Quantum Electronic Trap-to-Band Transitions in Chalcogenides Induced by Electron-Electron Interaction

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***Abstract*—Charge transport in amorphous-chalcogenide materials used for manufacturing memory devices is determined by two mechanisms: hopping of trapped electrons and motion of band electrons. Electron-electron interaction is investigated here as one of the mechanisms mainly responsible for the trap-to-band transitions. The problem is tackled using a fully quantum-mechanical approach by numerically solving the two-particle, time-dependent Schrödinger equation. 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 the determining the snap-back of the $I(V)$ characteristic in this kind of materials.**

I. Introduction

Chalcogenide materials have recently attracted a large interest as an emerging nonvolatile memory technology. In their amorphous phase, they exhibit a threshold switching in the conduction characteristic. The latter consists in a transition from a low- to a high-conductive state, once the applied bias reaches a critical threshold voltage, and an S-shaped negative differential resistance behavior in the curve is found [1]. A clear and correct understanding of the switching phenomenon in amorphous chalcogenide materials is of the utmost importance for exploiting such materials in the fabrication of alternative nonvolatile memories [2].

Carrier transport in chalcogenides is modeled by considering two contributions: electron hopping via localized states (traps), and motion of electrons in extended states (i.e., band electrons). The occurrence of the snap-back event has recently been related to the sharpness of the extraction mechanism responsible for the trap-to-band transition of the trapped electrons [3]. 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 self-sustained feedback mechanism, as required for the negative-differential resistance to occur. A third detrapping mechanism is the cooperative effect of band electrons over trapped electrons. In principle, this mechanism is similar to impact ionization, but involves lower-energy band electrons only. In a recent work [4], the effects of the collective Coulomb interactions have been included in a macroscopic simulative model relating the snap-back phenomenon to filamentation in energy. Such a model describes the generation process induced by the Coulomb interaction of a trapped electron with band electrons by means of a generation rate whose sharpness turns out to be critical for the appearance of the differential resistance in the $I(V)$ characteristics.

In this work, we derive from first principles a macroscopic generation rate describing trap-to-band transitions in amorphous chalcogenides. To this aim we use a numerical approach based on the investigation reported in [5], that exploits a solver of the two-electron, time-dependent Schrödinger equation. We consider a current of independent carriers, all having the same kinetic energy and interacting with a trapped electron. In this way, the Coulomb interaction between band- and trap-electrons can be modeled as a number of successive electron-electron scattering events, which can be investigated by means of a simple two-particle approach. Starting from the number of band electrons at a given initial energy one is eventually able to evaluate the detrapping probability as a function of the current density.

II. Physical model

To investigate the electron-electron interaction between band electrons and a trap electron, we consider a system made of a number of free propagating electrons, all of them in the same energy state, and an electron initially in the ground state of a potential well (Fig. 1). To simplify the problem, the case of a rectangular well is considered. Also, one scattered carrier at a time is examined, i.e., a band electron is supposed to interact with the trapped electron only when the previous scattering event is over. In this way the system always operates in a two-particle regime, and its Hamiltonian takes the form

$$H(x_1, x_2) = H_0(x_1) + H_0(x_2) + \frac{e^2}{4\pi\epsilon\,|x_1 - x_2|}\,, \quad (1)$$

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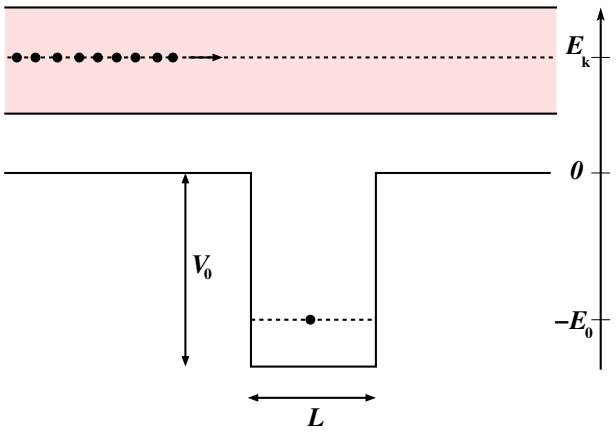

Fig. 1. A number of band electrons with energy E_k interact via successive Coulomb two-particle scatterings with an electron initially in the ground state E_0 of a rectangular well. The parameters used in the numerical calculation are $V_0 = 350$ meV, $E_0 = 189$ meV, and $L = 1$ nm. The standard deviation of the wavepackets describing the band electron is 5 nm.

where ϵ is the dielectric constant of the material, and

$$H_0(x) = -\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial x^2} + V_T(x)\,, \tag{2}$$

with V_T and m^* the well's potential energy and the material's effective mass, respectively.

The purpose of the calculation is determining the detrapping probability occurring as a consequence of the two-electron scattering. Initially, the incoming electron is represented by a minimum-uncertainty Gaussian wavepacket $w(x_1)$ with energy $E_k = \hbar^2 k^2/(2m^*)$, while the bound electron is in the ground state $\chi_0(x_2)$ of the single-particle Hamiltonian H_0 with energy $-E_0$. Thus, the two-particle wavefunction describing the system at $t = 0$ takes the form $\psi(x_1, x_2, 0) = w(x_1)\chi_0(x_2)$. The center of the incoming wavepacket is initially placed far away from the well in order to make the Coulomb interaction negligible at $t = 0$. The Schrödinger equation for the two-particle wavefunction,

$$i\hbar\,\frac{\partial}{\partial t}\psi(x_1, x_2, t) = H(x_1, x_2)\,\psi(x_1, x_2, t)\,, \tag{3}$$

is numerically solved using the Crank-Nicholson finite-difference scheme illustrated in section III. Spatial wavefunctions are obtained at each time step. In order to get a better insight into the electron-electron scattering dynamics, $\psi(x_1, x_2, t)$ has been used to evaluate at three different times (before, during and after the scattering) the single-particle density probability for the trapped electron (see Fig. 2). As a consequence of the electron-electron interaction, the free-propagating carrier can share part of its energy with the trapped electron, initially in the ground state χ_0 of the single-particle Hamiltonian (2). The trapped electron can be elevated to non-bound states with high energies, this meaning that its spatial-density probability, peaked around the well at $t = 0$, broadens up and takes non-vanishing values also in space regions far from the well. The broadening of the trapped-carrier wavepacket indicates the occurrence of a detrapping process.

At the final time t_f (i.e., when the interaction is negligible again), spatial wavefunctions are used to evaluate the detrapping probability, that is, the probability to find both electrons in an extended state. Since electron-electron scattering occurs in few hundreds of femtoseconds, ignoring the relaxation of the trapped electron to the ground level is reasonable. Thus, once a scattering occurs, the trapped electron is left in a linear superposition of states, namely,

$$\psi(x_1, x_2, t_f) = \sum_{n=0}^{N} \alpha_n\,\varphi_n(x_1)\,\chi_n(x_2)\,, \tag{4}$$

where $\chi_n(x_2)$ indicates the n-th eigenstate of the single-particle Hamiltonian H_0, and $\varphi_n(x_1)$ is a free-propagating state describing the incoming electron after the Coulomb scattering.

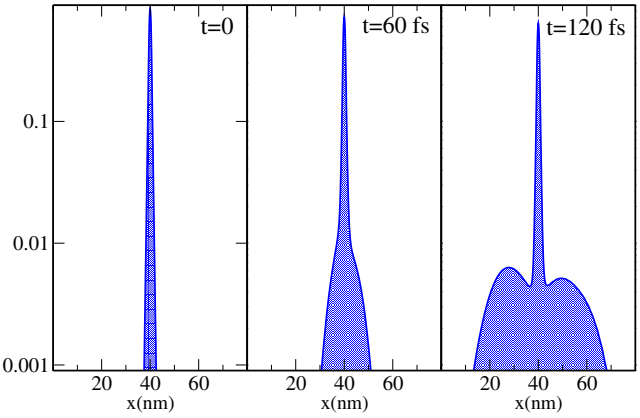

Fig. 2. Single-particle probability density $\int dx_1 |\psi(x_1, x_2, t)|^2$ of finding the trapped electron at different time steps, namely $t = 0$, $t = 60$ fs, and $t = 120$ fs. Note that at $t = 0$ the probability density is given by the square modulus of the wavefunction $\chi_0(x_2)$, and is peaked around the potential well centered at $x_0 = 40$ nm. Here the initial kinetic energy of the incoming carrier is equal to 50 meV.

III. Numerical Approach

The two-particle, time-dependent Schrödinger equation (3) has been solved by means of the Crank-Nicholson finite-difference scheme. The latter has also been used in other works [5], [6] to investigate the quantum dynamics of systems of interacting electrons in semiconductor nanostructures. Within a one-dimensional approach, we have considered an 80 nm-long region and discretized the spatial coordinates of the two carriers with a 640-point grid having a $\Delta x = 0.125$ nm resolution. The time step of the system's evolution has been taken equal to $\Delta t = 0.2$ fs.

By discretizing (3) and taking the unitary evolution operator in the Cailey form in order to guarantee the stability of the

numerical approach, we find

$$\begin{aligned}\psi_{j,l}^{k+1} - A\left(\psi_{j+1,l}^{k+1} - 2\psi_{j,l}^{k+1} + \psi_{j-1,l}^{k+1}\right) \\ -A\left(\psi_{j,l+1}^{k+1} - 2\psi_{j,l}^{k+1} + \psi_{j,l-1}^{k+1}\right) + \frac{i\Delta t}{2\hbar} V_{j,l}\,\psi_{j,l}^{k+1} = \\ \psi_{j,l}^{k} + A\left(\psi_{j+1,l}^{k} - 2\psi_{j,l}^{k} + \psi_{j-1,l}^{k}\right) \\ +A\left(\psi_{j,l+1}^{k} - 2\psi_{j,l}^{k} + \psi_{j,l-1}^{k}\right) - \frac{i\Delta t}{2\hbar} V_{j,l}\,\psi_{j,l}^{k}\,, \end{aligned} \tag{5}$$

where $A = (i\hbar\Delta t)/(4m^*\Delta x^2)$, and $\psi_{j,l}^k$ and $V_{j,l}$ stand for the wavefunction at the time step k and the potential energy involving the well and the Coulomb interaction terms, respectively, both evaluated at the two grid points j and l. Expression (5) represents a linear system of equations that can be written in compact form as

$$\boldsymbol{\psi}^{k+1} = \boldsymbol{M}\boldsymbol{b}^k\,, \tag{6}$$

where $\boldsymbol{b}^k$, the known term at time step k, incorporates the values of ψ that appear at the right hand side of (5), while the unknown quantity is the 640×640-element vector $\boldsymbol{\psi}^{k+1} = (\psi_{0,0}^{k+1}, \psi_{0,1}^{k+1}, \ldots, \psi_{j,l}^{k+1}, \ldots)$ describing the two-particle discretized wavefunction at the $(k+1)$-th time step. Finally, $\boldsymbol{M}$ is a so-called *diagonal-with-fringes* matrix, namely, a matrix with diagonal blocks that are themselves diagonal and sub- and super-diagonal blocks that are diagonal. Such a system has been solved by means of an iterative numerical algorithm based on the Gauss-Seidel scheme by imposing closed boundary conditions, that is, the wavefunction of the system is set equal to zero along the boundaries of the space grid. This procedure allows one to evaluate the time evolution of the quantum state of the two electrons.

IV. Results

At the final time t_f the detrapping probability due to a single scattering event can be evaluated from the wavepacket of the system by taking into account its spectral decomposition in terms of bound and non-bound states, given by (4). Due to the physical and geometrical parameters of the system under investigation, such as the carrier effective mass and trap-potential profile, the function χ_0 is the only eigenfunction of the single-particle Hamiltonian H_0 (2) that corresponds to a bound state describing a trapped carrier. Thus, the square modulus of the coefficient α_0 in (4) can be interpreted as the probability that a single scattering event leaves the trapped electron in the ground energy state when a band electron is injected with energy E_k.

Once the coefficient α_0 is known, the detrapping probability due to successive two-electron interactions can be evaluated. In fact, after the first electron-electron collision has occurred, the new incoming particle, again described by a Gaussian wavepacket w, interacts via the Coulomb potential with an electron which is now in a linear superposition of bound and non-bound states. As expected, the Coulomb scattering between the Gaussian wavepacket of the new injected carrier and the extended states of the other particle does not make the latter to relax while, as indicated above, the interaction of the incoming carrier with the particle in χ_0 has an $|\alpha_0|^2$ probability of leaving the electron state unchanged. Within the assumption of independent scattering events, the probability that a number n of collision leaves the trapped electron in the bound ground state is the product of the probabilities of no excitation in each scattering, namely, $|\alpha_0|^{2n}$. Thus, the quantity

$$P_D = 1 - |\alpha_0|^{2n} \tag{7}$$

represents the probability of finding the initially-trapped electron in an extended state as a consequence of multiple electron-electron scatterings, namely, the detrapping probability.

Fig. 3 shows the dependence of the detrapping probability P_D on the number n of the electrons injected at different values of E_k. As expected, the detrapping is more effective (that is, $|\alpha_0|$ is lower) when the energy of the injected electrons is larger. At a given injection energy, the detrapping probability increases with n and becomes very close to 1 within a few tens of interactions even for values of E_k of the order of the thermal energy. Considering such levels of energy of the band electrons is realistic in the case of amorphous-GST switching devices near threshold or in the snap-back regime, because the voltage across the device is relatively small.

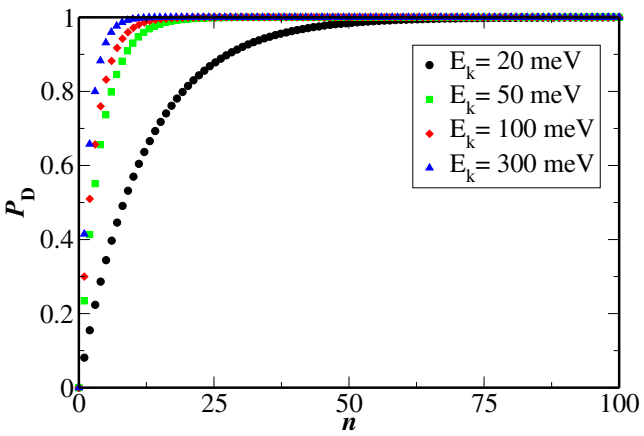

Fig. 3. Detrapping probability as a function of the number of injected electrons evaluated at four different values of the injection energy: 20 meV (circles), 50 meV (squares), 100 meV (diamonds), and 300 meV (triangles).

Thus, the current increase occurring in the snap-back region must be ascribed to a larger number of band electrons rather than to an increase in their velocity [3]. Note that a prescribed value of E_k fixes the electron drift velocity; consequently, the current density is proportional to n. In other terms, the behavior of P_D reported above indicates that the extraction of electrons from the traps sharply increases with the current density due to the carriers belonging to the extended states. Its functional form, an exponential dependence upon n and therefore upon the band-electron current density, is the origin of the function

$$r(I_n) = 1 - \exp(-I_n/I_k) \tag{8}$$

that describes the macroscopic rate used in [4], with I_n the band-electron current and I_k a fitting parameter. Such a rate

connects the generation process induced by the Coulomb interactions between trap and band electrons to the band-electron current. A simplified reasoning that justifies the form of (8) is made in the Appendix. The exponential form of (8) fulfills the sharpness requirement of the trap-to-extended-states transitions, that is essential for the occurrence of the negative-differential resistance in amorphous chalcogenides.

V. Conclusion

The electronic trap-to-band transitions, induced in chalcogenides by the Coulomb interactions of a trap electron with a number of band electrons, have been investigated. We obtained the detrapping probability P_D of such transitions by means of a fully quantum-mechanical approach that makes use of a solver for the two-particle, time-dependent Schrödinger equation. The assumption that a band electron interacts with the trapped one only when an earlier scattering event is over makes it possible to analyze the influence of the conduction-band current on a trapped electron in terms of a number of successive electron-electron interactions.

The numerical results indicate that the probability that controls the generation rate of the electronic trap-to-band transitions is an exponentially-increasing function of J_n, the current density of the conduction-band electrons. In the one-dimensional analysis carried out here it is $I_n = AJ_n$, with A the cross-sectional area of the device. The probability can thus be expressed in terms of I_n. The dependence on I_n in (8) is sufficiently strong to fulfill the sharpness requirements needed to give rise to a negative differential resistance in the device. In fact (as discussed, e.g., in [3]), the higher mobility of the conduction-band electrons is not sufficient in itself to justify the snap-back phenomenon. For the latter to occur it is necessary that the initially-trapped electrons be promoted to the conduction band by a mechanism that depends strongly on the current density. If that happens, the increase in the voltage across the device induced by an increasing current is overcome by a competitive effect, that is, the decrease in the same voltage induced by the sudden increase in the material's conductivity. Such a feed-back mechanism leads to the negative differential resistance experimentally observed in the amorphous-GST devices.

In conclusion, our microscopic analysis of the electron trap-to-band transitions supports and validates the idea that the cooperative effect of the interactions between a number of band electrons and a trap electron provides the self-sustained feedback mechanism leading to the switching phenomenon in amorphous chalcogenides.

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Appendix

In the parabolic-band approximation the conduction-band electrons have a kinetic energy $E_k = \hbar^2 k^2/(2m^*)$. The group velocity corresponding to it is

$$v = \sqrt{\frac{2E_k}{m^*}}\,. \tag{9}$$

Let τ be the time necessary for n equally-spaced band electrons, moving along the x axis with the same velocity (9), to reach the trap's location. The number n is taken high enough to make the detrapping probability significant (refer to Fig. 3). The total charge that crosses a plane normal to x near the trap is $n\,e$, whence the following relation holds:

$$I_n\,\tau = n\,e\,. \tag{10}$$

The above equality is realistic only if τ does not exceed the time $\tau_{\rm ph}$ necessary for the phonon-assisted relaxation process, which tends to bring the trapped electron back to the ground level, to occur. Letting λ be the spacing between two successive incoming electrons, one finds

$$n\,\lambda = \tau\,v\,. \tag{11}$$

Using $E_k = 50$ meV, $m^* = 4 \times 10^{-31}$ kg provides $v = 2 \times 10^7$ cm/s. Then, using $n = 20$, $\tau = \tau_{\rm ph} = 1.5$ ps yields the estimate $\lambda = 15$ nm, significantly larger than both the trap's width and the standard deviation of the conduction-band wavepackets. This is consistent with the assumption that the conduction-band electrons interact with the trapped electron one at the time.

Finally, from the relation $0 \le |\alpha_0|^2 \le 1$ one finds

$$P_D = 1 - \exp(-\sigma n)\,, \qquad \sigma \doteq -2\,\log|\alpha_0| \ge 0\,. \tag{12}$$

Replacing n from (10) yields

$$P_D = 1 - \exp(-I_n/I_k)\,, \tag{13}$$

with $I_k = e/(\sigma\tau)$. Although (13) is identical to (8), the simplifying assumptions involved in the reasoning leading to (13) are many, so that the above should not be considered a formal derivation of (8).

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