe accurately the dark current in CCDs.

3.1. The approximation of the completely depleted zone

Assuming that in the depletion zone, the electric field sweeps the holes to the p -substrate and the electrons to the potential wells, hence (in this region): $n, p \ll n_i^2$, the temperature dependence of the depletion dark current will be described by the expression [see relations (4) and (5)]:

$$De_{dep}^- = De_{0,dep}^- \cdot T^{3/2} \cdot \exp\left(-\frac{E_g}{2kT}\right) \cdot \text{sech}\left[\frac{E_t - E_i}{kT} + d\right] \quad (8)$$

where the depletion pre-exponential factor is given by the expression:

$$De_{0,dep}^- = \frac{x_{dep} A_{pix} c_n \sqrt{\sigma_p \sigma_n} \cdot V_{th} N_t}{2} \quad (8')$$

and “the polarization degree” d of the capture cross-sections for electrons and holes, respectively, is:

$$d = \arg \tanh \left(\frac{\sigma_n - \sigma_p}{\sigma_n + \sigma_p} \right) \quad (9)$$

Taking into account the possible concomitant presence of different traps j in each pixel, the previous expression (9) becomes:

$$De_{dep}^- = T^{3/2} \cdot \exp \left(-\frac{E_g}{2kT} \right) \cdot \sum_j De_{0,dep,j}^- \operatorname{sech} \left[\frac{E_{ij} - E_i}{kT} + d_j \right] = De_{0,dep,eff}^- \cdot T^{3/2} \cdot \exp \left(-\frac{E_g}{2kT} \right) \cdot \operatorname{sech} \left[\frac{E_{t,eff} - E_i}{kT} + d_{eff} \right]$$

where $De_{0,dep,eff}^-$, $E_{t,eff}$ and d_{eff} are the effective pre-exponential factor, trap energy and polarization degree of e^- , h capture cross-sections, corresponding to the considered pixel.

Assuming equal capture cross-sections for holes and electrons, hence a null polarization degree, the expression of the temperature dependence of the depletion dark current becomes:

$$De_{dep}^- = De_{0,dep,eff}^- \cdot T^{3/2} \cdot \exp \left(-\frac{E_g}{2kT} \right) \cdot \operatorname{sech} \left[\frac{E_{t,eff} - E_i}{kT} \right] \quad (10)$$

Because the temperature dependence of all physical parameters of the pre-exponential factor seems to be very weak (in comparison with the exponential dependence of the last 2 factors, especially), we can assume that the temperature dependence of the depletion dark current is due mainly to the last 3 factors of expression (10).

3.2. Choice of the uniqueness parameters

From relations (1) and (8), it results that the most suitable expression of the temperature dependence of the dark current in CCDs is given by the following relation:

$$De^-(T) = De_{diff}^-(T) + De_{dep}^-(T) = T^3 \exp \left(\ln De_{o,diff}^- - \frac{E_g}{kT} \right) + T^{3/2} \cdot \exp \left(\ln De_{o,dep}^- - \frac{E_g}{2kT} \right) \cdot \operatorname{sech} \left[\frac{E_i - E_t}{kT} + d \right] \quad (11)$$

The detailed analysis accomplished in the frame of works [13] pointed out that the most convenient choice of the uniqueness parameters corresponds to the order:

- a) $\ln De_{0,diff}^-$, $\ln De_{0,dep}^-$ (logarithms of the pre-exponential factors of the diffusion and depletion current, respectively) and E_g [the effective (temperature averaged) energy gap],
- b) the difference $E_t - E_i$ of the energies of the trap and of the intrinsic Fermi level, respectively, or its modulus $|E_t - E_i|$ [when the fitting relation (10) is used],
- c) the depolarization degree d of the capture cross-sections of electrons and holes, respectively, given by relation (9),
- d) the Varshni-Sze [8], [5] parameters (E_{g0} , α , β) of the temperature dependence of the energy gap.

A synthesis of the main features of the basic versions of the DCS method is presented by Table 1.

4. Main Implications of the Measurement Errors

Unlike the pure theoretical (“mathematical”) evaluation problems, where the researchers are concerned only by the obtainment of the least squares (“regression”) representation of the experimental data by means of a given (studied) function, in the frame of the physical evaluation problems the measurement errors affecting each experimental result achieve in fact the modeling of the considered evaluation study.

E.g., if the measurement errors are rather small¹ there appear some incompatibilities of the used theoretical model relative to certain experimental data [9c], which will lead to instabilities or pseudo-convergence of the evaluation process [13].

Conversely, for too large measurement errors the effects of many uniqueness parameters will be “hidden” (covered by errors). In fact, for certain given measurement errors, the best evaluation model has to be identified by a suitable choice of the number and nature of the representative (dominant) uniqueness parameters.

In order to apply these considerations to the DCS characterization of impurities and defects, the experimental results referring to the dark current and its corresponding standard deviation (error) for a set of 20 randomly chosen pixels of a CCD housed by the Spectra Video camera SC512V1 [6a], at 8 temperatures between 222 and 291 K, were reported and examined in the frame of works [13].

¹For extremely small measurement errors, the most theoretical models will be rejected, because the majority of the corresponding tiny confidence domains will not be crossed by the least-squares (regression) plot.

Table 1. Comparison of the main versions of the classical and computational approach of the Dark Current Spectroscopy (DCS) method

The DCS method version	Input Data	Accepted approximations	Basic expression(s)	Main evaluated parameter
1. Classical DCS method (CIDCS) a) McGrath [10a] b) McColgin [10b-e] c) Webster [10f]	<u>Histogram</u> : number of pixels vs dark current [10a]	Deep-depletion mode: $n, p \ll n_i$ Equal cross-sections: $\sigma_n = \sigma_p$	$j_{dark} = \frac{\sqrt{\sigma_n \sigma_p} \cdot V_{th} n_i n_t q W}{2}$	The average cross-section $\sigma \equiv \sigma_{ave} = \sqrt{\sigma_n \sigma_p}$
	Temperature dependence of the dark current [10d]	Deep-depletion mode: $n, p \ll n_i$ $ E_t - E_i \ll kT$	$j_d \propto \exp\left[-\frac{ E_t - E_i }{kT}\right]$	$ E_t - E_i $
	Traps concentration (n_t) and carrier velocity (V_{th}) from other methods [10c]	Deep-depletion mode: $n, p \ll n_i$ Equal cross-sections: $\sigma_n = \sigma_p$	$\frac{\Delta N_c}{\Delta t} = \frac{1}{\tau} = V_{th} \cdot \sigma \cdot n_t$	The generation (emission) rate, e^-/s , $e \equiv \frac{\Delta N_c}{\Delta t} = \frac{1}{\tau}$
	Temperature dependence of the generation (emission) rate [10f]	Validity of the Arrhenius equation	$\frac{\Delta N_c}{\Delta t} = \frac{1}{\tau} \equiv k = A \cdot \exp\left(-\frac{E_a}{kT}\right)$	The activation energy, E_a
2. Computational DCS approach (CA-DCS) a) Widenhorn-Bodegom [6a, b] b) & Iordache [12] c) & Tunaru [13]	Temperature dependence of the dark current [6a,b]	$n, p \ll n_i, \sigma_n = \sigma_p$ Very deep-level traps: $ E_t - E_i \ll kT$	$j_d = D_{o,diff} T^3 \exp\left(-\frac{E_g}{kT}\right) + D_{o,dep} T^{3/2} \exp\left(-\frac{E_g}{2kT}\right)$	The pre-exponential factors $D_{o,diff}; D_{o,dep} \rightarrow n_t$
	Idem and Arrhenius pre-exponential factor dependence on the activation energy [9], [11], [12]	The validity of the Arrhenius and Meyer-Neldel relations	$j_d = D_o \exp\left(-\frac{\Delta E}{kT}\right)$ $D_o = D_{oo} \exp\left(\frac{\Delta E}{E_{MN}}\right)$	The Meyer-Neldel energy E_{MN} and the pre-exponential factor D_{oo}
	The temperature dependence of the energy gap E_g [8], [5]	Negligible effect on dark current of $E_g = f(T)$, relative to those of $ E_t - E_i $ and even of $d = \arg \tanh \frac{\sigma_n - \sigma_p}{\sigma_n + \sigma_p}$ and $n, p \ll n_i$	$j_{d,dep} = D_{o,dep} T^{3/2} \exp\left(-\frac{E_g}{2kT}\right) \cdot \operatorname{sech}\left[\frac{ E_t - E_i }{kT} + d\right]$	$D_{o,diff}, D_{o,dep}, E_g$ (effective parameter), $ E_t - E_i $ and $d \rightarrow \sigma_n, \sigma_p$
	Results concerning $D_{o,diff}, D_{o,dep}, E_g$ (effective parameter), $ E_t - E_i $ and d [13]	Idem	Single or double linear co-relations between some effective parameters	Correlations coefficients, <u>High</u> : $\ln D_{o,diff} = f(E_g),$ $\ln D_{o,dep} = f(E_t - E_i)$ <u>Medium values</u> : $\ln D_{o,dep} = f(E_g),$ <u>Low values</u> : $\ln D_{Arrh} = f(E_g)$

4.1. Implications of the Measurement Errors on the Compatibility of the Theoretical Model relative to the Experimental Data (CTM/ED)

Table 2 synthesizes the: *a)* average relative measurement errors for the 8 studied temperatures, *b)* corresponding CTM/ED or incompatibility, as well as the lowest values of some average relative measurement errors able to ensure the compatibility.

Table 2. Average relative measurement errors (ARME) for the 8 studied temperatures [13] and the corresponding CTM/ED or incompatibility

Temperature (K)	222	232	242	252	262	271	281	291
ARME	35.85%	9.45%	3.53%	1.03%	0.486%	0.233%	0.233%	0.297%
CTM/ED or incompatibility	CTM/ED	CTM/ED	CTM/ED	CTM/ED for 60% of pixels	CTM/ED for 25% of pixels	CTM/ED for only 5% pixels	CTM/ED for only 5% pixels	CTM/ED for 65% of pixels
Lowest ARME value to ensure CTM/ED	Not necessary changes	Not necessary changes	Not necessary changes	1.12%	0.71%	0.71%	0.81%	0.37%

The analysis of the results reported by Table 2 (see also [9c], [13]) points out that:

a) the studied theoretical model (10) is compatible with 57.5% of experimental data,

b) the necessary corrections in order to re-establish the compatibility for the other experimental data are not too large, for the temperatures of 252, 262 and 291 K, especially,

c) the experimental standard errors for the temperatures 271 and 281 K (where the necessary changes are rather large) are in obvious disagreement with those for the neighbor temperatures (262 and 291 K).

One finds so that: *(i)* the studied theoretical model [expressed by relation (10)] is compatible with the obtained experimental data, *(ii)* some of the reported standard errors (involving even some discontinuities) were too optimistically estimated and can be corrected to ensure a general CTM/ED.

4.2. Implications on the choice of the representative uniqueness parameters

In order to complete the results of section 3.2 with the implications of the measurement errors on the choice of the best set of uniqueness parameters (hence of the theoretical model used to describe the studied experimental data), Table 3 reports the obtained results concerning the numbers of pixels whose experimental data [13] lead to instabilities or pseudo-convergence (attractor values without physical meaning) of the evaluation process.

Table 3. Results concerning the behavior (right attractor, or instability and pseudo-convergence, respectively) of the evaluation process for 3 choices of uniqueness parameters

Obtained results	Simplifying assumptions		
	$n, p \ll n_i, \sigma_n = \sigma_p$ $ E_t - E_i \ll kT$	$n, p \ll n_i$ $ E_t - E_i \ll kT$	$n, p \ll n_i$
The evaluated uniqueness parameters	$\ln D_{0,diff}^-, \ln D_{0,dep}^-, E_g$	$\ln D_{0,diff}^-, \ln D_{0,dep}^-, E_g$ and $ E_t - E_i $	$\ln D_{0,diff}^-, \ln D_{0,dep}^-, E_g$ $ E_t - E_i $ and d
Number of pixels data leading to instability or pseudo-convergence	0+1 pseudo-convergence (5%)	1 instability+1 pseudo-convergence (10%)	3 instability+2 pseudo-convergence (25%)
Average relative error for the highest 6 temperatures, %	2.722 %	2.361 %	-
Average relative error for all 8 temperatures	-	5.92 %	4.48 %

The examination of results synthesized by Table 3 points out that while the description accuracy is weakly improving for a larger number of evaluated uniqueness parameters, the evaluation process becomes considerably worse, due to the additional restrictions introduced by each new evaluation. Taking into account that for the evaluation of the 5 uniqueness parameters with the strongest influence on the dark current at different temperatures, already 25% of experimental data were lost due to the numerical phenomena of instability and pseudo-convergence, it results that the evaluation of the following 3 uniqueness parameters (the Varshni-Sze ones: E_{g0}, α, β) has to be postponed up to the achievement of considerably more accurate experimental measurements.

4.3. Evaluation of the effective (averaged over the 222÷291 K interval) energy gap

In order to achieve the assignment of the calculated values of $|E_t - E_i|$ for each pixel to some impurities or complexes, it is necessary to start from the evaluation of the effective (averaged for the considered temperature interval: 222÷291 K) energy gap. Together with the corresponding stability diameters, Table 4 reports the obtained results (by means of computational methods indicated by the monograph [14]) concerning this effective energy gap.

Eliminating the obviously erroneous (due to a local pseudo-convergence) value 1.19 eV for pixel 31, 247, from the examination of Table 4 it results that the (222÷291 K averaged) effective energy gap in silicon is $E_g \cong 1.08$ eV, in agreement with the results of work [10a].

Table 4. Obtained results concerning the: a) effective parameters of the semiconductor material (Si with different impurities), b) the stability diameters around the representative point of the “central” zero-order approximations*, starting from the temperature dependence of the dark current for 20 randomly selected pixels

Coordinates of the considered pixel	The effective value of the parameter (the “attractor coordinate”) The extreme values of the stability diameter along this parameter*			
	lnDiff	lnDep	E_g (eV)/ m ($m = 10 \times \frac{E_{gD} - E_{gAve}}{E_{gSze} - E_{gAve}}$)	$ E_t - E_i $, meV
41, 120	Instability			
61, 140	<u>31.079047</u> 27 ... 54	<u>17.524259</u> 15 ... 36	<u>1.072556 eV</u> $m = -6 ... +4$	<u>28.92 meV</u> 2 ... 169 meV
81, 160	<u>31.119436</u> 28 ... 56	<u>16.276704</u> 16 ... 35	<u>1.073807 eV</u> $m = -8 ... +4$	<u>17.0 meV</u> 3 ... 146 meV
101, 180	<u>31.353146</u> 28 ... 55	<u>15.706546</u> 15 ... 36	<u>1.079606 eV</u> $m = -8 ... +4$	<u>12.77 meV</u> 3 ... 145 meV
121, 200	<u>30.867372</u> 28 ... 55	<u>15.611681</u> 17 ... 35	<u>1.067257 eV</u> $m = -10 ... +2$	<u>13.23 meV</u> 0.9...137 meV
141, 220	<u>31.152358</u> 27 ... 54	<u>15.684044</u> 14 ... 36	<u>1.074538 eV</u> $m = -10 ... +4$	<u>12.96 meV</u> 3 ... 151 meV
161, 240	<u>32.355596</u> 28 ... 55	<u>19.409546</u> 17 ... 34	<u>1.105744 eV</u> $m = -6 ... +8$	<u>45.41 meV</u> 1 ... 188 meV
181, 260	<u>31.175348</u> 28 ... 54	<u>15.508352</u> 16 ... 34	<u>1.075505 eV</u> $m = -10 ... +4$	<u>12.48 meV</u> 1 ... 144 meV
201, 280	<u>31.072543</u> 27 ... 55	<u>16.904658</u> 15 ... 37	<u>1.071989 eV</u> $m = -6 ... +2$	<u>16.98 meV</u> 2 ... 155 meV
221, 300	<u>30.627558</u> 27 ... 54	<u>16.588115</u> 15 ... 37	<u>1.061095 eV</u> $m = -10 ... +4$	<u>19.14 meV</u> 2 ... 155 meV
241, 320	<u>31.203713</u> 28 ... 54	<u>15.338220</u> 17 ... 37	<u>1.075681 eV</u> $m = -10 ... +2$	<u>6.8 meV</u> 0.64...134meV
261, 340	<u>31.768681</u> 28 ... 53	<u>18.476570</u> 16 ... 34	<u>1.090382 eV</u> $m = -4 ... +8$	<u>30.22 meV</u> 2 ... 149 meV
281, 360	<u>31.117528</u> 27 ... 55	<u>18.011161</u> 16 ... 35	<u>1.073652 eV</u> $m = -10 ... +4$	<u>27.51 meV</u> 3 ... 164 meV
301, 380	<u>30.193521</u> 27 ... 53	<u>15.793308</u> 17 ... 33	<u>1.048424 eV</u> $m = -10 ... +2$	<u>11.58 meV</u> 2 ... 137 meV
321, 400	<u>31.241897</u> 28 ... 55	<u>14.748118</u> 14 ... 34	<u>1.076446 eV</u> $m = -8 ... +6$	<u>18.21 meV</u> 3 ... 160 meV
341, 420	<u>33.174582</u> 28 ... 56	<u>19.353229</u> 16 ... 33	<u>1.126693 eV</u> $m = -6 ... +4$	<u>30.77 meV</u> 1 ... 181 meV
31, 247	<u>35.635528</u> 27 ... 53	<u>19.859227</u> 17 ... 32	<u>1.190169 eV</u> $m = -6 ... +6$	<u>10.3 meV</u> 3 ... 180 meV
29, 88	<u>31.261229</u> 28 ... 54	<u>17.285039</u> 15 ... 35	<u>1.077355 eV</u> $m = -10 ... +4$	<u>24.15 meV</u> 3 ... 155 meV
188, 471	<u>31.097239</u> 28 ... 55	<u>16.070513</u> 15 ... 32	<u>1.071933 eV</u> $m = -10 ... +6$	<u>22.05 meV</u> 0.6 ... 151 meV
161, 289	<u>31.838808</u> 32 ... 57	<u>14.588399</u> 18 ... 30	<u>1.092433 eV</u> $m = -11 ... +10$	<u>28.36 meV</u> 3 ... 130 meV

*The values $\ln\text{Diff} = 34.9$, $\ln\text{Dep} = 19$ [3b], $m = 0$, $|E_t - E_i| = 100$ meV were considered as “central”. To determine the stability diameters, only one zero-order approximation is changed, the others remaining equal to the “central” values.

5. Study of the possibilities of identification of the impurities and/or defects embedded in the semiconductor crystalline lattice

5.1. Main characteristic parameters of the impurities and/or defects

The main characteristic parameters of the impurities and/or defects embedded in the forbidden band of a semiconductor are:

a) *the capture cross-sections of the free electrons σ_n and holes σ_p by the different types of traps, or their geometrical average: $\sigma_{ave} \equiv \sigma = \sqrt{\sigma_n \sigma_p}$ [10a] or the*

corresponding polarization degree: $d = \arg \tanh \left(\frac{\sigma_n - \sigma_p}{\sigma_n + \sigma_p} \right)$,

b) *different (and related) generation rates of the charge carriers:*

(i) *the emission rate, defined by the classical expression of the number of captures (through collisions) in the time unit, in terms of the mean thermal velocity V_{th} and the considered traps type concentration n_t in the volume unit:*

$$e = \frac{\Delta N}{\Delta t} = V_{th} \cdot \sigma_{em} \cdot n_t = \frac{V_{th} \cdot \sigma \cdot N_b}{g} \cdot \exp\left(-\frac{\Delta E}{kT}\right), \quad (12)$$

where N_b is the effective density of states at the border of the of the respective carriers band, g is the degeneracy of the trap level, while ΔE is the energy separation (the so-called *activation energy*) between the trap level and the border of the corresponding carriers band,

(ii) *the generation rate given by 1 trap in a cm^3 , defined as:*

$$r = \frac{e}{n_t} = \frac{1}{n_t} \cdot \frac{\Delta N}{\Delta t} = V_{th} \cdot \sigma, \quad (13)$$

with distinct values for the generation by one free electron capture (r_n) or by one hole capture (r_p),

(iii) *the emission time, defined as:*

$$\tau = \frac{1}{e} = \frac{g}{V_{th} \cdot \sigma \cdot N_b} \cdot \exp\left(\frac{\Delta E}{kT}\right), \quad (14)$$

c) *the energy level, given by its absolute value: $E_v + E_a$ or $E_c - E_a$ in terms of the energies corresponding to the upper/lower thresholds of the valence/conduction band and the activation energy, respectively, or by the modulus $|E_t - E_i|$ of the distance from the considered trap to the intrinsic Fermi level [taking into account we have chosen the value $E_g \approx 1.08$ eV for the effective (averaged on the temperature interval 222÷291 K) energy gap, we used the value $E_i \approx 0.54$ eV].*

5.2. Evaluation of the Polarization Degree of the Capture Cross-sections of free electrons and holes, respectively

As it was found [see e.g. relation (10)], the polarization degree d of the capture cross-sections of the free electrons and holes, respectively, intervenes in the expression of the depletion dark current, which is prevalent at low temperatures.

For this reason, even if the low temperatures dark currents are considerably weaker (hence, their use implies considerably higher errors) than those corresponding to higher temperatures, the evaluation of the polarization degree imposes the use of the dark current for all 8 studied temperatures.

Starting from the evaluated values of the logarithms of pre-exponential factors corresponding to the diffusion $\ln Diff$ and depletion $\ln Dep$ dark current, respectively, as well as from the evaluated effective energy gap E_g , it is evaluated also the last factor of the expression (10):

$$Fact = \operatorname{sech} \left[\frac{E_{t,eff} - E_i}{kT} + d_{eff} \right] \quad (15)$$

for all 8 studied temperatures.

In following, are determined the slope

$$\frac{E_t - E_i}{k}$$

and the intercept d of the least squares (regression) straight-line:

$$\arg \operatorname{sech}(Fact) = F \left(\frac{1}{T} \right),$$

as well as the correlation coefficient corresponding to this regression line.

5.3. Numerical results

The obtained results, as well as the corresponding description errors were synthesized in the frame of Table 5.

As it can be found easily, the description achieved by means of the 5 uniqueness parameters $\ln Diff$, $\ln Dep$, E_g , $|E_t - E_i|$ and d is considerably more accurate than that which neglects the “polarization” of the capture cross-sections, even if this evaluation is obliged to use also the weakest (hence, the most inaccurate) dark current (those at the lowest temperatures).

Table 5. Synthesis of the obtained results concerning the evaluations of the polarization degree (pdg) of the capture cross-sections of the free electrons and holes, respectively, for the 18 pixels whose dark current values ensure both the stability and the physical convergence of the successive approximations procedure

Computation version	$n, p \ll n_i$ and $\sigma_h = \sigma_n$	$\sigma_h \neq \sigma_n$, but $n, p \ll n_i$	Non-null polarization degree ($\sigma_h \neq \sigma_n$) of the capture cross-sections: $pdg = \arg th \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n} \neq 0$			
Coordinates of the pixel	Accuracy (%) in the simplifying hypotheses		Parameters of the $\arg \sec h(Fact) = F\left(\frac{1}{T}\right)$ least squares (regression) straight-line			
			Slope $\pm E_t - E_i $, meV	Intercept $\pm pdg$	Correlation Coefficient	Possible assignments
141, 220	40.984565	6.158345	8.491114	0.773062	0.209964	Au ₋ (?)
61, 140	29.835971	7.725308	35.506866	0.957512	0.791114	Mn, Co, Ni, Au ₁ , Cr-Al Pt ⁺ in n-Si
81, 160	31.684291	2.293766	33.589217	0.015198	0.833865	
101, 180	39.567260	2.453604	24.662637	0.045513	0.617421	
188, 471	12.726169	6.988253	28.043222	0.790385	0.550769	
201, 280	34.694638	1.770353	31.208078	0.117103	0.948588	
221, 300	27.815573	3.7973	28.027774	0.438159	0.820892	
321, 400	28.683876	17.46146	-30.07672	3.035967	0.23972	
121, 200	37.723976	5.297034	38.011142	-0.500201	0.735786	
301, 380	44.121581	3.002418	30.845741	-0.311215	0.79831	Pt, Fe ⁺ , Cr-Ga, E-center As-V
181, 260	41.189387	2.913412	23.866181	-0.052121	0.460874	
261, 340	54.276471	2.279811	57.224543	0.135146	0.986594	
341, 420	61.112558	2.276783	55.476258	0.259002	0.987388	
281, 360	23.007037	3.197787	45.695567	0.397229	0.961896	Mn-B and the above trap states
29, 88	3.0963128	2.472732	51.860567	-0.15476	0.957251	
161, 240	INSTABILITY					
241, 320	INSTABILITY produced by pseudo-convergence					
161, 289	INSTABILITY produced by pseudo-convergence					

One finds that, even if the use of the weakest dark current (those at the lowest temperatures, where the depletion dark current is prevalent) leads to more instability and pseudo-convergence numerical phenomena (only 14 pixels from the 20 selected ones lead to attractors with physical meaning), the studied procedure allows the evaluation of the polarization degree of the capture cross-sections of the free electrons and holes, respectively.

5.4. Basic features of the most efficient generation-recombination traps

The examination of Table 5 points out that the detected traps energy levels are less than approximately 60 meV.

In order to explain this finding, we will start from the effective generation - recombination life of electrical charge carriers in the depletion region (see e.g. [5]-[7]), defined and expressed as:

$$\tau = \frac{n_i}{2U} = \frac{x_{dep} A_{pix} n_i}{2D e^-} = \frac{\sigma_n \exp\left(\frac{E_t - E_i}{kT}\right) + \sigma_p \exp\left(\frac{E_i - E_t}{kT}\right)}{\sigma_p \sigma_n V_{th} N_t} \quad (16)$$

It is very easy to find that this effective generation-recombination life presents a sharp minimum (i.e. a maximum dark current emission) for:

$$0 = \frac{d\tau}{dE_t} = \frac{1}{\sigma_p \sigma_n V_{th} N_t} \left[\frac{\sigma_n \exp\left(\frac{E_t - E_i}{kT}\right)}{kT} - \frac{\sigma_p \exp\left(\frac{E_i - E_t}{kT}\right)}{kT} \right] \quad (17)$$

equivalent to the condition:

$$E_t = E_i + \frac{kT}{2} \ln\left(\frac{\sigma_p}{\sigma_n}\right) \quad (17')^1$$

Because in the middle of the temperature interval studied by us (≈ 260 K), we have: $\frac{kT}{2} \cong 11.2125$ meV, it results that: (i) $|E_t - E_i| / (E_g/2) \leq 0.2$, hence the most active impurities correspond to a rather deep energy levels (near to the Fermi level, i.e. they correspond to *deep-level traps*), (ii) $|E_t - E_i| / (kT/2) \cong 0.8 \div 5$, it results that the polarization degree of the capture cross-sections of holes and electrons, respectively, has to be rather large (of the magnitude order of 1). Of course, the experimentally found depletion dark current do not correspond exactly to the emission maximum, hence: a) some specific numerical calculations are necessary, but: b) the assumption on the possibility to consider the capture cross-sections of holes and electrons as equal seems to be wrong.

6. Study of the energy states corresponding to the typical traps in silicon

6.1. Main experimental methods intended to the characterization of impurities and/or defects embedded in the semiconductor crystalline lattice

The analysis [9]-[13], [15]-[18] of the experimental methods used presently to characterize the impurities and/or defects embedded in semiconductors points out that the most important ones are the:

¹From relations (17), (17'), it results also that: a) if the deep-level trap is located (slightly) above the intrinsic Fermi level, then the capture cross-sections of holes recombination will be prevail usually to those for the free electrons recombination, b) conversely, if this trap is located (slightly) below the intrinsic Fermi level, then the capture cross-section of electrons will prevail usually, but – at least, for moment – these features cannot be detected using only the temperature dependence of dark current.

a) *deep-level transient spectroscopy* (DLTS) method [16a],
b) *thermally stimulated capacitance* (TSCa, starting with the works [15d]-[15g]),
c) *electron paramagnetic resonance* (EPR) [17] and – of course:
d) the *dark current spectroscopy method* (DCS) [10], [6], [13]. In order to achieve the assignments of the traps states detected by our method (see Table 5), Table 6 presents the synthesis of the specialty literature results concerning the states whose energy position do not differ more than 75 meV from the intrinsic Fermi level position in the considered silicon semiconductor.

Table 6. Main nano-particles or nano-complexes embedded in the silicon lattice, with energy states located no more than 75 meV from the corresponding intrinsic Fermi level position*

$ E_t - E_i $, meV	Impurity or defect: its main features, used experimental methods, reference
≤ 15 meV	Au ₂ acceptor: $E_c - 0.54 \div -0.55$ eV; $\sigma_n = 0.7 \cdot 10^{-15}$ cm ² ; DLTS, DCS [15a, b], [10c] (MnB) ⁺ acceptor: $E_c - 0.55$ eV; EPR [17]
(15, 45]	Mn: $ E_t - E_i < 50$ meV; $\sigma_{ave} = \sim 10^{-15}$ cm ² ; $e = 6400$ e ⁻ /s (55°C); DCS [10e] Co, Ni: $ E_t - E_i < 30$ meV; $\sigma_{ave} = 6.6 \cdot 10^{-15}$ cm ² ; $e = 3700$ e ⁻ /s (55°C); DCS [10c, e] Au ₁ : $ E_t - E_i < 30$ meV; $\sigma_{ave} = 10^{-15}$ cm ² ; $e = 565$ e ⁻ /s (55°C); DCS [10e] (Mn ⁺ Au) ⁺ donor: $E_v + 0.57$ eV; $r_p = 3 \cdot 10^{-8}$ cm ³ /s (250 K); DLTS, TSCa [15b] Cr-Al donor: $E_v + 0.52$ eV; $r_p = 2 \cdot 10^{-9}$ cm ³ /s (240 K); DLTS [15b] Pt ⁺ in n-Si: $E_c - 0.52$ eV; $\sigma_{ave} = 6.6 \cdot 10^{-15}$ cm ² ; DLTS [16b]
(45, 75]	Pt: $ E_t - E_i = 60$ meV; $\sigma = 7 \cdot 10^{-15}$ cm ² ; DCS [10e] E-center As-V(acance) acceptor: $E_c - 0.47$ eV; DLTS [19] Fe ⁺ donor: $E_v + 0.47$ eV; DLTS [15c] Cr-Ga donor: $E_v + 0.47$ eV; $r_p = 2 \cdot 10^{-8}$ cm ³ /s (250 K); DLTS, TSCa [15c] Mn-B donor: $E_v + 0.60 \div 0.62$ eV; $r_p = 1 \cdot 10^{-14}$ cm ³ /s (90 K); DLTS [15c]

*According to our results from Table 4 and to the work [10a], we will assume that the energy corresponding to the silicon intrinsic Fermi level is: $E_i \cong 0.54$ eV.

6.2. Interpretation of the found numerical results

The main difficulties of our study correspond to the:

- (i) possible presence in each pixel of several types of traps and/or impurities, which means that the obtained values are in fact averages over the present traps/impurities,
- (ii) complexity of the used SRH theoretical model, which determines an effective character of all evaluated uniqueness parameters.

The analysis of the results presented by Table 5 points out that:

- a) the new Dark Current Spectroscopy version proposed by this work, presents the:
 - (i) *additional possibilities* of the: (*i*₁) study of the used theoretical model (Shockley-Read-Hall) compatibility with the existing experimental data, taking into account their errors, (*i*₂) evaluation of the polarization degree of capture cross-sections of free electrons and holes, respectively,
 - (ii) *limits of this method* to allow only the

determination only of the moduli $|E_t - E_i|$ and $|pdg|$, but not of the absolute values of the difference $E_t - E_i$ and polarization degree $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$, respectively;

b) due to the different possibilities of each experimental method – an accurate characterization of the traps states require the use of at least 2 different, but complementary experimental methods, the first envisaged one being that of the deep-level transient spectroscopy (DLTS), which allows also the determination of the sign of the difference $E_t - E_i$;

c) unfortunately, these DCS and DLTS methods have different basic assumptions: (i) the DCS method [10]-[13] refers to the truly deep-level traps, whose distance from the intrinsic Fermi level is not larger than 60 meV, usually, and to the capture cross-sections referring to the free electrons and holes *recombination* [7a, b] which have – in these circumstances – the same magnitude order, being possible to assume sometimes [6a] their equality: $\sigma_{n,rec} = \sigma_{p,rec}$, (ii) the DLTS method [16], [15], [18] refers in fact to the: (ii₁) forbidden band odd quarters (semi-)deep level traps, when $|E_t - E_i| \gg kT$, hence one of the recombination cross-sections is much larger than the other: $\sigma_{n,rec} \gg \sigma_{p,rec}$, or conversely, (ii₂) *emission* cross-sections [see relation (15)] after the recombination in the electron ($e_n \gg e_p$) or in the hole ($e_p \gg e_n$) traps, for the majority and minority carriers, respectively;

d) among the 15 pixels (from the total of 20 studied ones) whose experimental data were sufficiently accurate to evaluate the parameters $|E_t - E_i|$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$, not less than 5 ones (33.3%) had opposite signs of the slope

and intercept of the regression line $\arg \sec h(Fact) = F\left(\frac{1}{T}\right)$, hence opposite signs of the

parameters $E_t - E_i$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$, relative to relation (17');

e) because from the studied traps, some of the manganese impurities and complexes have the same “donor” character both in the bottom and the top part of the forbidden band: (i) $Mn^{+/++}$: $E_v + 0.25$ eV, EPR [17], (ii) Mn^{++} : $E_v + 0.30$ eV, (iii) Mn^+Au^- donor: $E_v + 0.57$ eV; $r_p = 3 \cdot 10^{-8} \text{ cm}^3/\text{s}$ (250 K); DLTS, TSCa [15b]; (iv) Mn-B: $+0.62$ eV, $r_p = 8 \cdot 10^{-14} \text{ cm}^3/\text{s}$ (90 K) DLTS, TSCa [15c], (v) Mn-Al: $+0.72$ eV, $r_p = 2 \cdot 10^{-10} \text{ cm}^3/\text{s}$ (90 K) DLTS [15c], (vi) Mn-Ga: $+0.76$ eV, $r_p = 10^{-11} \text{ cm}^3/\text{s}$ (90 K) DLTS [15c], the only one different complex identified with the same behavior being that of: (vii) n-GaAs: $+0.76$ eV, DLTS [16a], fig. 8, it seems that some of the above indicated manganese traps prevail in the content of pixels with different signs

of parameters $E_t - E_i$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$;

f) taking into account that the average number of impurities in the frame of one pixel of the studied Spectra-Video camera model SV512V1 was about 10 [6a], it results that: *(i)* the values of the parameters indicated by Table 5 are averages over (possibly) several different types of traps, *(ii)* the different opposite values of the polarization degree of the recombination capture cross-sections correspond to different contents of the prevailing manganese impurities and/or complexes mixed with the other “normal” (with the same sign of parameters $E_t - E_i$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$) traps characterized by values of the $|E_t - E_i|$ and $|pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}|$ in the same interval.

7. Assignment possibilities of the detected traps energy levels

Starting from the above indicated findings, the 15 pixels sufficiently accurate described experimentally to allow the evaluation of all 5 uniqueness parameters were divided in 5 groups, depending on the: *a)* interval of their $|E_t - E_i|$ values, *(b)* relative signs of parameters $E_t - E_i$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$.

Using the experimental data synthesized by Table 6, the possible assignments of the experimentally observed (by means of our computational approach of the DCS method) dark current temperature dependencies for the studied pixels were registered in the frame of the last column of Table 5.

One finds that for the sensitivity interval of our DCS version ($|E_t - E_i| < 75 \text{ meV}$), the intervening nano-impurities or defects (atoms, ions or complexes) belong mainly to the 6B (Cr), 7B (Mn), 8B (Fe, Co, Ni, Pt), 1B (Au) subgroups of the transition group of periodicity Table, but also to the neighbor groups relative to the silicon one (4A): 3A (B, Al, Ga) and 5A (As, in the E-center As-V).

According to the above analysis, it seems that the opposite signs of parameters $E_t - E_i$ and $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$ allow the detection of some energy states of manganese, as well as a qualitative characterization of Mn states proportion among the impurities intervening for a certain pixel.

8. Conclusions

The accomplished analysis allowed to point out some additional possibilities of the computational approach of the dark current spectroscopy [13] relative to the other existing experimental methods intended to the characterization of nano-impurities and complexes embedded in the silicon lattice:

a) the study of the compatibility of the Shockley-Read-Hall basic theoretical model [7] with some experimental results concerning to the temperature dependence of the dark current in silicon, starting from the measurement errors,

b) the evaluation of the polarization degree of the recombination capture cross-sections of free electrons and holes: $pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}$ for the truly deep-level traps, whose distance to the intrinsic Fermi level is less or of the same magnitude order as the thermal energy (not larger than about 60 meV),

c) the huge reserve of potential additional information existing in the evaluated values of the pre-exponential factors of the field-free regions (diffusion and substrate) and depletion current, respectively (see e.g. [6a] and the above findings from paragraphs 2 and 3).

The limits of the computational approach of the DCS method were also emphasized:

- a) Its insensitivity for the not very-deep traps ($|E_t - E_i| \gg kT$),
- b) The impossibility to determine the signs of parameters $E_t - E_i$ and

$$pdg = \operatorname{argth} \frac{\sigma_h - \sigma_n}{\sigma_h + \sigma_n}.$$

In order to achieve the assignments of the obtained values of uniqueness parameters to some nano-impurities or traps intervening in the frame of the studied pixels, a comparison of the most important experimental methods intended to the characterization of these impurities/defects was accomplished.

There were pointed out both the important differences between the basic notions and parameters of the Dark Current Spectroscopy method (DCS) and of the Deep-Level Transient Spectroscopy (the most important present alternative experimental method) one, as well as also the possibilities to combine their results.

Acknowledgements

The authors want express their best thanks to the leaderships of the Portland State University (Oregon, USA) and of the “Politehnica” University of Bucharest for their Memorandum of Understanding (PSU contract 9908/03.06.2006), which allowed the achievement of this work.

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