Microscopic Description of the Inter-Trap Transitions in *a*-Chalcogenides

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***Abstract*—An important contribution to charge transport in amorphous-chalcogenide materials used for manufacturing memory devices is due to the trap-to-trap transitions. Here the physics of the phenomenon is worked out as a combination of energy and space transitions, and its probability is expressed in closed form in terms of microscopic parameters. The results are useful for setting up the macroscopic master equation to be used in Monte Carlo analysis or TCAD codes.**

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]. An important contribution to carrier transport in chalcogenides is due to electron transitions via localized states (traps) [2]. In fact, in such materials the temperature and field dependences of the conductance show that transport occurs mainly via thermally-activated trap-limited mobility, with electrons moving from one site to another in the band or, at least, above the band-mobility edge [3].

This paper focuses on trap-to-trap transitions, and aims at working out a consistent expression of the current due to them. To this purpose, the localized traps within the chalcogenide material are associated to spatial sites that are labeled with an integer, e.g., i, j, while the volume and trap concentration of the ith site are Ω_i and N_i. A trap is neutral when filled with an electron, positive when empty. Letting $0 \leq \alpha_i \leq 1$ be the fraction of filled traps of the ith site, the current flowing between the ith and jth site is given by the macroscopic master equation (1), whose unknowns are the fractions α_i, α_j:

$$I_{ij} = q\,\bar{N}_i\,\bar{N}_j\left[S^{0+}_{ji}\,\alpha_j\,(1-\alpha_i) - S^{0+}_{ij}\,\alpha_i\,(1-\alpha_j)\right]. \quad (1)$$

In (1) it is $\bar{N}_i = \Omega_i N_i$, $q > 0$ is the electron charge, and S^{0+}_{ij} the probability per unit time that an electron makes a transition from a filled trap belonging to site i to an empty trap belonging to site j (in the symbols used here, the charge states are labeled "0" and "+", respectively). For the applications to Computer-Aided Design it is necessary to express the coefficients of (1) in terms of easily-accessible quantities, like electric potential and temperature. In the literature the probability transition per unit time S^{0+}_{ij} is usually expressed after Miller and Abrahams [4] as

$$S^{0+}_{ij} = \nu_0\,\exp[-r_{ij}/r_0 - q\,(u_i - u_j + |u_i - u_j|)/2], \quad (2)$$

where ν_0 is the attempt-to-escape frequency, r_{ij} the distance between the two trap sites, $u_i = \varphi_i/(k_B T_L)$ the normalized electric potential at the ith site, and r_0 a normalizing factor that depends on the energy barrier existing between the two sites. One notes that in (2) the electric potential plays a role only when $\varphi_i > \varphi_j$. In this paper the form of S^{0+}_{ij} is worked out starting from a microscopic analysis, and compared with the approaches of [4].

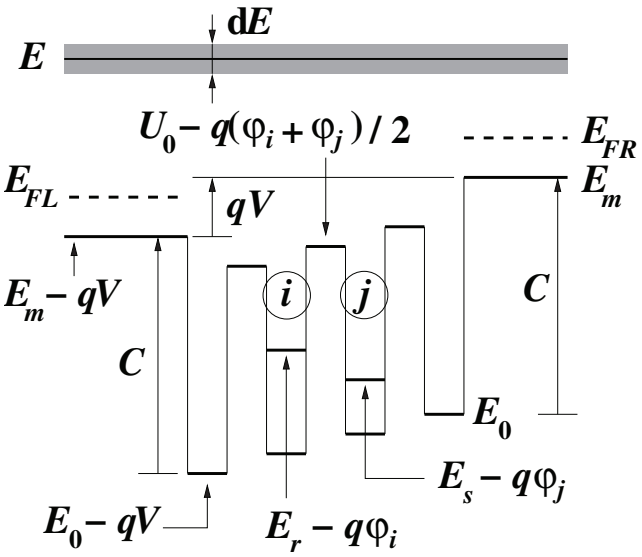

Fig. 1. Potential energy within a one-dimensional schematization of the chalcogenide material in a non-equilibrium condition, with $E_{FR(L)}$ the Fermi level of the right (left) lead. The bottom levels of the conduction band of the left and right lead are shifted by V with respect to each other. The relative shift in the ground levels of two adjacent traps due to the nonuniformity of φ is assumed to equally distribute over the two sides of the barrier between the traps.

II. Model

The process by which an electron moves from the ith to the jth site is described as the combination of phonon absorption, propagation at constant energy E, and phonon emission [5]. The traps are modeled as rectangular wells (this approximation is discussed later). A particle initially localized in an energy state $E_r - q\varphi_i$ of a trap in the ith site makes a transition to an energy state $E_s - q\varphi_j$ of a trap in the jth site, where $r, s = 0, 1, \ldots$ (Fig. 1). In principle, the electron may occupy any of

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the discrete energy states within the trap; however, it will be assumed for simplicity that in a filled trap the electron always belongs to the ground state due to the energy relaxation with the lattice. This approximation is easily removed by assuming that the population of electrons within Ω_i distribute over the trap states according to the Fermi statistics. The energy shift $q(\varphi_i - \varphi_j)$ between the ground levels of two adjacent traps, due to the external potential, is assumed to equally distribute over the two sides of the barrier between the traps. Consequently, the top of the barrier between the two traps has an energy $U_0 - q(\varphi_i + \varphi_j)/2$, with U_0 the energy of the top of the barrier at equilibrium. For the sake of clarity the energy E is drawn in Fig. 1 above the top of all barriers. In the actual cases it may happen for some barrier that $U_0 - q(\varphi_i + \varphi_j)/2 > E$. The important constraint is in fact that E be above the barriers between the device and the external leads; specifically, E must be larger than the the bottom of the conduction band of both left and right lead, otherwise the particle would not be able to propagate: with reference to Fig. 1, $E > E_m - qV$ and $E > E_m$, respectively, with V the voltage drop across the device. The use of the same symbol E_m for the left and right leads implies that they are made of same material. To calculate the transition of an electron from one trap to another it is useful to define $\eta = E_m - E_0 > 0$, with E_0 the ground energy of the traps at $\varphi = 0$. It follows that the wave vector k_L (k_R) to be associated to the electron on the left (right) side of the barrier is $k^2_{L(R)} = (1/\hbar)\,[(2\,m)\,(E - E_m + \eta + q\,\varphi_{i(j)})]^{1/2}$. The propagation of the electron from the left to the right of the barrier, or viceversa, is determined by the transmission coefficient T_{ij}, whose calculation is straightforward. Note that $E_m - U_0 = (E_{\rm vac} - U_0) - (E_{\rm vac} - E_m)$, with $E_{\rm vac}$ the vacuum level. The second term in parentheses at the right hand side of the above is the work function of the lead. By analogy, the first term may be thought of as the electron affinity of the material. Both terms in parentheses are positive. As a consequence, at the interface between the material and the lead a thin barrier is formed (not shown in figure 1), that is crossed by the electrons by tunneling.

Letting $E_r = E_0$, the first part of the transition process from the initial to the final state is assisted by the absorption of a phonon of energy $E - (E_0 - q\,\varphi_i)$. Assuming $V > 0$, the minimum value of E is E_m. Let $P(E_0 - q\varphi_i \rightarrow E)$ be the probability of the transition from $E_0 - q\varphi_i$ to E due to phonon absorption; in the Golden-Rule approximation, the probability of the transition from E to $E_0 - q\varphi_i$, due to the emission of a phonon of energy $E - (E_0 - q\varphi_i)$, is the same as above. Let P_i indicate the common value of the two, that reads

$$P_i = \theta_i\,[\delta(\Delta E - \hbar\,\omega) + \delta(\Delta E + \hbar\,\omega)]\,\Delta t_i\,, \qquad (3)$$

with $\theta_i = (2\,\pi/\hbar)\,|h_i^{(0)}|^2$ an energy over a time, $h_i^{(0)}$ the entry of the perturbation matrix involving the initial and final states of the electron ($[h_i^{(0)}] = {\rm J}$), $\Delta E = E_0 - q\,\varphi_i - E$, $\omega > 0$ the phonon's angular frequency, and Δt_i the duration of the electron-phonon interaction. Similarly, let $P(E' \rightarrow E_0 - q\varphi_j)$ be the probability of an electron transition from the energy E' to the energy $E_0 - q\varphi_j$ due to the emission of a phonon of energy $E' - (E_0 - q\varphi_j)$. The probability of the transition from the energy $E_0 - q\varphi_j$ to the energy E' due to the absorption of a phonon of energy $E' - (E_0 - q\varphi_j)$ is the same as above. The common value of the two is $P_j = \theta_j\,[\delta(\Delta E' - \hbar\,\omega') + \delta(\Delta E' + \hbar\,\omega')]\,\Delta t_j$, with $\theta_j = (2\,\pi/\hbar)\,|h_j^{(0)}|^2$. The meaning of the symbols in the above is analogous to that in (3). The above treatment can be extended to incorporate the multi-phonon absorption/emission processes using, e.g., the multiphonon probability in the single-energy phonon approximation [6].

Let $\Omega_i N_i\,\alpha_i = \bar{N}_i\,\alpha_i$ be the number of filled traps at site i, and $\alpha(E)\,g(E)\,{\rm d}E$ the number of filled states in the interval ${\rm d}E$ around $E > E_m$, with $g(E)$ the density of states and $\alpha(E)$ the fraction of occupied states of the band. Then, let $n^{\rm ph}\,g^{\rm ph}\,{\rm d}\hbar\omega$ be the number of phonons in the interval ${\rm d}\hbar\omega$ centered on the energy $\hbar\omega$, with $n^{\rm ph}(\hbar\omega)$ the phonons' average occupation number and $g^{\rm ph}(\hbar\omega)$ the corresponding density of states. The product $Q_i(E,\omega)\,{\rm d}\omega\,{\rm d}E = \bar{N}_i\,\alpha_i\,P_i\,n^{\rm ph}g^{\rm ph}\,{\rm d}\hbar\omega\,[1 - \alpha(E)]\,g(E)\,{\rm d}E$ is the number of transitions from $E_0 - q\varphi_i$ to the interval ${\rm d}E$ centered on E due to the absorption of the phonons belonging to the interval ${\rm d}\hbar\omega$ centered on $\hbar\omega$. In turn, the product $Q_j(E',\omega')\,{\rm d}\omega'{\rm d}E' = \bar{N}_j\,(1 - \alpha_j)\,P_j\,(n^{\rm ph} + 1)\,g^{\rm ph}\,{\rm d}\hbar\omega'\,\alpha(E')\,g(E')\,{\rm d}E'$ is the number of transitions to $E_0 - q\varphi_j$ from the interval ${\rm d}E'$ centered on E' due to the emission of phonons belonging to the interval ${\rm d}\hbar\omega'$ centered on $\hbar\omega'$. Integrating the product $T_{ij}\,\bar{E}\,\delta(E' - E)\,Q_i\,Q_j\,{\rm d}\omega'\,{\rm d}\omega\,{\rm d}E'\,{\rm d}E$, first over $\hbar\omega$ and $\hbar\omega'$ from 0 to ∞, then over E' from E_m to ∞, yields the number of phonon-assisted transitions from site i to site j associated to the energy E. The factor $\bar{E}\,\delta(E' - E)$, with $\bar{E}$ a constant energy, accounts for the fact that the transmission occurs only for $E' = E > E_m$. Due to the δs in P_i and P_j, the first integration fixes $\hbar\omega$ to $\hbar\omega_i = E - (E_0 - q\,\varphi_i) = E - E_m + \eta + q\,\varphi_i$ in the absorption term, and fixes $\hbar\omega'$ to $\hbar\omega_j = E' - (E_0 - q\,\varphi_j) = E' - E_m + \eta + q\varphi_j$ in the emission term.

If the expressions worked out so far are considered in the equilibrium case, using the principle of microscopic balance with $n_i^{\rm ph} = 1/\{\exp[\hbar\omega_i/(k_B T)] - 1\}$ yields for α_i the Fermi statistics, as should be. In the non-equilibrium case the number Γ_{ij} of the $i \rightarrow j$ transitions differs from the number Γ_{ji} of the $j \rightarrow i$ transitions. Letting $\Delta t_j = \Delta t_i$, defining the dimensionless quantity $G_{ij} = g_i^{\rm ph}\theta_i\,g_j^{\rm ph}\theta_j\,t_P^2$, and indicating the common value with t_P, and remembering that $T_{ji} = T_{ij}$, one finds

$$\begin{aligned}{\rm d}\Gamma_{ij} = \bar{N}_i\,\bar{N}_j\,(1 - \alpha_j)\,\alpha_i\,G_{ij}\,n_i^{\rm ph}\,(n_j^{\rm ph} + 1)\,T_{ij}(E)\times \\ \times\alpha(E)[1 - \alpha(E)]\,\left\{\bar{E}\,g^2(E)\,{\rm d}E\right\}\,, \qquad (4)\end{aligned}$$

while Γ_{ji} is found by interchanging the indices in (4). The current flowing between sites i and j is given by the net number of transitions per unit time multiplied by $-q$. In turn, the net number of transitions per unit time for each energy E is ${\rm d}\Gamma_{ij}/{\rm d}t_P - {\rm d}\Gamma_{ji}/{\rm d}t_P$. As all energies above E_m are

possible, the result of the differentiation must be integrated over E from E_m to ∞, to yield

$$I_{ij} = -q \int_{E_m}^{\infty} \frac{\mathrm{d}}{\mathrm{d}t_P} \left(\Gamma_{ij} - \Gamma_{ji}\right) \mathrm{d}E \,. \tag{5}$$

Comparing (5) with (1) and using (4) yields the coefficients sought:

$$S_{ij}^{0+} = \int_{E_m}^{\infty} F_{ij}\, n_i^{\mathrm{ph}} \left(n_j^{\mathrm{ph}} + 1\right) \mathrm{d}E \,,$$
$$S_{ji}^{0+} = \int_{E_m}^{\infty} F_{ji}\, n_j^{\mathrm{ph}} \left(n_i^{\mathrm{ph}} + 1\right) \mathrm{d}E \,, \tag{6}$$

where $F_{ij} = T_{ij}(E)\,\alpha(E)\left[1-\alpha(E)\right](2\,G_{ij}/t_P)\,\bar{E}\,g^2(E)$ is the inverse of an action, $F_{ji} = F_{ij}$. It follows that (6) are the inverse of a time as should be. The transition rates S_{ij}^{0+}, S_{ji}^{0+} are different from each other due to the extra phonon present in the emission events, and transform into each other when i and j are interchanged. It is worth noting that the assumption that the barriers are rectangular has not played a role so far. In fact, expressions (6) are general and do not depend on how the term T_{ij} is calculated. The use of rectangular barriers will in fact be exploited below to obtain an analytical form of S_{ij}^{0+}, suitable for the implementation into Monte Carlo or general-purpose TCAD simulators.

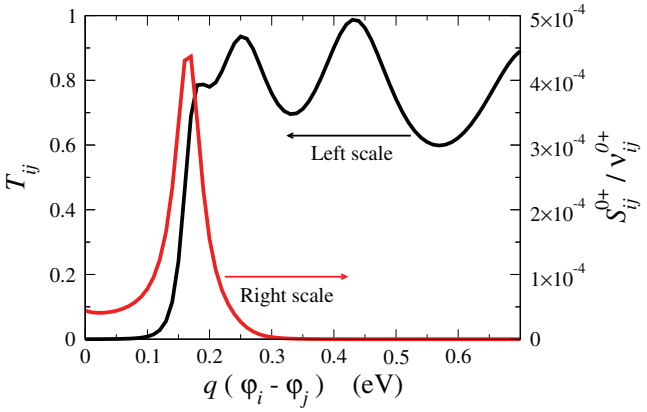

Fig. 2. Normalized probability per unit time $S_{ij}^{0+}/\nu_{ij}^{0+}$ (right scale) and transmission coefficient T_{ij} (left scale) as a function of the energy difference $q\,(\varphi_i - \varphi_j)$ between traps, at $T_L = 300$K. A rectangular barrier with a 4 nm thickness has been considered, with $\eta = 50$ meV, and φ_j has been set to zero. The parameters have been calibrated to obtain both the real-exponential and the oscillatory behavior of T_{ij}, depending on $q\,\varphi_i$.

III. Discussion

As shown earlier, the terms n_i^{ph}, g_i^{ph} depend on $\hbar\omega_i = E - E_0 + q\varphi_i$ while the terms n_j^{ph}, g_j^{ph} depend on $\hbar\omega_j = E - E_0 + q\varphi_j$. It is expected that the average occupation numbers monotonically vanish as E increases. To specify their form it is reasonable to use the equilibrium expression $n_i^{\mathrm{ph}} = 1/\{\exp[\hbar\omega_i/(k_B T)]-1\}$. In contrast, little information is available about the densities of states g_i^{ph} and g_j^{ph}. However, for estimating the dependence of the integrals (6) on the electric potential, one may assume that the dependence of the densities of states on the arguments ($E - E_0 + q\varphi_i$ or $E - E_0 + q\varphi_j$) is weaker than that of n_i^{ph} and n_j^{ph}. The band-density of states $g(E)$ does not depend on the electric potential. It may be approximated by that of free space, this yielding $g^2(E) \propto E$. The remaining factors θ_i, θ_j appearing within F_{ij}, being related to the conservation of momentum of the electron-phonon interaction, are independent of the arguments $E - E_0 + q\,\varphi_i$ or $E - E_0 + q\,\varphi_j$. The dependence of the transmission coefficient T_{ij} on E, φ is calculated by assuming a rectangular barrier as anticipated.

Finally, the band-occupation fraction $\alpha(E)$ is described by a Fermi statistics where the Fermi level is replaced with the local quasi-Fermi level E_{ni}, E_{nj}. In the macroscopic analyses carried out by TCAD simulators, the quasi-Fermi level is available because it is extracted from the carrier concentration and the electric potential. As E_{ni} and E_{nj} are close to each other, the product $\alpha(E, E_{ni})\,[1-\alpha(E, E_{nj})]$ has a peak at $E_{\mathrm{av}} = (E_{ni} + E_{nj})/2$ and an area of the order of $k_B\,T_L$, with T_L the lattice temperature: to obtain an analytical approximation of (6), such a product is approximated with $k_B\,T_L\,\delta(E - E_{\mathrm{av}})$, to yield

$$S_{ij}^{0+} = \nu_{ij}^{0+} \left[T_{ij}\, n_i^{\mathrm{ph}} \left(n_j^{\mathrm{ph}} + 1\right)\right]_{E_{\mathrm{av}}} \,,$$
$$S_{ji}^{0+} = \nu_{ji}^{0+} \left[T_{ji}\, n_j^{\mathrm{ph}} \left(n_i^{\mathrm{ph}} + 1\right)\right]_{E_{\mathrm{av}}} \,, \tag{7}$$

with

$$\nu_{ij}^{0+} = \nu_{ji}^{0+} = \zeta_{ij} k_B T_L \left(g_i^{\mathrm{ph}} g_j^{\mathrm{ph}}\, g^2\right)_{E_{\mathrm{av}}} \,, \tag{8}$$

the attempt-to-escape frequency ($\zeta_{ij} = 2\,\bar{E}\,t_P\,\theta_i\theta_j$ is independent of T_L). The normalized probability per unit time $S_{ij}^{0+}/\nu_{ij}^{0+}$ calculated from (7) is shown on the right scale of Fig. 2 as a function of the energy difference $q\,(\varphi_i - \varphi_j)$ between two adjacent traps, for a barrier whose thickness is 4 nm. The calculation has been carried out by fixing $\varphi_j = 0$. It follows that n_j^{ph} becomes a constant; also, when $\varphi_i \to 0$ the barrier encountered by the electron in the $i \to j$ transition increases. The transmission coefficient T_{ij} is drawn in the same figure on the left scale. The parameters have been calibrated to obtain both the real-exponential behavior of T_{ij}, corresponding to $q\,\varphi_i < 2\,(U_0 - E_{\mathrm{av}})$, and the oscillatory behavior, corresponding to $q\,\varphi_i > 2\,(U_0 - E_{\mathrm{av}})$. It is found that $S_{ij}^{0+}/\nu_{ij}^{0+}$ has a peak near the transition between the real-exponential and the oscillatory behavior of T_{ij}. Its fast drop on the right of the peak is due to the vanishing behavior of $n_i^{\mathrm{ph}} = 1/\{\exp[(E_{\mathrm{av}} - E_0 + q\,\varphi_i)/(k_B T)] - 1\}$, that prevails over the oscillatory behavior of T_{ij}. In turn, the form of the left side of the peak is due to the competition between the decreasing exponential within n_i^{ph} and the increasing one that is present within T_{ij} as long as $q\,\varphi_i < 2\,(U_0 - E_{\mathrm{av}})$. The same quantities as in Fig. 2 are reported in Fig. 3 for different barrier thicknesses and, respectively, in Fig. 4 for different lattice temperatures.

IV. Conclusion

Eqs. (6), along with the expression of F_{ij}, provide the first-principle derivation of the coefficients of the master equation

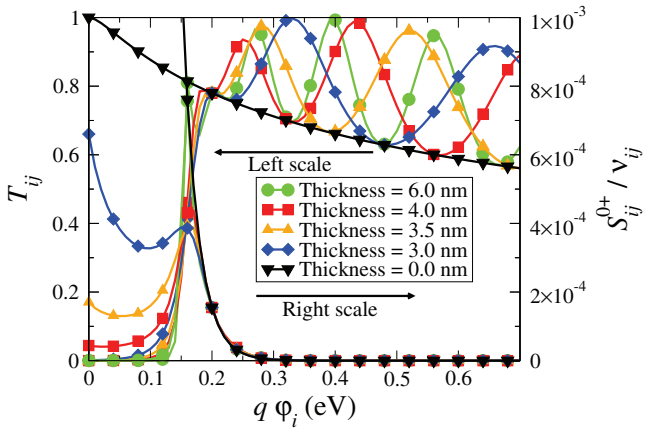

Fig. 3. The same plot as in Fig. 2 at different values of the barrier thickness, with $T_L = 300$K.

for the current (1) in terms of the local potential φ, traps' properties, and other parameters. In turn, (7,8) provide a closed-form simplification of (6) suitable for implementation into Monte Carlo or TCAD device simulators. The behavior of S_{ij}^{0+} differs substantially from that of [4], as shown by Fig. 5 that reports the normalized probability per unit time calculated with (7) and (2). In fact, in (2) the effect of the local potential disappears when $\varphi_j > \varphi_i$, namely, the probability of a phonon emission that brings the electron into the destination site equals unity; also, the real-exponential dependence on r_{ij} used in (2) is correct only in a specific range of the final energy E of an absorption event. The model proposed in this paper does not suffer from the above limitations: both the absorption and emission probabilities are considered, and the propagation at constant energy is accounted for by the transmission coefficient T_{ij} in both the real-exponential and oscillatory cases.

Coupling (1) with the Poisson equation, and using the potential φ_i and the fraction α_i of filled traps as unknowns, makes the model applicable to both Monte Carlo analyses and standard TCAD codes for device design.

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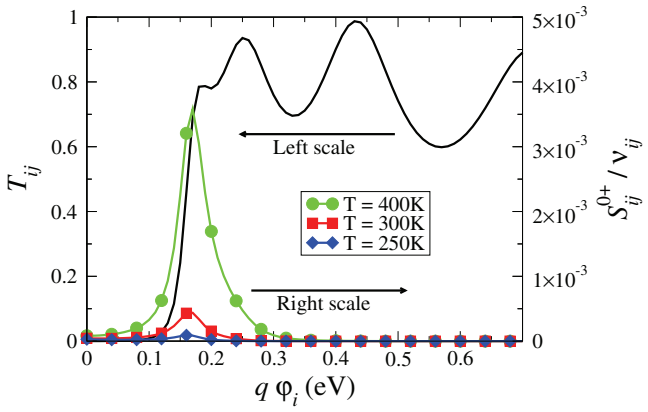

Fig. 4. The same plot as in Fig. 2 at different temperatures. The barrier thickness is 4 nm.

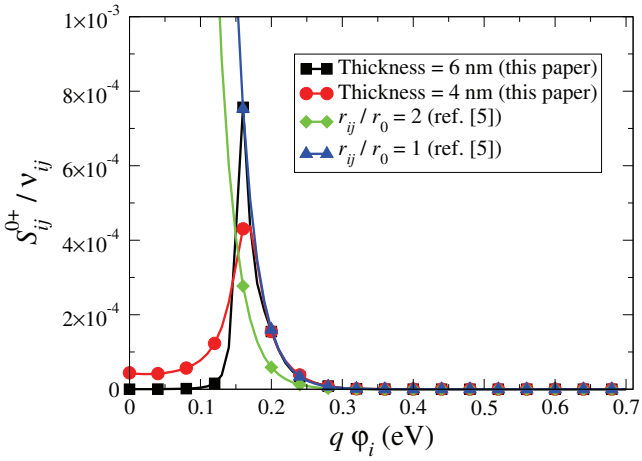

Fig. 5. Comparison between the normalized probability per unit time of Eq. (7) with that of [4], reported here as Eq. (2).