Model and results for a deep level with two different configurations in $Hg_{0.3}Cd_{0.7}Te$

M. Koehler and E. F. Ferrari
Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19081, 81531-990 Curitiba Paraná, Brazil

J. F. Barbot*
The Case School of Engineering, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106-7204

I. A. Hümmelgen
Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19081, 81531-990 Curitiba Paraná, Brazil
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We consider a model for a defect which presents two distinct configurations at two different states of charge and discuss its behavior as observed via deep-level transient spectroscopy (DLTS) experiments. A general solution is obtained for the occupation fractions of the defect at each of both possible configurations. The obtained results are applied to explain the unusual dependence of DLTS line amplitudes as a function of filling pulse length in $Hg_{0.3}Cd_{0.7}Te$ submitted to ion implantation.

I. INTRODUCTION

Defect induced deep levels is an investigation subject whose development has been strongly enhanced by the deep-level transient spectroscopy (DLTS) technique. Apart from simple cases, many examples of intricate unusual phenomena observed using this technique and associated with charge state controlled metastable defects are reported in the literature.[1–8] This unusual behavior has its origin, for example, due to the strong coupling to the lattice, to negative correlation energy (negative U center), and to entropy driven spontaneous configurational changes that can be observed at a critical temperature.

In CdTe, defects with an unusual dependence between DLTS line amplitude and filling pulse length has been reported.[3,5] Zoth and Schröter[3] observed a multiple charged defect in p-CdTe: two DLTS lines corresponding to two different configurations were observed. They found a relation between occupation fractions for both configurations, similar to a previously reported behavior observed in InP [1]. Hümmelgen and Schröter[5] observed deformation induced defects in p-CdTe whose DLTS line presents a decreasing amplitude with increasing filling pulse length. A similar behavior has been observed in n-type $Hg_{0.3}Cd_{0.7}Te$, by Barbot *et al.*[8] They investigated samples containing dislocation loops generated by ion implantation and found two lines, labeled $E2$ and $E4$, with unusual dependence between their amplitudes and the filling pulse length. The amplitude of line $E2$ rises with increasing filling pulse time up to a maximum at approximately 10 μs and decreases for longer filling pulse times. The amplitude of line $E4$ behaves like a point defect for filling pulses of duration lower than 1000 μs. However, for longer filling pulses its amplitude does not saturate as expected for point defects (see Fig. 1).

We consider a defect with two charge states, as well as the finite capture rates for both defect configurations, and discuss the implications for each phase of a DLTS measurement.

We succesfully apply our model to explain the results presented by Barbot *et al.*[8] and obtain the expressions used by Levinson *et al.*,[1] and Zoth and Schröter,[3] as a particular case.

II. MODEL

The unusual dependence of the DLTS amplitude of lines $E2$ and $E4$ with the filling pulse can be explained by considering them as two distinct configurations of the same defect in differents states of charge. We assume that this deep level can capture two electrons; DLTS line $E2$ corresponds to the emission of the fraction of defects occupied by one carrier [called $E2(A)$] and the nonsaturation of line $E4$ originates from the emission of the fraction filled with two electrons [$E2(B)$]. Further dependence of $E4$ maximun amplitude with the filling pulse length t_p, which clearly presents neither a pointlike nor an extendedlike character, results from the superposition of two independent emissions: one of a point defect and the other of the simultaneous emissions of the two electrons in $E2(B)$.

The kinetics of the transition between the two configura-

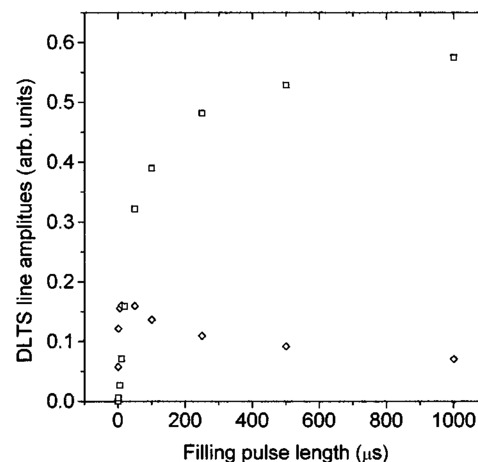

FIG. 1. Variation of DLTS amplitude with filling pulse length t_p for $E2$ (◇) and $E4$ (□) as abtained by Barbot *et al.* (Ref. 8).

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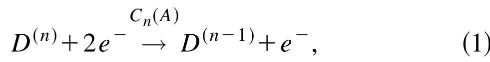
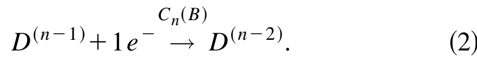
tions $[E2(A) \leftrightarrow E2(B)]$ is driven by the capture and emission of the second carrier. Therefore, the activation enthalpies measured by DLTS are considered as real binding energies of the captured electrons; i.e., the transition is not thermically activated.

The follow description assumed that the magnitude of the depletion layer motion is large compared to the Debye length. This ignores any effects due to the inhomogenities of the free-carrier distribution in the transition region.[11] During the filling pulse the thermodinamicaly stable configuration is the one with two capturated carriers. Calling the unspecified initial value of the charge state n, the capture rate of the first charge carrier $c_n(A)$, and the capture rate of the second charge carrier $c_n(B)$, the system proceeds according to the following reaction:



$$D^{(n)}+2e^{-} \xrightarrow{C_n(A)} D^{(n-1)}+e^{-}, \tag{1}$$



$$D^{(n-1)}+1e^{-} \xrightarrow{C_n(B)} D^{(n-2)}. \tag{2}$$

In the filling period (denoted by I), the temporal variation of the defect occupation fractions with one electron f_A^I and with two electrons f_B^I is governed by the coupled differential equations

$$\frac{\partial f_A^I}{\partial t}=c_n(A)(1-f_A^I-f_B^I)-c_n(B)f_A^I,$$
$$\frac{\partial f_B^I}{\partial t}=c_n(B)f_A^I. \tag{3}$$

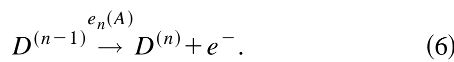
The general solution of this system is

$$f_A^I(t)=B_1e^{-c_n(B)t}+\frac{c_n(A)B_2}{c_n(B)}e^{-c_n(A)t}, \tag{4}$$

$$f_B^I(t)= 1-B_1e^{-c_n(B)t}-B_2e^{-c_n(A)t}, \tag{5}$$

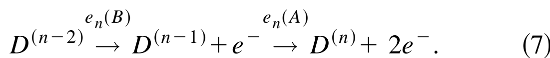
where B_1 and B_2 are constants and $0 \leqslant t \leqslant t_p$.

During the relaxation time ($t_i=(1/f)-t_p$, where f is pulse repetition frequency) the defect returns to its original state of charge n. If it is initially occupied by one electron it emits the captured charge carrier at emission rate $e_n(A)$ following the process



$$D^{(n-1)} \xrightarrow{e_n(A)} D^{(n)}+e^{-}. \tag{6}$$

Instead, if it binds two carriers, the defect emits any charge carrier at emission rate $e_n(B)$ and the next one at emission rate $e_n(A)$, following the reaction



$$D^{(n-2)} \xrightarrow{e_n(B)} D^{(n-1)}+e^{-} \xrightarrow{e_n(A)} D^{(n)}+ 2e^{-}. \tag{7}$$

In the relaxation period (denoted by II), the defect occupation fractions with one electron f_A^{II} and with two electrons f_B^{II} satisfies the following system of differential equations:

$$\frac{\partial f_A^{II}}{\partial t}=e_n(B)f_B^{II}-e_n(A)f_A^{II},$$
$$\frac{\partial f_B^{II}}{\partial t}=-e_n(B)f_B^{II}. \tag{8}$$

The general solution of (8) is

$$f_A^{II}(t)=\frac{e_n(B)}{e_n(A)-e_n(B)}B_3e^{-e_n(B)t}+B_4e^{-e_n(A)t}, \tag{9}$$

$$f_B^{II}(t)=B_3e^{-e_n(B)t}, \tag{10}$$

where B_3 and B_4 are constants and $0 \leqslant t \leqslant t_i$.

The constants B_1, B_2, B_3, and B_4 are determined by the conditions imposed by the DLTS measurement procedure: a periodical sequence of filling pulses followed by relaxation time. The initial state of the relaxation period is the final state of the filling period and vice versa.

The occupation fractions of configurations A and B at the beginning of period II are equal to the occupation fractions at the end of period I. Applying this condition of continuity,

$$f_A^{II}|_{t_i=0}=f_A^I(t_p),$$
$$f_B^{II}|_{t_i=0}=f_B^I(t_p),$$

we obtain

$$B_3=f_B^I(t_p)$$

and

$$B_4=f_A^I(t_p)-\frac{e_n(B)}{e_n(A)-e_n(B)}f_B^I(t_p).$$

Thus, substituting in Eq. (9) and in Eq. (10) one obtains the following result:

$$f_A^{II}(t)=f_A^I(t_p)e^{-e_n(A)t}+\frac{e_n(B)}{e_n(A)-e_n(B)}f_B^I(t_p) \times[e^{-e_n(B)t}-e^{-e_n(A)t}], \tag{11}$$

$$f_B^{II}(t)=f_B^I(t_p)e^{-e_n(B)t}, \tag{12}$$

where $0 \leqslant t \leqslant t_i$.

Similary, the occupation fractions of configurations A and B at the beginning of period I are equal to the occupation fractions at the end of period II. Again, applying this condition of continuity,

$$f_A^I|_{t_p=0}=f_A^{II}(t_i),$$
$$f_B^I|_{t_p=0}=f_B^{II}(t_i),$$

we obtain the following system of linear algebraic equations for B_1 and B_2:

$$\left[(1-e^{-e_n(A)t_i-c_n(B)t_p})+\frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i})e^{-c_n(B)t_p}\right]B_1 + \left[\frac{c_n(A)}{c_n(B)}(1-e^{-e_n(A)t_i-c_n(A)t_p})+\frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i})e^{-c_n(A)t_p}\right]B_2 = \frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i}), \quad (13)$$

$$(1-e^{-e_n(B)t_i-c_n(B)t_p})B_1+(1-e^{-e_n(B)t_i-c_n(A)t_p})B_2 = (1-e^{-e_n(B)t_i}). \quad (14)$$

Solving this system of equations, B_1 and B_2 are determined:

$$B_1=\frac{c_1b_2-c_2b_1}{a_1b_2-a_2b_1}, \quad (15)$$

$$B_2=\frac{a_1c_2-a_2c_1}{a_1b_2-a_2b_1}, \quad (16)$$

where a_1, a_2, b_1, b_2, c_1, and c_2 are the following parameters:

$$a_1= 1-e^{-e_n(B)t_i-c_n(B)t_p}, \quad (17)$$

$$b_1= 1-e^{-e_n(B)t_i-c_n(A)t_p}, \quad (18)$$

$$c_1= 1-e^{-e_n(B)t_i}, \quad (19)$$

$$a_2=(1-e^{-e_n(A)t_i-c_n(B)t_p})+\frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i})e^{-c_n(B)t_p}, \quad (20)$$

$$b_2=\frac{c_n(A)}{c_n(B)}(1-e^{-e_n(A)t_i-c_n(A)t_p})+\frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i})e^{-c_n(A)t_p}, \quad (21)$$

$$c_2=\frac{e_n(B)}{e_n(A)-e_n(B)}(e^{-e_n(B)t_i}-e^{-e_n(A)t_i}). \quad (22)$$

By replacing this solution in the expressions for $f_A^I(t_p)$ in Eq. (4) and for $f_B^I(t_p)$ in Eq. (5), we can find the occupation fractions of the states A and B at the end of the filling pulse as a function of capture rates [$c_n(A)$ and $c_n(B)$], emission rates [$e_n(A)$ and $e_n(B)$], filling pulse length t_p and relaxation time t_i.

As a particular case, for high values of $c_n(A)>10^7\ \mathrm{s}^{-1}$, we find the same formula presented by Refs. 1 and 3, in the limit $c_n(A)\rightarrow\infty$:

$$f_B^I(t_p)=1-f_A^I(t_p)=\frac{1-\exp[-c_n(B)t_p]}{1-\exp[-e_n(B)t_i-c_n(B)t_p]}. \quad (23)$$

III. APPLICATION

In this section we shall apply the model to describe the anomalous behavior of lines $E2$ and $E4$ identified by Barbot *et al.*[8] in $\mathrm{Hg_{0.3}Cd_{0.7}Te}$.

We assume that line $E2$ corresponds to the process described by Eq. (6) and that line $E4$ corresponds to the summatory of the process described by Eq. (7) and the emission from another pointlike defect with usual dependence with the filling pulse length.

We explain the behavior of lines $E2$ and $E4$ using our model supposing that (i) line $E2$ is associated with configuration $E2(A)$; and (ii) line $E4$ results from the superposition of configuration $E2(B)$ and another pointlike defect labeled $E4P$.

In the fitting of $E2(A)$, we adjust Eq. (4) for $t=t_p$, the constants B_1 and B_2 given by Eqs. (15) and (16), and the emission rate,

$$e_n(A)=2.51\times f=200.8\ \mathrm{s}^{-1}$$

determined by the correlation used in the DLTS system. In this way we obtain the following values for the capture and emission rates at 187 K:

$$c_n(A)=7\times10^5\ \mathrm{s}^{-1},$$

$$c_n(B)=230\ \mathrm{s}^{-1},$$

$$e_n(B)=15\ \mathrm{s}^{-1}.$$

Employing the relation (A1) presented in the Appendix, we derived the capture cross sections of $E2(A)$ and $E2(B)$:

$$\sigma_A=2.5\times10^{-17}\ \mathrm{cm}^2,$$

$$\sigma_B=8\times10^{-21}\ \mathrm{cm}^2.$$

The comparison between σ_A and the prefactor for the $E2$ emission rate, obtained by Barbot *et al.*[8] as $\sigma_A\chi_A=5\times10^{-15}\ \mathrm{cm}^2$, yields the entropy of ionization,

$$\Delta S_A=2.6\times10^{-4}\ \mathrm{eV/K}.$$

This value lies in the range of estimates and measurements of ΔS in other semiconductors at higher temperatures.[9,10]

Supposing $\Delta S_B = 0$ and using the values of $e_n(B)$ and σ_B from the fitting of line $E2(A)$ we obtain from Eq. (A2):

$$\Delta H_B = 0.134 \text{ eV}.$$

We ascribe the anomolous dependence of line $E4$ amplitudes on the filling pulse to the sum of two contributions:[8] the characteristic emissions of an isolated point defect $(E4P)$ and the simultaneous emissions of the two electrons in $E2(B)$. In other words, we suppose that at the temperature of the peak of line $E4$ ($T=261$ K), the emission rate of configuration B is

$$e_n(B)|_{T=261\text{ K}} = 2.51 \times f = 200.8 \text{ s}^{-1}.$$

Applying, for $\Delta H_A = 0.27$ eV,[8] the formula (A.2) in the Appendix at $T=267$ K, we obtain

$$e_n(A)|_{T=261\text{ K}} = 4.5 \times 10^4 \text{ s}^{-1}.$$

Since $e_n(A)|_{T=261\text{ K}} >> e_n(B)|_{T=261\text{ K}}$, the transition described by Eq. (7) is a two-electron emission; the emission of the electron from $E2(A)$ occurs immediately after the emission of the electron from $E2(B)$. As in the case described by Ref. 3, the $E2(B)$ emission rate is the limiting step. Therefore, the contributions of $E2(B)$ to the amplitude of line $E4$ are twice what is expected for a single-electron emission $[2 \times f_B^I(t_p)$, given by Eq. (5)]. Supposing again $\Delta S_B = 0$ and using the values of $e_n(B)|_{T=261\text{ K}}$ and σ_B from the fitting of line $E2(A)$, we obtain, from Eq. (A.2),

$$\Delta H_B = 0.144 \text{ eV}.$$

Therefore, the resulting values for configuration B parameters are comprehended in the intervals

$$\sigma_B \chi_B \sim 10^{-20} - 10^{-21} \text{ cm}^2,$$

$$\Delta H_B \sim 0.13 - 0.15 \text{ eV}. \tag{24}$$

Comparing the above values for ΔH_B with the activation enthalpy for configuration A ($\Delta H_A = 0.27$ eV),[8] it is clear that in the positive-U ordering of this defect[12] the first electron is more strongly bounded than the second. In this regard, our deep level behaves like the one already observed by Zoth and Schröter.[3]

In Figs. 2 and 3 we show the fitted curves for lines $E2$ and $E4$. The observed apparent linear increase of $f_B^I(t_p)$ with the filling pulse of Fig. 3 has its origin in the great value of $e_n(A)|_{T=261\text{ K}}$: as $c_n(B)$ is temperature independent, a faster emission rate of configuration A represents less defect in this configuration and a slower increase of defects in configuration B. Hence, the exponential growth of $f_B^I(t_p)$ would be revealed only for long filling pulses ($t_p \gg 1000$ μs).

IV. CONCLUSION

This article is divided into two complementary parts. First, in Sec. II, we describe a model for a defect which presents two configurations determined by its state of charge. Configuration A corresponds to the fraction of defects occupied by one carrier and configuration B corresponds to the one occupied by two carriers. We find the expressions for the occupation fractions of each configuration during the two phases of a DLTS measurement: filling pulse time and relaxation time. Finally, we show that the relation presented by Levinson *et al.*[1] and used by Zoth and Schröter[3] is a particular case of our expressions.

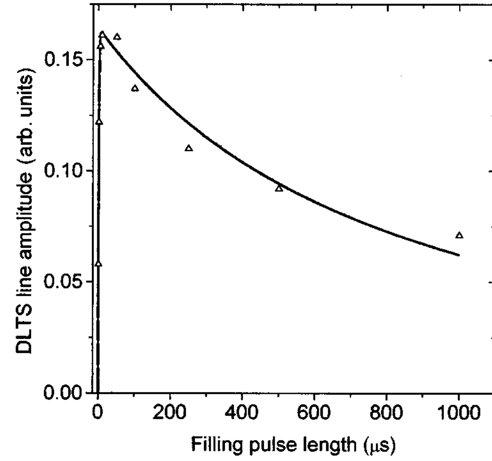


FIG. 2. DLTS line $E2$ ($\triangle$) as a function of pulse length t_p and a continuous line representing the theoretical curve according to Eq. (6) $[E2(A)]$.

Second, in Sec. III, we apply our model to explain the unusual dependence of lines $E2$ and $E4$ on filling pulse length, observed by Barbot *et al.*[8] in $Hg_{0.3}Cd_{0.7}Te$. The line $E2$ originates from the electron emission of the defects in configuration A and the line $E4$ from the superposition of two independent emissions: the two electrons from the defects in configuration B and the electron from another point-like defect. This application yields an estimation of the capture cross sections for both configurations and also the activation enthalpy for configuration B.

What emerges from our analysis is the clear evidence that the defect observed by Barbot *et al.* has the same behavior as that described by Zoth and Schröter. The main difference between the two cases is in the values of the capture rates; the defect in p-type CdTe has capture rates for configurations A and B higher than that ones in $Hg_{0.3}Cd_{0.7}Te$. Following

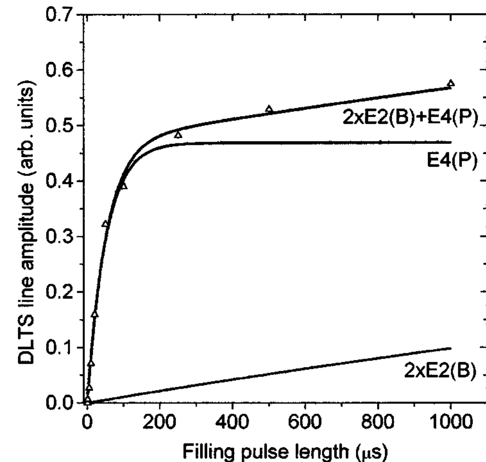


FIG. 3. DLTS line $E4$ ($\triangle$) as a function of pulse length t_p compared with a continuous line representing the theoretical curve. The line $E4(P)$ is obtained by taking the DLTS line amplitude proportional to $[1-\exp(-t_p/\tau_c)]$ with $\tau_c = 5 \times 10^{-5}$ s.

from this are other consequences: (i) In the case of Barbot, the increase of the amplitudes of line $E2(A)$ with short filling pulse length is observed, whereas, in the case of Zoth and Schröter, the line $H4(A)$ reached its maximum value even for the shortest available pulse length. (ii) The line $E2(B)$ is detectable only at a relatively high temperature that makes the increase of its occupation fraction seem linear even for the longest filling pulse available. Therefore, the association of the unusual behavior for line $E2$ with that for line $E4$ is not direct. It depends on a detailed analysis under the scope of our theory.

APPENDIX

The capture rates of the two configurations are related to theirs capture cross sections (σ_A and σ_B) by the equation

$$c_n = \sigma n \langle v\,\mathrm{th} \rangle, \tag{A1}$$

where n is the density of majority free carriers and $\langle v\,\mathrm{th}\rangle$ their the mean thermal velocity. In addition, the emission rates are given by the relationship

$$e_n = \sigma \chi N_c \langle v\,\mathrm{th} \rangle e^{\frac{-\Delta H}{kT}}, \tag{A2}$$

where N_c is the effective density of states in the conduction band,

$$\chi = \exp\left(\frac{\Delta S}{k}\right), \tag{A3}$$

ΔH and ΔS are the activation enthalpies and entropies of ionization.

*Permanent address: Laboratoire de Metallurgie Physique, URA 131 CNRS, Université de Poitiers, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France.

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