Many-Level Trap-to-Band Transitions in Chalcogenide Memories

M. Rudan[1], F. Buscemi[1], G. Marcolini[1], F. Giovanardi[1], A. Cappelli[2], E. Piccinini[1], and R. Brunetti[2]
[1]"E. De Castro" Advanced Research Center on Electronic Systems (ARCES) and Department DEIS
University of Bologna, Viale Risorgimento 2, I-40136 Bologna, Italy — mrudan@arces.unibo.it
[2]Physics Department, University of Modena and Reggio Emilia, and CNR-Institute of NanoSciences S3
Via Campi 213/A, I-41125, Modena, Italy

Abstract. The cooperative electron-electron interaction is one of the mechanisms for the occurrence of trap-to-band transitions in chalcogenide memories. Here its analysis is tackled by considering the presence of several trap levels, this removing the limitations of earlier approaches. Also, the action of two feed-back mechanisms is demonstrated. The results show that the detrapping probability increases with the current density, this supporting the interpretation by which successive electron-electron scattering events may play a major role in determining the snap-back of the $I(V)$ characteristic in this kind of materials.

I. Introduction

Some of the amorphous chalcogenide materials exhibit a transition from a highly resistive to a conductive state, characterized by a voltage snap-back. Thanks to this feature they are used in the fabrication of nonvolatile memories [1]. Carrier transport in chalcogenides is modeled by considering two contributions: electron hopping via localized states (traps), and motion of electron in extended states (i.e., band electrons). The snap-back event is related to the sharp energy dependence of the extraction mechanism responsible for the trap-to-band transition of the trapped electrons [2]. This transition can be started by different phenomena, such as impact ionization or field-induced emission. While the former is not sufficiently frequent at the operating condition of the device near threshold, the second one cannot always provide a positive self-sustained feedback mechanism, as required for the negative-differential resistance to occur. A third detrapping mechanism is is ascribed to the cooperative effect of band electrons over trapped electrons [3], [4]. This mechanism is similar to impact ionization, but involves only low-energy band electrons. It seems a promising candidate to explain the feed-back effect.

Macroscopic models describing the generation process induced by the Coulomb interaction of a trapped electron with band electrons make use of a generation rate. To derive the latter from first principles we used a numerical approach [3], exploiting a solver of the two-electron, time-dependent Schrödinger equation. Basing on this approach one evaluates the detrapping probability as a function of the current density in terms of the number of band electrons at a given initial energy. While in [2], [4] a single trap level was considered (the ground state), here the analysis is generalized to the case of several levels. The restriction of assuming that the band electrons have the same energy is removed as well. The analysis confirms the dependence of the snap-back phenomenon on the driving current. It also shows that the feed-back process is actually made of the combination of two mechanisms.

Letting f_k be the filling fraction of the kth level E_k of a trap, in the equilibrium condition the Fermi statistics for f_k holds, which keeps the majority of traps filled and makes the population of the band and of the upper trap levels negligible. An external perturbation (typically produced by a current generator) results in an increase in the band population. The electron concentration n of the band is described through a modified Fermi statistics in which the Fermi level E_F is replaced with the quasi-Fermi level E_n. This is equivalent to shifting the statistics along the energy axis. This description is acceptable because in the typical operating conditions the band electrons do not become significantly hot [2]. The higher number of band electrons increases the probability of the trap-to-band transitions per unit time due to the cooperative effect. Such a probability is the largest for the highest trap level (E_M in figure 1) because the transition energy $E_C - E_M$ (with E_C the bottom of the band) is the smallest. However, as the population of E_M is initially negligible, so is the number of electrons that are promoted to the band. On the other hand the cooperative effect induces transitions among all pairs of trap levels; such transitions, in turn, tend to equalize the level populations, including that of E_M. The increased population of E_M provides a larger supply of electrons that can be promoted to the band, this providing one of the two contributions to the feed-back mechanism. Finally, the larger concentration of band electrons makes the cooperative effect stronger, this providing the other contribution to feed-back. As more current is injected into the device, n keeps increasing at the expense of the population of the trap levels. The two contributions to feed-back are investigated in the next sections.

II. Transition Probabilities

The $E_s \leftrightarrow E_k$ transition probabilities per unit time between the levels of indices s, k combine the effects of the phonon stimulated-emission/absorption and electron interactions, $\dot{P}_{ks} = \dot{P}_{sk} = \dot{P}^P_{sk} + \dot{P}^E_{sk}$. These terms do not include the spontaneous emissions, which are treated separately. For

 ISBN 978-0-615-71756-2

$\dot{P}_{sk}^{E}$ we adopt the same approach as that used in [5], [6], [7] to model the degradation phenomena related to interface traps; namely, indicating with γ the density of states per unit volume of the band, with f the filling fraction of the band states, with $u = u(E_e)$ the angular average of the group velocity of the band electrons, and letting $\Delta_{sk} = |E_s - E_k|$, one has

$$\dot{P}_{sk}^{E} = \int_{\Delta_{sk}}^{\infty} \gamma\, u\, \sigma\, f\, \mathrm{d}E_e\,. \tag{1}$$

In the above,

$$\sigma = \sigma_0 \left(\frac{E_e - \Delta_{sk}}{E_0}\right)^r , \qquad E_e \geq \Delta_{sk}\,, \quad r > 0\,, \tag{2}$$

is the Keldysh-like cross section of the interaction between the trap electron belonging to level E_k and the band electrons, while E_e is the band-electron energy relative to the minimum E_C of the band and E_0 a constant. The discussion focuses on the integrand of (1), where all factors are non negative. The energy dependence of the product γu, albeit complicated, is fixed by the lattice structure; the cross section σ is a sharply increasing function of energy because the exponent r is large. In fact, in the problem of [5] the value $r = 11$ is used; in the fully quantum-mechanical approach of [4], a power of the order of a few tens enters the probability that an electron leaves the trap due to multiple scattering with band electrons. For a power law of the type of (1), with $r \sim 10$, the sharp increase of σ starts at the threshold energy $\Delta_{sk} + E_0$. As the filling fraction f has an exponentially-decreasing tail, the product σf is expected to have a peak, whose value depends on the position of the tail along the energy axis. As discussed in the introduction, such a position shifts when the device is driven into a non-equilibrium condition by the application of an external current.

The product σf is shown in figure 2; as expected, the curves exhibit a peak, whose value turns out to depend strongly on the shift of the quasi-Fermi level E_n. In the figure, the shift in the Fermi distributions is obtained by changing $\eta_n = (E_n - E_C - \Delta_{sk})/(k_B T_L)$ by one unit (k_B is the Boltzmann constant, T_L the lattice temperature). In contrast, the dependence of the peaks' position on η_n is much weaker: solving $r \exp(\eta_n - \eta) = \eta - r$ for η with $r = 11$ shows that a change $\Delta\eta_n = 2$ moves the peak by $\Delta\eta \simeq 0.02$; in the more realistic case $r = 15$ one needs $\Delta\eta_n \simeq 5.5$ to obtain the same $\Delta\eta$. As a consequence, the integration domain in (1) is not changed appreciably by the shift of E_n. This is important for the purpose of the present discussion, because in the calculation of the integral one leaves the structural factor γu unchanged when E_n changes. As a consequence, the changes in σf are not masked by the local features of γu, and the exponential-like dependence of σf on E_n is inherited by the integral.

It is worth mentioning that the analysis of [6] provides a different model for the cross section, namely, σ is approximated by a step function

$$\begin{cases} \sigma = 0\,, & E_e < \Delta_{sk} \\ \sigma = \sigma_0\,, & E_e > \Delta_{sk} \end{cases} \tag{3}$$

whose two branches are connected by an exponential. However, the outcome of the analysis is similar, and yields an approximation to $\dot{P}_{sk}^{E}$ in the form

$$\dot{P}_{sk}^{E} = \int_{\Delta_{sk}}^{\infty} \gamma\, u\, \sigma\, f\, \mathrm{d}E_e \simeq \frac{\sigma_0}{q}\, J_n(\Delta_{sk})\,, \tag{4}$$

with $q = 1.602 \times 10^{-19}$ C the electron charge, and $J_n(\Delta_{sk}) \geq 0$ the current density due to the band electrons having a kinetic energy $E_e > \Delta_{sk} + E_0$ (Keldish-like cross section) or $E_e > \Delta_{sk}$ (step-function cross section).

III. Band Population

The derivation of the balance equations for the energy levels is formally the same as, e.g., in laser theory. All traps are equal to each other and provide a set of M energy levels $E_1 < E_2 < \ldots < E_M$. The trap concentration is N, while $N_k = N f_k$ is the concentration of traps whose E_k level is filled. The time variation of N_k due to the $E_i \leftrightarrow E_k$ transitions is $R_{ik} = \dot{P}_{ik}\,(N_i - N_k) - N_k\,(1 - f_i)/\tau_{ki}$, with $1 < k < M$, $E_i < E_k$, and τ_{ki} the lifetime of spontaneous phonon emission. The expression for the $E_k < E_i$ case is found by exchanging i with k.

The exchange rate between E_k and the band has a slightly different form because empty band states are always available. It reads $R_{kB} = (\dot{P}_{kB}^{P} + \dot{P}_{kB}^{E}) N_k - \alpha_{Bk} n N (1 - f_k)$, where $\dot{P}_{kB}^{P}$, $\dot{P}_{kB}^{E}$ are the trap-to-band emission coefficients for the phonon and electron interactions, and α_{Bk} the band-to-trap transition coefficient including the effect of spontaneous phonon emission. An Auger-like term is not included in the above expression; this approximation does not violate the microscopic-balance condition because (4) vanishes at equilibrium. In this case from $R_{kB} = 0$ one finds

$$[\dot{P}_{kB}^{P}\, f_k]^{\mathrm{eq}} = [\alpha_{Bk} n (1 - f_k)]^{\mathrm{eq}}\,, \tag{5}$$

with f_k^{eq} the Fermi statistics. It follows

$$\left[\dot{P}_{kB}^{P}/\alpha_{Bk}\right]^{\mathrm{eq}} = n^{\mathrm{eq}}\, d\, \exp\left(\frac{E_k - E_F}{k_B T_L}\right), \tag{6}$$

where d is the degeneracy coefficient.

The form of the exchange rates simplifies considerably if one assumes that the transitions occurring between neighboring levels are dominant. This is justified by the observation that in this case the energy required to induce the transition is minimum. If, in addition, the electron-interaction perturbation is large enough to make $\dot{P}_{rs}^{E}$ dominant with respect to the phonon-related coefficients $\dot{P}_{rs}^{P}$ and $1/\tau_{sr}$, expressions similar to (2a,b,c) of [5] are reached. It follows that in steady state the level populations N_k equalize, $N_1 = \ldots = N_M$, as is ascertained easily starting from the balance equation for the ground level E_1 and continuing with those for $E_2, E_3, \ldots$. Finally, a spatially-uniform case is considered. Due to the form of the balance equation for level E_M, the equalization makes the exchange rate R_{MB} to vanish. From this, the expression of the common value of the populations is found to be

$$N_1 = \ldots = N_M = \frac{nN}{n + b_M}\,, \quad b_M = \frac{\dot{P}_{MB}^{P} + \dot{P}_{MB}^{E}}{\alpha_{BM}}\,. \tag{7}$$

In the spatially-uniform case the charge density

$$\varrho = q(N - n - \sum_k N_k) \tag{8}$$

vanishes; still considering the situation where $\dot{P}_{rs}^{E}$ is dominant, the vanishing of ϱ coupled with the equalization of the level populations yields

$$N - n - M \frac{nN}{n + b_M} = 0 \,. \tag{9}$$

Then, letting $\nu = b_M + (M-1)\,N$, the band concentration is found to be

$$n = \sqrt{\nu^2/4 + N b_M} - \nu/2 \,. \tag{10}$$

Note that (10) holds only above the threshold-switching condition of the device (that is, after the onset of the positive feed-back mechanism typical of the device [2]), because the equalization of the level population is implied in its derivation. This, in turn, holds only when the electron-interaction perturbation is dominant.

IV. Threshold Condition

Combining the results of sections II and III one finds that the electron-kinetic energy that defines the threshold-switching condition of the device is $\Delta_{MB} + E_0 = E_C - E_M + E_0$ (for the symbols refer also to figure 1). Above the threshold-switching condition one splits the current density of the band as $J_n = J_n^{\rm th} + J_n(\Delta_{MB})$, with $J_n^{\rm th} = $ const the current density due to the band electrons having a kinetic energy $E_e \le \Delta_{sk} + E_0$. From (4) it follows

$$\dot{P}_{MB}^{E} = \frac{\sigma_0}{q}\,\left(J_n - J_n^{\rm th}\right) \tag{11}$$

which, combined with the second of (7), makes ν and b_M to depend linearly on $J_n - J_n^{\rm th}$. Inserting such dependences into (10) provides the relation between n and $J_n - J_n^{\rm th}$ that holds above threshold. In particular, the band-electron concentration at threshold, $n^{\rm th}$, is found by calculating n with $J_n = J_n^{\rm th}$.
When $\nu^2 \gg 4 N b_M$ the band concentration (10) saturates to $b_M N/\nu$ (if the trap levels are grouped into a single one, then $M = 1$, $\nu = b_M$, the expression for n simplifies to (14) of [2], and the saturation value of n becomes N). The expression of ν can be recast as

$$\nu = n_B + (M-1)N + \beta\,(J_n - J_n^{\rm th}) \,, \tag{12}$$

with

$$n_B = \frac{\dot{P}_{MB}^{P}}{\alpha_{BM}} \,, \qquad \beta = \frac{\sigma_0}{q\alpha_{BM}} \,. \tag{13}$$

The definition of n_B in (13) is the same as in [2, Eqs. (5,6)]. The form of $n = n(J_n - J_n^{\rm th})$ is shown in figure 3 where, following [2], we have set $n_B = 10^{14}$ cm^{-3}, $N = 10^{19}$ cm^{-3}. The values of the other parameters have been fixed to $\sigma_0 = 5 \times 10^{-15}$ cm^2, $\alpha_{BM} = 10^{-7}$ cm^3/s, $J_n^{\rm th} = 10^2$ A/cm^2, $M = 5$. The figure shows that near threshold the concentration of the band electrons increases sharply, to eventually saturate. In figure 4, the $n(b_M)$ relation is zoomed in to better show its behavior near threshold.
In the spatially-uniform case considered here, the relation between the total current density J and the band-electron current density J_n is [2, Eqs. (17,18)]

$$\frac{J_n}{J} = \theta(n) \,, \qquad \theta(n) = \frac{\mu_n n}{\mu_n n + \mu_T (N - n)} \,, \tag{14}$$

where μ_n, μ_T are the band and trap mobility, respectively. Inserting the expression $n(J_n - J_n^{\rm th})$ worked out above into (14) provides an intrinsic relation $J_n(J)$. After calculating J_n for each value of the bias current density J, one determines the corresponding concentration n. Then, the electric field $\mathcal{E}$ for each bias point is found from $J_n = q\mu_n n \mathcal{E}$. In this way the branch of the $V(I)$ characteristic above threshold is determined.
Finally, the total current density at threshold $J^{\rm th}$ is determined from

$$J^{\rm th} = \frac{\mu_n n^{\rm th} + \mu_T (N - n^{\rm th})}{\mu_n n^{\rm th}}\, J_n^{\rm th} \,. \tag{15}$$

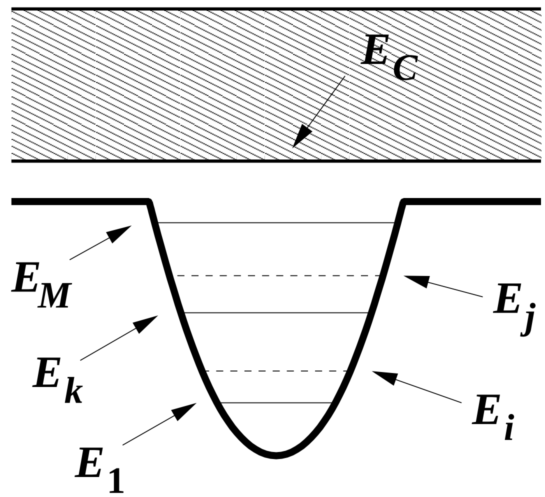

Fig. 1. Schematic view of a trap with energy levels $E_1 < E_2 \ldots < E_M$. The grey area above indicates the energy band, whose minimum energy is E_C.

V. Conclusions

The effect of the many-level transitions induced by the co-operative interactions between band and trap electrons has been investigated in this work. The main results are *i)* the role of the power-like energy dependence of the cross section σ has been clarified: the parameters Δ_{sk}, E_0, and r fix the threshold energy and the sharpness of the behavior of $\dot{P}_{sk}^{E}$ around threshold. *ii)* The dependence of $\dot{P}_{sk}^{E}$ on the external perturbation is due to the form of the energy distribution of the band electrons; the estimate of the integral (1) confirms that $\dot{P}_{sk}^{E}$ is an exponentially-increasing function of E_n, which in turn explains the positive feed-back mechanism in the transport process [2]. *iii)* The analysis also shows that two mechanisms contribute to the feed-back: they are the tendency of the level populations to equalize and the increase in $\dot{P}_{sk}^{E}$ with the band population; the first one provides a larger supply of electrons able to make a transition from E_M to the band; then, the second one makes n to further increase at the expense of the traps' population. *iv)* In the uniform case the dependence $n = n(J_n)$ is worked out analytically. The heuristic expression of [2] for the J_n dependence has been replaced here by a

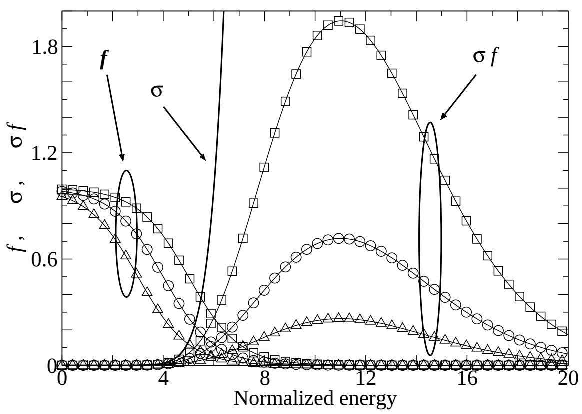

Fig. 2. The continuous line shows the interaction cross section σ calculated by letting $\sigma_0 = 1$, $r = 11$ in (1). Using the normalized energy $\eta = (E - \Delta_{sk})/(k_B T_L)$ yields $\sigma = \eta^r$. Each bell-shaped curve shows the product of σ by the shifted Fermi distribution $1/[\exp(\eta - \eta_n) + 1]$ indicated with the same symbols on the left part of figure (η_n is defined in the text). The shift in the Fermi distributions is obtained by changing $\eta_n = (E_n - E_C - \Delta_{sk})/(k_B T_L)$ by one unit. The corresponding shift in the peak value of the bell-shaped curves is found by solving $r \exp(\eta_n - \eta) = \eta - r$ for η. The area of each bell-shaped curve is $\Gamma(r+1)\Phi_r(\eta_n)$, thus its dependence on η_n is the same as that of the Fermi integral. In the classical limit it becomes $\Gamma(r+1)\exp(\eta_n)$.

physical derivation through equation (4) combined with the analysis of the trap and band populations.

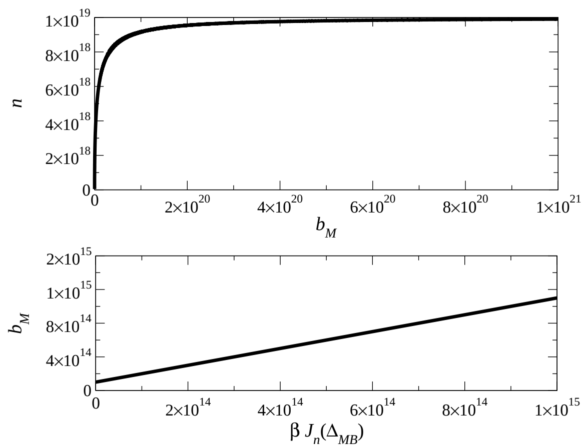

Fig. 3. The relation $n = n[J_n(\Delta_{MB})]$ for $n \geq n_{\rm th}$, as found from (10). It is $J_n(\Delta_{MB}) = J_n - J_n^{\rm th}$. The definition of β is given in (13).

Acknowledgment

This work has been carried out under the contract 3477131/2011 of the Intel Corporation whose support is gratefully acknowledged. We also thank Prof. S. Reggiani for useful discussions about the theories of [5], [6], [7].

References

[1] D.C. Kau et al., *A stackable cross point phase change memory*, Proc. IEDM09, p. 617–620 (2009).

[2] M. Rudan et al., *Voltage Snapback in Amorphous-GST Memory Devices: Transport Model and Validation*, IEEE Trans. on Electron Devices **58**, 4361 (2011).

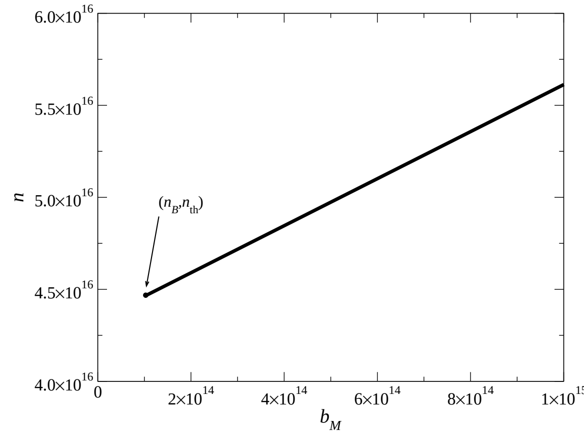

Fig. 4. Zoom of the $n(b_M)$ graph of figure 3 near threshold.

[3] F. Buscemi, P. Bordone, and A. Bertoni, *Entanglement dynamics of electron-electron scattering in low-dimensional semiconductor systems*, Phys. Rev. A **73**, 052312 (2006).

[4] F. Buscemi et al., *Quantum Electronic Trap to Band Transitions in Chalcogenides Induced by Electron-Electron Interaction*, Proc. SISPAD-2011, Osaka, 231 (2011).

[5] S.E. Tyaginov et al., *Interface traps density-of-states as a vital component for hot-carrier degradation model*, Microelectronics Reliability **50**, 1267 (2010).

[6] C. Hess et al., *The Physics of Determining Chip Reliability*, Circ. Dev. Mag., 33 (May 2010).

[7] A. Bravaix et al., *Hot-carrier acceleration factors for low power management in DC-AC stressed 40 nm NMOS node at high temperature*, Proc. of Int. Reliab. Phys. Symp., 531 (2009).