

Charge transport through electrically active interfaces revisited

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Abstract

We present a model of low-field steady and non-steady state charge transport through electrically active interfaces that unifies and extends previous ones. Within the limits of linear response theory, it provides a theoretical framework for the electrical response of material systems with electrically active interfaces. We pay particular attention to the (non-radiative) recombination properties of defects at the interface, thus allowing to characterize surface traps as well as bulk deep levels. The model is of direct application to many materials in polycrystalline phases (Si, GaAs, ZnO, BaTiO₃,...), whose functionality depends upon charge transport properties, which, in turn, are defined by the electronic structure and interface recombination rates. For these materials, the model allows a meaningful interpretation of the electrical response in terms of electronic structure and recombination properties, covering a very broad spectral range (~ 14 orders of magnitude), as well as broad temperature and applied bias ranges.

I. INTRODUCTION

An electrically active interface (EAI) is a boundary between crystals characterized by the presence of surface electronic states that capture and emit electrical charge. This paper presents a new model for the electrical response of one such a structure. The model fully accounts for the effects of charge trapping and emission at the interface, and it allows to identify surface traps through their dynamic signature (energy position and capture cross-section).

When the interface lies between two crystals of the same phase, as in the case of inversion boundaries or grain boundaries within polycrystalline materials, then the structure is called an electrically active homophase interface (EAHI).¹ The electronic structure of EAHIs controls the charge transport properties of a huge range of materials in polycrystalline form (either bulk ceramic or thin film), whose electrical response plays a major role in many modern technologies. Examples include, among many others, Si²⁻⁴ or GaAs^{5,6} for transistors or efficient solar cells, GaN for optoelectronic applications,⁷ ZnO for luminescent devices,⁸ transparent electrodes,⁹ or thin film transistors,¹⁰ SnO₂ for varistors¹¹ or gas sensors,¹² perovskite materials such as BaTiO₃^{13,14} or SrTiO₃¹⁵ for PTC devices, multi-layer capacitors, or ferroelectric memories, or YBa₂Cu₃O_δ for high T_c superconductors.¹⁶ The functional properties of these materials depend crucially upon their interface/depletion layer electronic structure, which, in turn, is defined by their chemistry and microstructure: an understanding of the native defects or impurities which confer functionality to a certain interface electronic structure would be a very first step towards a true electronic structure engineering for this huge class of materials. Therefore, the microscopic origin of the electrical activity in EAHIs has been the subject of intensive theoretical and experimental research in the last years. For example, the electrical activity of grain boundaries in SrTiO₃ has been analyzed¹⁵ in terms of the intrinsic nonstoichiometry of these interfaces; calcium doping has been found¹⁶ to passivate YBa₂Cu₃O_δ grain boundaries hence reducing the barrier height and improving charge transport; and Bi-doped *n*-type ZnO has been the subject of recent experimental^{17,18} and theoretical¹⁹ studies, leading to a better understanding of the role of Bi as electrical activator,¹⁸ and to the proposal that an interfacial Bi_{Zn}+V_{Zn}+O_i complex is responsible for the electrical activity of interfaces in this system.¹⁹ In the context of these research efforts, one important achievement is the recent development of powerful spectroscopic scanning

probe techniques, based on the concepts of admittance spectroscopy,²⁰⁻²² which allow for the study of electronic structures at single interfaces. However, these techniques rely on highly simplified models of the electrical behaviour of a charged interface. Hence, despite its great potential, it is widely recognized^{20,22} that a comprehensive theoretical framework is needed in order to meaningfully interpret the local electrical response of the interface, hence allowing the relevant physical information to be extracted. In this sense, a comprehensive model for the low-field charge transport through EAHI has become increasingly necessary in recent years.

The interface/depletion layer electronic structure of an EAHI has been frequently described through a geometrical model called double Schottky barrier (DSB) model. The DSB structure has been found to accurately represent all the relevant features of electrically active interfaces in materials such as Si,^{2,4} Ge,²³ GaN,⁷ ZnO,^{17,19} or even in carbon nanotubes.²⁴ It also provides accurate description of charge transport in ionic conductors such as zirconia,²⁵ one of the fastest known ionic conductors and one of the most widely used in fuel cell technology. Additionally, the authors have recently shown²⁶ that a proper analysis of non-steady state charge transport within the DSB model is able to explain the commonly observed frequency-domain non-Debye and time-domain non-exponential dielectric response of polycrystalline materials. We have also shown how this kind of analysis, based on a DSB model, provides empirical evidence in favour of the recently predicted²⁷ lack of a dominant shallow donor in ZnO.²⁶ In the case of the ferroelectric perovskites such as BaTiO₃ or SrTiO₃, the exact conditions of validity of the DSB model are currently under active discussion: while the DSB model provides an accurate macroscopic description of transport properties in BaTiO₃,^{13,28} some recent works suggest that the model is microscopically inaccurate⁶⁸ in the case of SrTiO₃.^{15,29} Note that, in the case of scanning probe spectroscopic techniques, the highly localized nature of the electrical measurements, which involve just one interface in contrast with a measurement on a ceramic sample which involves hundreds, makes it further reasonable to represent the EAI as a double Schottky barrier. Charge transport through double Schottky barriers was first studied in the works of Pike and Seager,^{30,31} and two general models were established independently by Pike³² (neglecting deep levels in the depletion layers) and by Blatter and Greuter³³ (incorporating the effect of deep levels). Very similar theoretical frameworks were later applied to single sided Schottky barriers.^{34,35} The formalisms developed in these models are different and, in fact, are not known to be

equivalent.³⁶ Most important, all models assume a simplifying assumption in which the interface density of states, whatever its shape and value, is characterized by a single, constant capture cross-section. This prevents the models from being useful to analyze interface recombination properties, which critically determine charge transport.

In this paper, we present a model for charge transport that, by introducing an energy distributed capture cross-section, takes recombination properties at the interface into account. The model provides the framework for a meaningful physical interpretation of electrical spectroscopic techniques, such as admittance spectroscopy or the recently developed scanning probe spectroscopic techniques. It provides detailed guidance to assess when these processes, which have been commonly neglected,^{7,34} introduce a relevant contribution to current flow and, therefore, must be taken into account. Certain simple limits of this formalism have been already introduced,^{18,26,37,38} but this is the first report of the whole theoretical framework in its full generality. The plan of the paper is as follows: In section II we briefly summarize the DSB model. In sec. III we introduce the distributed capture coefficient and obtain the relevant steady-state charge transport properties. In section IV we present the formalism for non-steady state transport properties, in the case of negligible concentration of deep donors in the depletion region: this simplified case allows an explicit analytical calculation of the system's admittance. In section V we present the extension of the previous formalism to the more general and realistic case in which deep donors play a relevant role. Then, section VI presents our conclusions. Three appendixes present some relevant calculational details, and provide additional arguments and explanations on certain aspects of the model. Additional applications of the formalism, as well as a detailed exposition of the broadband spectroscopic technique that the model originates, will be the subject of a forthcoming paper.

II. DOUBLE SCHOTTKY BARRIER MODEL

The double Schottky barrier model is a geometrical electronic structure model that interrelates three different microscopic regions around any electrically active interface (see Fig. 1, depicted for an n -type material): the interface or grain boundary (GB), the depletion region around the GB, and the bulk grain region. The interface becomes electrically active by trapping majority carriers, thereby originating the DSB, and its electronic structure controls dc and ac conduction, barrier height, barrier pinning, and charge transport properties.

The model is explicitly formulated for grain boundaries or any other type of double-sided interfaces, but it can be easily adapted for the case of Schottky barriers in diodes or any kind of metal-semiconductor junctions.

Figure 1 depicts the typical band geometry around a GB in a polycrystalline semiconductor. The notation is the same for one-sided junctions (such as Schottky barriers), which would be essentially represented by the right side of this diagram. A steady-state situation, under a constant bias V , is represented in Fig. 1. Under a constant bias $V = V_0$, the geometry of the conduction band is $E_C(x, V) = -q_e \times \Phi(x, V)$, the associated electrostatic potential is $\Phi(x, V)$, and the barrier height is $\Phi_B(V) \equiv -\Phi(x, V)|_{x=0}$. The carrier concentration in the conduction band is $N_0 \equiv n$, defining the Fermi level position in the bulk $E_F(-\infty)$ [with $\xi = E_C(-\infty) - E_F(-\infty)$]. We assume that $N_0 = N_S - N_A$, where N_S is the density of an everywhere ionized shallow donor of energy $E_0(x, V)$ while N_A is the density of an eventual shallow acceptor. Deep lying defects are assumed to be donor-like (neutral when occupied), and to have densities N_α capture cross-sections σ_α and energies $E_\alpha(x, V)$ where $\alpha = 1 \dots d$ numbered from shallower to deeper. The junction is assumed homogeneous, so the defect densities are constant throughout. The conduction band and the defect energies bend in parallel, so the energy separation $\xi_\alpha \equiv E_C(x, V) - E_\alpha(x, V)$ ($\alpha = 0, \dots, d$) remains constant everywhere for any bias. An interface surface density of states (IDOS) $N_S(E)$ exists at the interface, so that $N_S(E)dE$ is the number of available energy levels between E and $E + dE$ by unit area. Associated with this IDOS is an interface distribution of capture cross sections given by a certain function $\sigma_S(E)$. We henceforth call Q_S the total charge per unit area trapped in the interface. Free carriers are assumed to be negligible within the well defined limits $x = -x_{L0}$ and $x = x_{R0}$ of the space charge (depletion) region, where neutrality is maintained between the positive screening charge due to ionized donors and the excess negative charge trapped in the interface; away from this region into the bulk, the positive charge due to the shallow donor is balanced by electrons in the conduction band. Deep acceptor defects can be incorporated to the model by subtracting their density from that of the everywhere ionized shallow defect, and treating them as donors.

In a steady state, the occupation statistics of all these states can be described by a quasi-Fermi level $E_F(x, V, Q_S)$ that, under the homogeneous junction hypothesis, can be written as:³⁹

$$E_{Fi}(V, Q_S) \equiv E_F(x, V, Q_S)|_{x=0}, \quad (3)$$

hence introducing the convention of attaching a subscript i to any quantity specifically evaluated at the interface. Now, under a constant $V = V_0$, it is possible to evaluate the quantity V_{1i} , which happens to depend on the applied bias only:^{32,40}

$$\begin{aligned} q_e V_{1i}(V_0) &\equiv q_e V_1(x, V_0)|_{x=0} \\ &= k_B T \ln(2/(1 + e^{-q_e V_0/k_B T})), \end{aligned} \quad (4)$$

Therefore, if we fix the energy origin in the conduction band of the direct biased side,⁶⁹ the quasi-Fermi level at the interface in steady state may be written as

$$E_{Fi}(V_0) = -\xi - q_e V_{1i}(V_0), \quad (5)$$

where we write V_0 to emphasize that this expression is valid only in steady state. However, for the quantities, explicitly evaluated in the interface, it is much more convenient to fix the energy origin in the top of the valence band at the interface, because is with respect to this origin that the IDOS $N_S(E)$ is constant through the subsequent dynamic evolution of the barrier. Therefore, for any interface quantity, we take $E_V(x)|_{x=0} = 0$ and we write

$$E_{Fi} = E_{Fg} - q_e \Phi_B - q_e V_{1i}, \quad (6)$$

where

$$E_{Fg} = E_G - \xi \quad (7)$$

is the Fermi level in the bulk crystal given with respect to the valence band in the direct biased side. E_G is the band gap. We can now write:

$$\begin{aligned} -Q_S &\equiv -Q_S(V; N_S(E)) \\ &= q_e \int_{E_V}^{E_C} N_S(E) f_{Fi}(E, E_{Fi}) dE, \end{aligned} \quad (8)$$

where $f_{Fi}(E, E_{Fi})$ is the interface Fermi distribution function, which depends upon the applied bias through Eq. (6) for E_{Fi} . Please note that both the quantity V_{1i} and the barrier height Φ_B depend upon the bias V .

The DSB geometry is found by solving the Poisson equation for the potential $\Phi(x, V)$ in $-x_{L0} \leq x \leq x_{R0}$, with boundary conditions $\Phi(-\infty) = \Phi(-x_{L0}) = 0$ and $\Phi(+\infty) = \Phi(x_{R0}) = V (> 0)$. The corresponding charge density is non-uniform due the spatial variation of the defect energies E_α and the Fermi level E_F inside the Fermi distribution function $f_F(E_\alpha, E_F)$:

$$\rho(x) = \sum_{\nu=0}^d Q_\nu(x) = \sum_{\nu=0}^d q_e N_\nu^+(x), \quad (9)$$

where

$$Q_\nu(x) = q_e N_\nu^+(x) = q_e N_\nu [1 - f_{F,\nu}(E_\nu, E_F; x)], \quad (10)$$

$$f_{F,\nu}(E_\nu, E_F; x) = \frac{1}{1 + g_\nu \exp[(E_\nu(x) - \xi(x))/(k_B T)]}, \quad (11)$$

where g_ν is the degeneration factor, essentially equal to the inverse of the degeneration of the level.⁴¹ The quantity $E_\nu(x)$ is given by $E_\nu(x) = E_C(x, V) - \varepsilon_\nu = -q_e \Phi(x, V) - \varepsilon_\nu$. Note that the charges $Q_\nu(x)$, associated with each of the deep levels in the depletion layers, and defined through Eq. (10), are actually *volume charge densities*. At this point we also introduce the densities

$$Q_{L\nu} \equiv \int_{-\infty}^0 Q_\nu(x) dx \quad \text{and} \quad Q_{R\nu} \equiv \int_0^{+\infty} Q_\nu(x) dx, \quad (12)$$

which represent a *charge per unit area* associated with each deep level, as well as the total charges per unit area

$$Q_L = \sum_{\nu=0}^d Q_{L\nu} \quad \text{and} \quad Q_R = \sum_{\nu=0}^d Q_{R\nu}, \quad (13)$$

which allow us to write the electroneutrality condition as

$$Q_S = Q_R + Q_L. \quad (14)$$

At this point the Schottky approximation is assumed, turning the charge density into a sum of uniform regions:

$$\rho(x) = q_e \sum_{\alpha=0}^d N_\alpha (\theta(x + x_{L\alpha}) - \theta(x - x_{R\alpha})), \quad (15)$$

the total charges per unit area at the edges of the depletion region into

$$Q_R = q_e \sum_{\nu=0}^d N_\nu x_{R\nu}, \quad Q_L = q_e \sum_{\nu=0}^d N_\nu x_{L\nu}, \quad (16)$$

and, finally, the solution of the Poisson equation into a sum of parabolas:

$$\Phi(x, V) = \frac{-q_e}{2\varepsilon_0\varepsilon_r} \sum_{\alpha=0}^d N_\alpha \theta(x + x_{L\alpha})(x + x_{L\alpha})^2 \quad (17)$$

for $-x_{L0} \leq x \leq 0$, and

$$\Phi(x, V) = V - \frac{q_e}{2\varepsilon_0\varepsilon_r} \sum_{\alpha=0}^d N_\alpha (1 - \theta(x - x_{R\alpha}))(x - x_{R\alpha})^2 \quad (18)$$

for $0 \leq x \leq x_{R0}$. The energy zero lies at the bottom of the conduction band in the direct-biased side (see Note 65). The equations that determine the $2d + 3$ unknowns $x_{L\alpha}$, $x_{R\alpha}$ and Φ_B ($\alpha = 0, \dots, d$), were written and solved by Blatter and Greuter,³³ who obtained:

$$\Phi_B(V, Q_S) = \frac{V_C}{4} \left(1 - \frac{V}{V_C}\right)^2 + \frac{1}{q_e \gamma} \sum_{\nu=1}^d \gamma_\nu \varepsilon'_\nu, \quad (19)$$

where $\gamma_\nu = q_e N_\nu / \varepsilon_0 \varepsilon_r$,

$$V_C = \frac{1}{2\gamma} \left(\frac{Q_S^2}{\varepsilon_0 \varepsilon_r} \right)^2, \quad \gamma = \sum_{\nu=0}^d \gamma_\nu, \quad (20)$$

and

$$\varepsilon'_\nu \equiv \xi_\nu - \xi, \quad \forall \nu \geq 1. \quad (21)$$

Equations (19) and (20) imply that any increase in V tends to reduce the barrier height but, at the same time, by dragging an increased portion of $N_S(E)$ below E_{Fi} , it also tends to increase the trapped charge and, therefore, the very barrier height. From a computational point of view this means that the quantities Q_S and Φ_B must be found in a self-consistent calculation for each value of the bias. From a physical point of view, this effect is responsible for the so called *strong barrier pinning*, a phenomenon whose practical and theoretical implications have been recently discussed.³⁷

III. STEADY STATE CHARGE TRANSPORT

The seminal work of Taylor, Odell, and Fan⁴² on polycrystalline Ge was the first on considering charge transport through EAHIs from the point of view of electrostatic barriers at

the interfaces. These authors assumed a diffusion mechanism for charge transport, and completely neglected any effect due to carrier recombination at the interface. It was Mueller⁴³ who first considered the thermionic emission mechanism and incorporated the recombination processes into the theory. Since then, a number of works have evaluated many transport mechanisms (such as tunnel effect or drift-diffusion) in many materials (Si, Ge, ZnO, SnO₂, BaTiO₃),⁴⁴⁻⁴⁷ finding that the thermionic emission mechanism is the most suitable one as long as $q_e V < E_G$. We therefore start from the thermionic emission mechanism, modifying it to include the effect of recombination processes at the interface. The carriers with enough thermal energy to surmount the barrier are given by

$$J_{inc,LR} = A \exp [-(\xi + q_e \Phi_B)/k_B T] \quad (22)$$

and

$$J_{inc,RL} = A \exp [-(\xi + q_e \Phi_B + q_e V)/k_B T], \quad (23)$$

where $A \equiv A^* T^2$ where A^* is Richardson's constant. In these equations L and R stand from left and right side in Fig. (1) so, e.g., $J_{inc,LR}$ means the current travelling from left to right. We also need to evaluate the amount of charge trapped at and the amount of charge emitted from the interface in states between E and $E + dE$. These quantities are:

$$dJ_{capt} = q_e c_S(E) n p_t(E) dE, \quad (24)$$

and

$$dJ_{emis} = q_e e_S(E) n_t(E) dE, \quad (25)$$

where n is the free electron density, $n_t(E) = N_S(E) \times f_{Fi}(E, E_{Fi})$ is the density of electrons trapped at the interface (occupied interface states), and $p_t(E) = N_S(E) \times (1 - f_{Fi}(E, E_{Fi})) = N_S(E) - n_t(E)$ is the density of empty interface states. These equations actually define the capture and emission coefficients, where the capture coefficient is given by

$$c_S \equiv c_S(E) = \sigma_S(E) v_{th}. \quad (26)$$

Please, note that we have introduced an energy dependent capture coefficient coming from an energy dependent capture cross section $\sigma_S(E)$. There is convincing evidence⁴⁸⁻⁵⁰

that recombination at the interfaces and in the depletion layers of material systems with EAHIs proceeds chiefly via a non-radiative multi-phonon emission mechanism.^{51,52} Atomistic models of this type of recombination events⁵³⁻⁵⁵ clearly demonstrate the strong dependence of the capture cross-section upon the atomic-scale properties of the defect. Different defects are therefore expected to present very different recombination properties, i.e., very different capture cross-section. However, up to now, all the models attempting to describe charge recombination at an EAI have arbitrarily assumed a constant value for $\sigma_S(E)$. When the main current concern is to identify the defects that confer determined properties to a particular interface, this assumption is clearly untenable. The actual IDOS will be determined by the distribution of intrinsic and extrinsic defects, and each of these defects will be characterized by a particular recombination behavior, as a function of the atomic-scale properties of the defect. The dynamic response of the various defects needs by no means be the same. In order to illustrate the relevance of this point, let us consider passivation of polycrystalline Si, which is a major issue in the search for cheap and effective materials for solar cells.⁵⁶ Admittance spectroscopy measurements of poly-Si properties, interpreted within the current models, do not distinguish between highly dense defects with low recombination activity or diluted defects with high recombination rates. The essential physics of the process is therefore lost. A complete picture should account not only for the densities and energies of the various defect species, but also for their dynamic (recombination) properties. Introduction of a distributed capture cross-section is therefore a step towards a better understanding of interface charge dynamics and a better determination of these dynamics from electric measurements.

The product $q_e v_{th} n$ represents the total charge per unit time and unit area available to be trapped at the interface. Therefore, we can use Eqs. (22), (23), and (4) to write (in steady state):

$$\begin{aligned}
 dJ_{capt} &= A\sigma_S(E)N_S(E)(1 - f_{Fi}(E, E_{Fi})) \\
 &\quad \times (1 + \exp(-q_e V/k_B T)) \\
 &\quad \times \exp[-(\xi + q_e \Phi_B)/k_B T] dE.
 \end{aligned}
 \tag{27}$$

The detailed balance condition in thermodynamic equilibrium imposes the following relation between the capture cross-section and the emission coefficient:

$$e_S \equiv e_S(E) = \sigma_S(E)v_{th}ne^{-(E_{Fi}-E)/k_B T},
 \tag{28}$$

so, using Eqs. (6) y (7), we write:

$$dJ_{emis} = 2A\sigma_S(E)N_S(E)(1 - f_{Fi}(E, E_{Fi})) \times e^{-(\xi+q_e\Phi_B+q_eV_{1i})/k_B T} dE \quad (29)$$

The total current density flowing through the external measurement circuit is therefore

$$\begin{aligned} J_R &= J_{inc,LR} - J_{inc,RL} + \frac{1}{2} \int dJ_{emis}dE - \int dJ_{capt,LR}dE \\ &= A [1 - \exp(-q_eV/k_B T)] \exp[-(\xi + q_e\Phi_B)/k_B T] \\ &\quad + A \exp[-(\xi + q_e\Phi_B)/k_B T] \times \int \sigma_S(E)N_S(E)(1 - f_{Fi}(E, E_{Fi})) [\exp(-q_eV_{1i}/k_B T) - 1]. \end{aligned} \quad (30)$$

Now, using Eq. (4) and defining a modified capture cross section as

$$\hat{c} = \int_{E_V}^{E_C} \sigma_S(E)N_S(E)(1 - f_{Fi}(E, E_{Fi})), \quad (31)$$

we can write the simple expression

$$\begin{aligned} J_R(V_0, \Phi_B) &= A e^{-(\xi+q_e\Phi_B)/k_B T} \left(1 - \frac{\hat{c}}{2}\right) \\ &\quad \times \left(1 - e^{-q_eV_0/k_B T}\right) \end{aligned} \quad (32)$$

where we have written V_0 instead of V to emphasize the steady-state nature of this equation. The modified capture coefficient \hat{c} depends upon the amount of *unoccupied* states at the interface and, therefore, upon the applied bias (indirectly through the Fermi function). Note that this model for steady-state charge transport is not valid under high field regimes $q_eV \approx E_G$.^{57,58}

It should be stressed that the presence of the energy dependent capture cross section $\sigma_S(E)$ below the integral in Eq. (31) has non trivial consequences: it can not be factored out from the integrals as in previous models.^{32,33} This modifies all the calculations, as well as the final expressions for the electrical response.

IV. NON-STEADY STATE TRANSPORT WITHOUT DEEP LEVELS

We will study the non-steady state response of a DSB within linear response theory. This means that we perturb the steady state conditions with a time-dependent harmonic signal

$$V \equiv V(t) = V_0 + \Delta V = V_0 + \tilde{V}e^{i\omega t}, \quad (33)$$

which is small in the sense that

$$\tilde{V} \ll k_B T, \quad (34)$$

and we expand all quantities in a Taylor series around the steady state conditions retaining only those terms that are linear in ΔV . As long as Eq. (34) is satisfied, linear response theory provides a very general and accurate framework. The very few treatments that have analyzed non small-signal electrical responses,^{37,59} only deal with very restricted sets of experimental conditions.

Under excitation (33), all quantities become armonically time-dependent: $\Phi_0(x) \equiv \Phi(x, V)|_{V=V_0} \Rightarrow \Phi(x, t) = \Phi_0(x) - \Delta\Phi(x, t) = \Phi_0(x) - \tilde{\Phi}(x)e^{i\omega t}$, $Q_{S0} \equiv Q_S(V)|_{V=V_0} \Rightarrow Q_S(t) = Q_{S0} + \Delta Q_S = Q_{S0} + \tilde{Q}_S e^{i\omega t}$, $V_{1i0} \equiv V_{1i}(V)|_{V=V_0} \Rightarrow V_{1i}(t) = V_{1i0} + \Delta V_{1i} = V_{1i0} + \tilde{V}_{1i} e^{i\omega t}$, or $Q_{\nu 0}(x) \equiv Q_\nu(x, V)|_{V=V_0} \Rightarrow Q_\nu(x, t) = Q_{\nu 0}(x) + \Delta Q_\nu(x, t) = Q_{\nu 0}(x) + \tilde{Q}_\nu(x) e^{i\omega t}$. We distinguish with a zero subscript the stationary part of the armonic time dependent quantities.⁷⁰ Note that also the Fermi distribution function f_{Fi} acquires a time dependent component, in such a way that the steady-state distribution $f_{Fi0}(E, E_{Fi0}) \equiv f_{Fi}(E, E_{Fi}; V)|_{V=V_0}$ becomes t-dependent: $f_{Fi}(t) = f_{Fi0}(E, E_{Fi0}) + \Delta f_{Fi}(t) = f_{Fi0}(E, E_{Fi0}) + \tilde{f}_{Fi} e^{i\omega t}$.

Now, under the transient regime imposed by Eq. (33), two different types of oscillating currents appear: (1) *Transport currents*, which are oscillating currents originated in the steady state conduction current J_{R0} of Eq. (32), which is now also time-dependent: $J_{R0} \Rightarrow J_R(t) = J_{R0} + \Delta J_R = J_{R0} + \tilde{J}_R e^{i\omega t}$. (2) *Displacement currents*, due to the oscilation of the free charge densities Q_R and Q_L at the limits of the space charge region. These currents are intrinsically tied to the non-steady state regime and they did not exist at all under steady state conditions. The total current is therefore

$$J(t) = J_R(t) + J_{Rd}(t) = J_R + \dot{Q}_R, \quad (35)$$

where the transport component J_R is given by Eq. (30), while the displacement component J_{Rd} is given by

$$J_{Rd} \equiv \frac{d}{dt} \sqrt{2q_e \varepsilon_0 \varepsilon_r N_0 (\Phi_B + V)}$$

$$= \frac{C_R}{q_e} \left\{ \left(\frac{\partial \Phi_B}{\partial Q_S} \right) \dot{Q} + \left(\frac{\partial \Phi_B}{\partial V} \right) \dot{V} + q_e \dot{V} \right\}. \quad (36)$$

We now proceed by expanding $J(t)$ in Taylor series around its steady state value, retaining only the terms linear in $\Delta V(t)$. Our aim is then to factorize ΔV and obtain the admittance as $\Delta J/\Delta V$. Actually, in the case without deep levels, Eq. (18) greatly simplifies and the partial derivatives in Eq. (36) become straightforward. This allows to write an explicit expression for Eq. (36), to first order in ΔV :

$$J_{Rd} = \dot{Q}_R = i\omega \Delta Q_R = \frac{i\omega C_R}{C_L + C_R} \Delta Q_S + \frac{i\omega C_L C_R}{C_L + C_R} \Delta V. \quad (37)$$

Where we have introduced the geometrical capacitances of the direct and reverse biased sides of the depletion layer

$$C_L(V) = \frac{\varepsilon_0 \varepsilon_r}{x_{L0}(V)} = \sqrt{\frac{q_e \varepsilon_0 \varepsilon_r N_0}{2\Phi_B}}, \quad (38)$$

$$C_R(V) = \frac{\varepsilon_0 \varepsilon_r}{x_{R0}(V)} = \sqrt{\frac{q_e \varepsilon_0 \varepsilon_r N_0}{2(\Phi_B + V)}}. \quad (39)$$

Analogously, we can expand $\Phi_B(t)$ and $q_e V_{1i}(t)$ in Taylor series up to first order in ΔV . The expression for $\Phi_B(t)$ is straightforward:

$$\begin{aligned} \Phi_B(t) &= \Phi_{B0} - \Delta \Phi_B = \Phi_{B0} - \tilde{\Phi}_B e^{i\omega t} \\ &= \Phi_{B0} - \frac{C_{R0}}{C_{L0} + C_{R0}} \Delta V + \frac{1}{C_{L0} + C_{R0}} \Delta Q_S, \end{aligned} \quad (40)$$

which may be written as

$$-\Delta \Phi_B = \frac{\Delta Q_R}{C_{R0}} - \Delta V = \frac{\Delta Q_L}{C_{L0}}. \quad (41)$$

The calculation for $q_e V_{1i}(t)$ is not so straightforward, and is presented in Appendix A. The result is:

$$\begin{aligned} q_e V_{1i}(E, t) &= q_e V_{1i0} + \frac{C_{R0}}{C_{L0} + C_{R0}} q_e \Delta V \\ &\quad - \frac{q_e}{C_{L0} + C_{R0}} \Delta Q_S \\ &\quad + \frac{k_B T}{q_e N_S(E) f'_{F_{i0}}} \Delta q_S(E), \end{aligned} \quad (42)$$

where the function $q_S(E)$ has been introduced, whose dimensions are *charge/(area × energy)*. It represents the amount of charge per unit area trapped at the interface in

electronic states within a range dE around E . Therefore, the total charge per unit area at the interface is obtained as

$$Q_S = \int_{E_V}^{E_C} q_S(E) dE. \quad (43)$$

Recall that Q_S (hence also $q_S(E)$) are functions of the bias and the barrier height: $Q_S \equiv Q_S(V, \Phi_B)$.

Equations (37)-(40), and (42), involve a crucial term: $\Delta Q_S \equiv \Delta Q_S(t) \equiv \Delta Q_S(t; V, \Phi_B)$, representing the oscillation of the interface trapped charge and, therefore, containing all the information about the electrical dynamics of the interface. The calculation of the quantity ΔQ_S follows the ideas originally introduced by Pike,³² modified in such a way so as to incorporate a distribution of interface recombination properties. It is given in Appendix B. The result is that we can describe interface dynamics through a complex capacitance $C_Q(\omega) \equiv C_Q(\omega; V_0, \Phi_{B0})$, which contains all the information about the interface electronic structure and recombination properties

$$\Delta Q_S(t) = C_Q(\omega) \Delta V(t), \quad (44)$$

and which is given by Eqs. (B2)-(B5). With the aid of Eqs. (40), (42), (44), and (A13), we can now expand the transport component J_R in Eq. (35) [which, in turn, is given by Eq. (30)], in Taylor series around the steady state values (see Appendix C) obtaining:

$$\begin{aligned} Y(V_0, \omega) = & G_0 + \frac{q_e J_0 (C_{Q0} - C_Q(\omega))}{k_B T (C_{L0} + C_{R0})} \\ & - \left[\frac{1}{2\tau_{Fi0}} \left(1 + \frac{2}{1 + e^{-q_e V_0 / k_B T}} \right) + \frac{q_e^2 N_{T1}(E_{Fi0})}{2(C_{L0} + C_{R0})} \right] (C_{Q0} - C_Q(\omega)) \\ & + \frac{i\omega C_{R0} C_Q(\omega)}{C_{L0} + C_{R0}} + i\omega C_{s0}, \end{aligned} \quad (45)$$

where $J_0 \equiv J_0^{tot} = J_{R0}^{trav} + J_{R0}^{ce}$ is given by Eq. (32), while the steady state conductance, limit $\omega \rightarrow 0$ of Eq. (45), is given by:

$$\begin{aligned} G_0 = & \left[\frac{q_e J_0}{k_B T (C_{L0} + C_{R0})} - \frac{q_e^2 N_{T1}(E_{Fi0})}{2(C_{L0} + C_{R0})} \right] \\ & \times (C_{R0} - C_{Q0}) + \frac{C_{Q0}}{2\tau_{Fi0}} \left(1 + \frac{2}{1 + e^{-q_e V_0 / k_B T}} \right) \\ & + \frac{q_e A}{k_B T} e^{-(\xi + q_e \Phi_{B0} + q_e V_0) / k_B T}. \end{aligned} \quad (46)$$

In these expressions we have used Eqs. (B3), (C3), and (C4). Also, we have introduced the total series geometrical capacitance:

$$C_s \equiv C_s(V, \Phi_B) = \frac{C_L C_R}{C_L + C_R}. \quad (47)$$

V. NON-STEADY STATE CHARGE TRANSPORT IN THE PRESENCE OF DEEP LEVELS

A. Bulk trap dynamics

Under the transient conditions imposed by Eqs. (33) and (34), the Fermi distribution function for the deep traps becomes time dependent $f_{F\nu} \equiv f_{F\nu}(E_\nu, E_F; x, t) \equiv f_{F\nu}(x, t)$:

$$\begin{aligned} E_\nu(x) &\Rightarrow E_\nu(x, t) \\ \xi(x) &\Rightarrow \xi(x, t) \\ f_{F\nu 0}(x) \equiv f_{F\nu}(x, V_0) &\Rightarrow f_{F\nu}(x, t) = f_{F\nu 0}(x) + \tilde{f}_{F\nu} e^{i\omega t}. \end{aligned} \quad (48)$$

Note that the time-dependence of the Fermi distribution function has different origins in the case of the bulk levels than in the case of the interface. Under the transient conditions given by Eqs. (33) and (34), the function

$$f_{Fi}(E, E_{Fi}) = \frac{1}{1 + \exp[(E - E_{Fi})/k_B T]} \quad (49)$$

acquires a time-dependence

$$f_{Fi 0} \equiv f_{Fi}(V)|_{V=V_0 \equiv cte.} \Rightarrow f_{Fi}(t) = f_{Fi 0} + \tilde{f}_{Fi} e^{i\omega t}, \quad (50)$$

which is a consequence of the harmonic oscillation of both the barrier height Φ_B and the function V_1 ; on the contrary, the time variation of $f_{F\nu}$ is a consequence of the harmonic modulation that the time-dependent external field imposes over the relative positions of $E_C(x)$ and $E_F(x)$.

The dynamics of the charge trapped in the ν -th deep level is determined from the kinetic detailed-balance equation within the Shockley-Read-Hall statistics:

$$\left(\frac{dn_\nu}{dt} \right) = c_\nu n p_\nu - e_\nu n_\nu, \quad (51)$$

where n is the free carrier density in the conduction band, $n_\nu = N_\nu \times f_{F\nu}(E_\nu, E_F)$ and $p_\nu = N_\nu - (N_\nu \times f_{F\nu}(E_\nu, E_F)) = N_\nu - n_\nu$ are, respectively, the densities of occupied and unoccupied states at the ν -th level, and $f_{F\nu}$ is given by Eq. (11). The former equations define the so called emission and capture coefficients e_ν and c_ν . These coefficients are not independent, but they are mutually related through the detailed balance principle in thermodynamic equilibrium:⁶⁰

$$e_\nu = g_\nu \tau_c^{-1} \exp\left(-\frac{E_F - E_\nu}{k_B T}\right) = g_\nu c_\nu n \exp\left(-\frac{E_F - E_\nu}{k_B T}\right) \quad (52)$$

Under the additional hypothesis of non-degenerate semiconductor, we can use Maxwell-Boltzmann statistics in order to write

$$n = N_C \exp\left(-\frac{E_C - E_F}{k_B T}\right) \quad (53)$$

with $N_C = 2(2\pi m_{DOS}^* k_B T / h^2)^{3/2} M_C$, where M_C is the number of equivalent minima in the conduction band, $m_{DOS}^* \equiv (m_1 m_2 m_3)^{1/3}$ is the density of states effective mass, and m_1 , m_2 , and m_3 are effective masses along the main axis on the energy surface. Introducing Eq. (53) in Eq. (52) we finally write

$$\begin{aligned} e_\nu &= g_\nu c_\nu N_C \exp\left(-\frac{E_C - E_T}{k_B T}\right) \\ &= g_\nu v_{th} \sigma_\nu N_C \exp\left(-\frac{E_C - E_T}{k_B T}\right) \end{aligned} \quad (54)$$

Note that

$$\frac{dn_\nu}{dt} = -\frac{dp_\nu}{dt}, \quad (55)$$

so

$$\left(-\frac{dp_\nu}{dt}\right) = c_\nu n p_\nu - e_\nu n_\nu, \quad (56)$$

which may be written as

$$\begin{aligned} \left(-\frac{dQ_\nu}{dt}\right) &= c_\nu n q_e N_\nu (1 - f_{F\nu}(E_\nu, E_F)) \\ &\quad - e_\nu q_e N_\nu f_{F\nu}(E_\nu, E_F), \end{aligned} \quad (57)$$

Now, by using Eqs. (53) and (54), we finally rewrite Eq. (57) as

$$\begin{aligned} \frac{d}{dt} Q_\nu &= -c_\nu N_C q_e N_\nu (1 - f_{F\nu}(E_\nu, E_F)) \\ &\quad \times \exp\left(-\frac{E_C(x) - E_F}{k_B T}\right) \\ &\quad + g_\nu c_\nu q_e N_C N_\nu f_{F\nu}(E_\nu, E_F) \exp(-\varepsilon_\nu / k_B T) \end{aligned} \quad (58)$$

Note that we made use of the fact that, despite E_C and E_ν being x -dependent, the quantity $\xi_\nu \equiv E_C(x) - E_\nu(x)$ is constant. In linear response theory, the charge dynamics is obtained by expanding to first order any time-dependent quantity in Eq. (58). This procedure is straightforward once we define the quantity

$$\begin{aligned} n(x, t) &= n_0(x) + \Delta n(x, t) = n_0(x) + \tilde{n}(x)e^{i\omega t} \\ &= N_C \exp\left(-\frac{E_{C0}(x) - E_F}{k_B T}\right) \\ &\quad + N_C \exp\left(-\frac{E_C(x, t) - E_F}{k_B T}\right) \end{aligned} \quad (59)$$

where $E_C(x, t)$ is given by $E_C(x, t) = E_{C0}(x) - \Delta E_C(x, t) = E_{C0}(x) - \tilde{E}_C(x)e^{i\omega t}$, with $\tilde{E}_C(x) = -q_e \tilde{\Phi}(x)$. We can now apply standard procedures⁶¹ to obtain

$$\tilde{Q}_\nu(x) = \frac{f_{F\nu 0}(x)(1 - f_{F\nu 0}(x))}{k_B T} \frac{q_e N_\nu}{1 + i\omega\tau_\nu(x)} q_e \tilde{\Phi}(x), \quad (60)$$

with the relaxation time

$$\tau_\nu(x) = \frac{q_e}{A\sigma_\nu} f_{F\nu 0}(x) \exp[(E_{C0}(x) - E_F)/k_B T]. \quad (61)$$

We can now introduce the Schottky approximation by writing

$$\begin{aligned} f_{F\nu 0}(x)(1 - f_{F\nu 0}(x)) &= \delta[E_{\nu 0}(x) - \xi(x)] \\ &= \delta[-\varepsilon'_\nu + q_e \Phi_0(x)] \end{aligned} \quad (62)$$

and, using

$$\delta[h(x)] = \sum_j \frac{1}{|h'(x_j)|} \delta(x - x_j) \quad \forall x_j : h(x_j) = 0, \quad (63)$$

and bearing in mind that ε'_ν is a constant, and using $h(x) = -\varepsilon'_\nu + q_e \Phi_0(x)$, we finally write

$$\delta[-\varepsilon'_\nu + q_e \Phi_0(x)] = \frac{1}{q_e |\Phi'_0(-x_{L\nu 0})|} \delta(x + x_{L\nu 0}). \quad (64)$$

This last step is only possible by virtue that the function $h(x) = -\varepsilon'_\nu + q_e \Phi_0(x) = E_{\nu 0}(x) - \xi$ vanishes when x is exactly equal to $-x_{L\nu 0}$, i.e., when the trap energy crosses the Fermi level. A straightforward calculation yields

$$|\Phi'_0(-x_{L\nu 0})| = \frac{1}{\varepsilon_0 \varepsilon_r} \sum_{\mu=0}^{\nu-1} q_e N_\mu (x_{L\mu 0} - x_{L\nu 0}), \quad (65)$$

in such a way that

$$\tilde{Q}_\nu(x) = \frac{q_e N_\nu}{k_B T} \frac{1}{1 + i\omega\tau_\nu(x)} \frac{1}{|\Phi'_0(-x_{L\nu 0})|} \delta(x + x_{L\nu 0}) \tilde{\Phi}(x), \quad (66)$$

and

$$\begin{aligned} \tilde{Q}_{L\nu} &\equiv \int_{-\infty}^0 \tilde{Q}_\nu(x) dx \\ &= \frac{q_e N_\nu}{k_B T} \frac{1}{|\Phi'_0(-x_{L\nu 0})|} \frac{\tilde{\Phi}(-x_{L\nu 0})}{1 + i\omega\tau_\nu(-x_{L\nu 0})}, \end{aligned} \quad (67)$$

where $\tau_\nu(x)$ is given by Eq. (61). Equation (67) is the analytical expression of the *Dirac delta approximation* discussed by Shiua and Bube;⁶² its physical meaning is that, when $x_{L\nu 0} \rightarrow x_{L\nu 0} + \delta x_{L\nu 0}$ as a consequence of an increase in the steady state component of the applied field, the increase in ionized charge due to the ν -th trap is assumed to be perfectly localized at $x = -x_{L\nu 0}$. This assumption has been shown^{62,63} to affect only very slightly all those *integrated* quantities as the capacitance, whose actual value only depends upon the total charge supplied to the external circuit. At this point, by directly applying Gauss theorem, the variation in the electrostatic potential at $x = -x_{L\nu 0}$ depends upon charge variations in each one of the points $x = -x_{L\mu 0}$ with $\mu < \nu$ according to

$$\tilde{\Phi}(-x_{L\nu 0}) = \frac{1}{\varepsilon_0 \varepsilon_r} \sum_{\mu=0}^{\nu-1} (x_{L\mu 0} - x_{L\nu 0}) \tilde{Q}_{L\mu}, \quad (68)$$

so, taking Eq. (65) into account,

$$\frac{\tilde{\Phi}(-x_{L\nu 0})}{|\Phi'_0(-x_{L\nu 0})|} = \frac{\sum_{\mu=0}^{\nu-1} (x_{L\mu 0} - x_{L\nu 0}) \tilde{Q}_{L\mu}}{\sum_{\mu=0}^{\nu-1} q_e N_\mu (x_{L\mu 0} - x_{L\nu 0})}. \quad (69)$$

Equations (67), (68), and (69) lead to the following relation between the retarded dynamics of the deep levels and the instantaneous response of the shallow donor:

$$\tilde{Q}_{L\nu} = r_\nu \tilde{Q}_{L0}, \quad (70)$$

where the coefficients r_ν are given by $r_0(\omega) \equiv 1$ and

$$r_\nu(\omega) = \frac{1}{1 + i\omega\tau_\nu} \frac{\sum_{\mu=0}^{\nu-1} (x_{L\mu 0} - x_{L\nu 0}) r_\mu(\omega)}{\sum_{\mu=0}^{\nu-1} (x_{L\mu 0} - x_{L\nu 0}) (N_\mu/N_\nu)}, \quad (71)$$

$$\tau_\nu = \frac{q_e}{AT^2\sigma_\nu(1 + g_\nu)} e^{\xi_\nu/k_B T}. \quad (72)$$

$\forall \nu > 1$. If we now apply Gauss theorem again, we find

$$\begin{aligned} -\tilde{\Phi}_B \equiv \tilde{\Phi}(x=0) &= \frac{1}{\varepsilon_0\varepsilon_r} \sum_{\nu=0}^d x_{L\nu 0} \tilde{Q}_{L\nu} \\ &= \sum_{\nu=0}^d \frac{x_{L\nu 0}}{\varepsilon_0\varepsilon_r} r_\nu \tilde{Q}_{L0} \\ &= \left(\sum_{\nu=0}^d \frac{x_{L\nu 0}}{\varepsilon_0\varepsilon_r} r_\nu \right) \tilde{Q}_{L0} \\ &= \left(\sum_{\nu=0}^d \frac{x_{L\nu 0}}{\varepsilon_0\varepsilon_r} r_\nu \right) \tilde{Q}_{R0} - \tilde{V} \end{aligned} \quad (73)$$

Comparing Eq. (73) with Eq. (41) we see that, defining

$$C_L(\omega) = \varepsilon_0\varepsilon_r \frac{\sum_{\alpha=0}^d r_\alpha(\omega)}{\sum_{\alpha=0}^d x_{L\alpha 0} r_\alpha(\omega)}, \quad (74)$$

and

$$C_R(\omega) = \varepsilon_0\varepsilon_r \frac{\sum_{\alpha=0}^d r_\alpha(\omega)}{\sum_{\alpha=0}^d x_{R\alpha 0} r_\alpha(\omega)}, \quad (75)$$

then Eqs. (41) and (73) are identical except for the change from real-valued constants C_{R0} y C_{L0} to complex-valued and ω -dependent quantities $C_R(\omega)$ and $C_L(\omega)$:

$$-\Delta\Phi_B = \frac{\Delta Q_R}{C_R(\omega)} - \Delta V = \frac{\Delta Q_L}{C_L(\omega)}. \quad (76)$$

Equations (74) and (75) are the same as those deduced by Blatter and Greuter³³ from a different charge-balance equation. However, these authors (as well as all subsequent studies) assumed that Eqs. (74) and (75) are reducible to a simple sum of independent Debye-like terms, which amounts to the particular case in which a dominant shallow donor exists, i.e., to

the case $N_0 \gg N_\nu \forall \nu$. Only very recently we have noticed²⁶ that Eqs. (74) and (75) represent a strongly coupled system, in which the various deep levels are strongly coupled among themselves through the solution of the Poisson equation. The assumption $N_0 \gg N_\nu \forall \nu$ was found to be generally incorrect and the electrostatic coupling between the deep levels was shown to provide a consistent explanation for typical non-Debye dielectric responses. We can say that the set of equations (74) and (75) do indeed fulfill the requirements suggested by several authors,⁶⁴ who emphasized the inappropriateness of usual assumptions for dielectric analysis, which involve distributions of uncoupled relaxation times describing parallel, independent processes.

B. Electrical response

We first note that

$$\frac{dq_S(E, t)}{dt} = q_e N_S(E) \frac{df_{Fi}(E, t)}{dt}, \quad (77)$$

i.e.,

$$\Delta f_{Fi}(E, t) = \frac{\Delta q_S(E, t)}{q_e N_S(E)}. \quad (78)$$

Now, from Eqs. (27) y (29), we can write the interface charge balance equation as:

$$\begin{aligned} \dot{q}_S(E, t) dE &= dJ_{capt} - dJ_{emis} \\ &= q_e N_S(E) c_S(E) [1 - f_{Fi}(t)] n_S(t) dE \\ &\quad - q_e N_S(E) e_S f_{Fi}(t) dE \end{aligned} \quad (79)$$

with [recall Eq. (26)]

$$\begin{aligned} q_e c_S(E) n_S(t) dE &\equiv A \sigma_S(E) (1 + \exp(-q_e V / k_B T)) \\ &\quad \times \exp(-(\xi + q_e \Phi_B) / k_B T) dE, \end{aligned} \quad (80)$$

and

$$q_e e_S(E) dE \equiv 2A \sigma_S e^{-(E_C - E) / k_B T} dE. \quad (81)$$

All the time dependent quantities are contained in $f_{Fi}(t)$ and $n_S(t)$. Therefore, Taylor expansion of Eq. (79) only involves the quantities $\Delta f_{Fi}(t) \equiv \Delta f_{Fi}(E, t)$ and $\Delta n_S(t)$. Hence, substituting

$$f_{Fi}(t) = f_{Fi0} + \Delta f_{Fi}(t) = f_{Fi0} + \tilde{f}_{Fi} e^{i\omega t}, \quad (82)$$

and

$$n_S(t) = n_{S0} + \Delta n_S(t) = n_{S0} + \tilde{n}_S e^{i\omega t}, \quad (83)$$

in Eq. (79), we obtain:

$$\begin{aligned} \dot{q}_S(E, t) &= q_e N_S(E) c_S(E) \\ &= \times [(1 - f_{Fi0}) n_{S0} + (1 - f_{Fi0}) \Delta n_S - n_{S0} \Delta f_{Fi}] \\ &\quad - q_e N_S(E) e_S (f_{Fi0} + \Delta f_{Fi}). \end{aligned}$$

This equation may be simplified through the use of the relation between the capture and emission coefficients provided by the detailed balance condition:

$$q_e N_S(E) c_S (1 - f_{Fi0}) n_{S0} = q_e N_S(E) e_S f_{Fi0}.$$

so that

$$\dot{q}_S(E, t) = q_e N_S(E) c_S \left[(1 - f_{Fi0}) \Delta n_S - n_{S0} \frac{\Delta f_{Fi}}{f_{Fi0}} \right]. \quad (84)$$

Now, given that

$$\dot{q}_S(E, t) = i\omega \Delta q_S(E, t),$$

we can substitute Eq. (78) in Eq. (84) in order to obtain an expression for $\Delta f_{Fi}(t)$:

$$i\omega \Delta f_{Fi} = c_S (1 - f_{Fi0}) \Delta n_S - c_S n_{S0} \frac{\Delta f_{Fi}}{f_{Fi0}}. \quad (85)$$

so

$$\Delta f_{Fi} = \frac{f_{Fi0} (1 - f_{Fi0})}{1 + i\omega f_{Fi0} / c_S n_{S0}} \frac{\Delta n_S}{n_{S0}}, \quad (86)$$

which, substituted back into (84), finally yields

$$\begin{aligned}\Delta q_S(E, t) &= q_e N_S(E) f_{Fi0} (1 - f_{Fi0}) \\ &= \times \frac{1}{1 + i\omega f_{Fi0}/c_S(E) n_{S0}} \frac{\Delta n_S}{n_{S0}}.\end{aligned}\quad (87)$$

Additionally, by expanding Eq. (80) around the steady state, one finds:

$$\frac{\Delta n_S}{n_{S0}} = \frac{q_e}{k_B T} \left(\Delta \Phi_B - \frac{\Delta V}{1 + e^{q_e V_0/k_B T}} \right), \quad (88)$$

so Eq. (87) becomes

$$\begin{aligned}\Delta q_S(E, t) &= \frac{q_e^2}{k_B T} N_S(E) f_{Fi0} (1 - f_{Fi0}) \\ &= \times \frac{1}{1 + i\omega f_{Fi0}/c_S(E) n_{S0}} \\ &\quad \times \left(\Delta \Phi_B - \frac{\Delta V}{1 + e^{q_e V_0/k_B T}} \right).\end{aligned}\quad (89)$$

We can finally integrate Eq. (89) over energies and, by using the definition (B4):

$$\begin{aligned}\Delta Q_S(t) &= \frac{q_e^2}{k_B T} \left(\Delta \Phi_B - \frac{\Delta V}{1 + e^{q_e V_0/k_B T}} \right) \times \lim_{s \rightarrow i\omega} I(s) \\ &\equiv \frac{q_e^2}{k_B T} I(i\omega) \left(\Delta \Phi_B - \frac{\Delta V}{1 + e^{q_e V_0/k_B T}} \right).\end{aligned}\quad (90)$$

It must be stressed that Eq. (90) is completely general: it has been obtained from the kinetic equation for capture/emission at the interface, without any mention to any particular shape for the barrier geometry: any information about this is contained within $\Delta \Phi_B$. In fact, it is possible to check the consistency of the formalism by substituting back the specific form of $\Delta \Phi_B$, as given in Eq. (40) in the absence of deep levels, and verifying that one obtains Eqs. (B2)-(B5), which were obtained by explicit calculation from the without-deep-levels case.

We now realize that the whole model is based on the following set of equations: First, the electroneutrality condition, Eq. (14):

$$Q_S = Q_R + Q_L, \quad (91)$$

then, Gauss theorem in the reverse biased side, Eq. (73):

$$-\Delta\Phi_B = \frac{\Delta Q_R}{C_R} - \Delta V, \quad (92)$$

and Gauss theorem in the direct biased side, Eq. (73):

$$-\Delta\Phi_B = \frac{\Delta Q_L}{C_L}. \quad (93)$$

We now realize that Eqs. (90)-(93) are a set of four algebraic equations with four unknowns ($\Delta\Phi_B$, ΔQ_S , ΔQ_R , and ΔQ_L), which are to be obtained as a function of ΔV . The solution of this system reproduces Eqs. (37)-(40), and (44), which are the basis to obtain the general expression (45). Recall that Eqs.(92) and (93), in the case of a non-negligible amount of deep levels, require the use of the complex and frequency-dependent quantities $C_L(\omega) \in C$ y $C_R(\omega) \in C$ instead of the real constants $C_R \in R$ and $C_L \in R$. These quantities $C_L(\omega)$ and $C_R(\omega)$ contain all the information about the energetics and dynamic properties of deep levels in the space charge region. Hence, we find the following scenario: when deep levels are accounted for, Eq. (90) holds on as it is not supported on the absence or presence of deep levels; Eq. (93) implements the charge neutrality condition and is perfectly valid as long as one interprets that the total charges per unit area Q_R and Q_L are given by Eq. (13); finally, Eqs. (91) and (92) hold the same with the change $C_R \rightarrow C_R(\omega)$ and $C_L \rightarrow C_L(\omega)$. In this way, the set of equations that determine $\Delta\Phi_B$, ΔQ_S , ΔQ_R , and ΔQ_L , as a function of ΔV , is formally identical: Eqs. (40)-(42), (44) and, most prominently, Eq. (45) are identically valid in the presence of deep levels, even when substantially more complicated due to the change $C_R \rightarrow C_R(\omega)$ and $C_L \rightarrow C_L(\omega)$. In particular, the real quantity C_{s0} turns into the complex quantity $C_s(\omega)$:

$$C_{s0} = \frac{C_{L0}C_{R0}}{C_{L0} + C_{R0}} \quad \Rightarrow \quad C_s(\omega) = \frac{C_L(\omega)C_R(\omega)}{C_L(\omega) + C_R(\omega)}, \quad (94)$$

and $C_s(\omega)$ is only the same as the geometrical capacitance per unit area of the DSB structure

$$C_{geom} = \frac{\varepsilon_0\varepsilon_r}{x_{R00} + x_{L00}}, \quad (95)$$

in the very high frequency limit $\omega \rightarrow \infty$ [see Eqs. (70)-(75)].

The final expression for the admittance of the DSB structure is therefore analogous to Eq. (45):

$$\begin{aligned}
Y(V_0, \omega) &= \frac{q_e A}{k_B T} e^{-(\xi + q_e \Phi_{B0} + q_e V_0)/k_B T} \\
&+ \left\{ \frac{q_e J_0}{k_B T [C_L(\omega) + C_R(\omega)]} - \frac{q_e^2 N_{T1}(E_{Fi0})}{2 [C_L(\omega) + C_R(\omega)]} \right\} [C_R(\omega) - C_Q(\omega)] \\
&+ \left[\frac{1}{2\tau_{Fi0}} \left(1 + \frac{2}{1 + e^{-q_e V_0/k_B T}} \right) \right] C_Q(\omega) \\
&+ \frac{i\omega C_R(\omega) C_Q(\omega)}{[C_L(\omega) + C_R(\omega)]} + i\omega C_s(\omega).
\end{aligned} \tag{96}$$

Note that, from Eqs. (B4)-(B5), the expression for $C_Q(\omega)$ becomes:

$$C_Q(\omega) = \frac{K_{V_0} I(i\omega)}{[C_L(\omega) + C_R(\omega)] k_B T / q_e^2 + I(i\omega)}, \tag{97}$$

where

$$\begin{aligned}
K_{V_0} &\equiv C_R(\omega) - f_{V_0} \times [C_L(\omega) + C_R(\omega)] \\
&= C_R(\omega) - \frac{C_L(\omega) + C_R(\omega)}{1 + e^{q_e V_0/k_B T}},
\end{aligned} \tag{98}$$

while Eqs. (B3) and (B4) for $I(s)$ remain literally valid. Note finally that, in thermodynamic equilibrium,

$$C_s^{(0)}(\omega) = \frac{C_L^{(0)}(\omega)}{2} = \frac{C_R^{(0)}(\omega)}{2}. \tag{99}$$

an expression that yields in the basis of the recently explained²⁶ non-Debye spectral response of polycrystalline semiconductors.

Note that, in order for Eqs. (96)-(98), (B3), and (B4) to be useful in spectroscopic procedures, we need to parametrize the functions $N_S(E)$ and $\sigma_S(E)$. A parametrization has been already presented,⁶⁵ based in the results of Ref. 18, where $N_S(E)$ is chosen to be $N_S(E) = N_0(E) + N_1(E) + N_2(E)$, where $N_1(E)$ and $N_2(E)$ are three-parameter gaussian functions intersecting the interface quasi-Fermi level, while $N_0(E)$ is a gaussian that lies well below the interface quasi-Fermi level, providing a certain amount of static interface charge, and therefore carrying just one parameter:

$$N_S(E) = \frac{N_{S0}}{\sqrt{2\pi}} e^{-\frac{(E-2)^2}{2}} + \frac{N_{S1}}{\sqrt{2\pi}} e^{-\frac{(E-E_{S1})^2}{\Sigma_1^2}} + \frac{N_{S2}}{\sqrt{2\pi}} e^{-\frac{(E-E_{S2})^2}{\Sigma_2^2}}.$$

Consequently, the distributed capture cross-section is chosen to be

$$\sigma_S(E) = \frac{\sigma_{S1} N_1(E) + \sigma_{S2} N_2(E)}{N_1(E) + N_2(E)},$$

where σ_{S1} and σ_{S2} are constants.

VI. CONCLUSIONS

We have developed a theoretical framework for the study of the electrical response of material systems with electrically active interfaces. This framework extends previous ones, allowing the analysis of relevant physical properties not covered by previous models. It also provides a unified formalism that was lacking up to now. Our model yields closed equations in which all the relevant physical quantities appear as parameters that can be adjusted from experimental data covering a huge range of frequencies (up to 14 orders of magnitude have been measured in Ref. 66), and a broad range of temperatures and externally applied fields.

In providing a meaningful interpretation for the electrical response, our model allows for the development of new spectroscopic techniques that have already revealed part of its potential. We have already explored some simple limits of the formalism and have shown its usefulness. Thus, for example, in Ref. 37, we have proved the important role that the strong barrier pinning property plays in C-V characterization techniques: this role was not clearly understood, leading to conceptually and quantitatively erroneous characterization procedures. We have also given some first steps towards a comprehensive broadband spectroscopic technique, based on simple limits of the equations here presented, that, despite its simplicity, have already yielded relevant results^{18,26,38}. However, more general parametrizations and extended measuring ranges are much desirable. In this sense, numerical examples of the general equations presented here, as well as the full broadband spectroscopic technique, exploiting the equations here presented in its full power and generality, will be the subject of a forthcoming paper.

APPENDIX A: TIME DEPENDENCE OF V_{1i} AND THE FERMI DISTRIBUTION

We initially assume that the interface density of states is the sum of several monoenergetic levels:

$$N_S(E) = \sum_{k=1}^M N_{Sk} \delta(E - E_{Sk}). \quad (\text{A1})$$

Under non-steady state conditions, there is no single quasi-Fermi level governing the occupation statistics of interface traps. Instead, each of the levels E_{Sk} appearing in Eq. A1

will be governed by a different quasi-Fermi level.^{32,67} In this way, both the interface quasi-Fermi level E_{Fi} and the function V_{1i} take yet another subscript that identifies the particular level they govern:

$$\begin{aligned} E_{Fi} &\Rightarrow E_{Fik} \quad k = 1, \dots, M \\ V_{1i} &\Rightarrow V_{1ik} \quad k = 1, \dots, M. \end{aligned}$$

Under the excitation given by Eq. (33), the functions V_{1ik} change $\forall k = 1, \dots, M$ from a constant quantity $V_{1ik0} \equiv V_{1ik}(V, Q_S)|_{V=V_0, Q_S=Q_{S0}}$ to a time dependent one $V_{1ik}(t) \equiv V_{1ik}(V(t), Q_S(t)) = V_{1ik0} + \Delta V_{1ik}(t) = V_{1ik0} + \tilde{V}_{1ik} e^{i\omega t}$, where

$$\begin{aligned} E_{Fik0} \Rightarrow E_{Fik}(t) &= E_G - \xi - q_e \Phi_B(t) - q_e V_{1ik}(t) \\ &= E_{Fik0} + \Delta E_{Fik}(t) = E_{Fik0} + \tilde{E}_{Fik} e^{i\omega t}. \end{aligned} \quad (\text{A2})$$

Expanding V_{1ik} in Taylor series around V_{1ik0} up to first order,

$$\begin{aligned} q_e V_{1ik}(t) &= q_e V_{1ik0} + \frac{\partial V_{1ik}}{\partial V} q_e \Delta V \\ &+ q_e \left(\frac{\partial V_{1ik}}{\partial Q_{Sk}} \right)_{V, Q_{Sj \neq k}} \Delta Q_{Sk} \\ &+ q_e \sum_{j=1, j \neq k}^M \left(\frac{\partial V_{1ik}}{\partial Q_{Sj}} \right)_{V, Q_{Sm \neq j}} \Delta Q_{Sj}, \end{aligned} \quad (\text{A3})$$

where the k -th charge $Q_{Sk}(t) = Q_{Sk0} + \Delta Q_{Sk}(t) = Q_{Sk0} + \tilde{Q}_{Sk} e^{i\omega t}$ is obtained from the Fermi distribution in the usual way:

$$Q_{Sk}(t) \equiv Q_{Sk}(V, \Phi_B; E_{Sk}) = q_e N_{Sk} f_{Fi}(E_{Sk}, E_{Fik}). \quad (\text{A4})$$

Note that the relation between the time variation of the charge trapped at the k -th level and the corresponding Fermi distribution describing the occupation statistics of that trap is just $\Delta Q_{Sk}(t) = q_e N_{Sk} \Delta f_{Fik}$. Also, note carefully the meaning of the various subscripts. For example, in V_{1ik0} , the first subscript belongs to the name of the very quantity; the second, i , identifies this quantity as being evaluated at the interface; the third one, k , means that we are dealing with the quasi-Fermi level associated with the k -th energy level E_{Sk} , with density N_{Sk} ; the last subscript, 0, refers to the convention by which we attach a subscript 0 to any quantity when evaluated in steady-state, i.e., to the stationary part or any time-dependent quantity.

The partial derivatives in Eq. (A3) are easily by deriving Eq. (A4) with respect to Q_k , $Q_{j \neq k}$, and $q_e V$. In this way, the following expression is obtained:³²

$$\begin{aligned} q_e V_{1ik}(t) &= q_e V_{1ik0} + \frac{C_{R0}}{C_{R0} + C_{L0}} q_e \Delta V \\ &\quad - \frac{q_e}{C_{L0} + C_{R0}} \Delta Q_S \\ &\quad + \frac{k_B T}{q_e N_{Sk} f'_{Fik0}} \Delta Q_{Sk}. \end{aligned} \quad (\text{A5})$$

with $Q_S = \sum Q_{Sk}$ and f'_{Fik} is the derivative of the Fermi distribution with respect to its absolute argument x_k , with

$$x_k \equiv \frac{E_k - E_{Fik}}{k_B T} = \frac{E_k - E_G + \xi}{k_B T} + \frac{q_e \Phi_B + q_e V_{1ik}}{k_B T}. \quad (\text{A6})$$

In the last term of Eq. (A5), a derivative of the Fermi distribution appears. One must note that

$$f_{Fik}(E_{Sk}, E_{Fik}) = \frac{1}{1 + e^{(E_{Sk} - E_{Fik})/k_B T}},$$

which, for each E_{Sk} , is a function of the variable $E_{Fik} \equiv E_{Fik}(t)$. The derivative of the Fermi distribution is

$$\begin{aligned} f'_{Fik0} &\equiv -f_{Fik0}(1 - f_{Fik0}) \\ &= -\frac{1}{1 + e^{(E_{Sk} - E_{Fik0})/k_B T}} \\ &\quad \times \left(1 - \frac{1}{1 + e^{(E_{Sk} - E_{Fik0})/k_B T}} \right), \end{aligned}$$

which is a real number for each (V_0, Φ_{B0}) such that, if $E_{Fik0} \equiv E_{Fik0}(V_0, \Phi_{B0})$ lies several $k_B T$ above E_{Sk} , then $f'_{Fik0} \approx 0$, hence contributing a diverging amount to Eq. (A5). However, the actual term that appears in Eq. (A5) is $\Delta Q_{Sk}/f'_{Fik0}$, and the factor ΔQ_{Sk} represents the variation in trapped charge at the k -th level. This variation happens because of the oscillation of Φ_B y V_{1i} inside E_{Fik} . The possibility $f'_{Fik0} \approx 0$ due to $E_{Fik0} - E_{Sk} > 4k_B T$ automatically implies $\Delta Q_{Sk} \approx 0$, as the level occupation can only change if its quasi-Fermi level is oscillating close to the actual energy level. Thus, for example, in case $E_{Fik0} - E_{Sk} > 4k_B T$, then the k -th level is almost completely occupied and the amount of charge trapped at this level is not going to change due to small oscillations [smaller than $k_B T$ due to Eq. (34) of its quasi-Fermi level. The quotient $\Delta Q_{Sk}/f'_{Fik0}$ keeps therefore, finite.

We can now generalize Eq. (A5), turning the discrete index i into a continuous variable E :

$$\begin{aligned}\Delta Q_{Sk} &\equiv \Delta Q_{Sk}(t) \rightarrow \Delta q_S(E)dE \equiv \Delta q_S(E,t)dE \\ N_{Sk} &\rightarrow N_S(E) \\ V_{1ik} &\rightarrow V_{1i}(E)\end{aligned}\tag{A7}$$

where the function $q_S(E)$ [see Eq. (42)] has been introduced. Note that the quantity q_S is actually $q_S \equiv q_S(E, V, \Phi_B; t)$ although we usually write simply $q_S(E, t) = q_{S0}(E) + \Delta q_S(E, t) = q_{S0}(E) + \tilde{q}_S e^{i\omega t}$. Also, note that

$$\Delta Q_S(t) = \int_{E_V}^{E_C} \Delta q_S(E, t) dE.\tag{A8}$$

With these definitions, Eq. (42) emerges immediately as the continuous version of Eq. (A5). Equation (42) should be interpreted as follows. Under non-steady state regime, the quasi-Fermi level $E_{Fi0} = E_G - \xi - q_e \Phi_{B0} - q_e V_{1i0}$ becomes *distributed*, i.e., becomes an E -dependent quantity, $E_{Fi} \equiv E_{Fi}(V, \Phi_B, E, t) = E_G - \xi - q_e \Phi_B - q_e V_{1i}(E, t) = E_{Fi0} - q_e(\Delta \Phi_B + \Delta V_{1i}) = E_{Fi0} + \Delta E_{Fi}(E, t)$. Clearly, if $\Delta V \ll k_B T$, then $\Delta E_{Fi}(E, t) \ll k_B T, \forall E$ and $\forall t$. Therefore, the quasi-Fermi level E_{Fi0} is distributed through a narrow energy region, restricted around the value it had under steady-state conditions. Each energy E in the gap, whose occupation was governed in steady-state by a single, well defined, quasi-Fermi level E_{Fi0} , is now governed by a particular $E_{Fi}(E)$, but this $E_{Fi}(E)$ is numerically very similar to the original E_{Fi0} except for a small correction which is less than $k_B T$. If the energy E lies close to E_{Fi0} , then the change from E_{Fi0} to the new $E_{Fi}(E)$ may have strong effects upon $\Delta q_S(E)$, but otherwise it will be $\Delta q_S(E) \approx 0$. Therefore, to a very good accuracy, we can write

$$\Delta q_S(E) \sim \Delta Q_S \times \delta(E - E_{Fi0}),\tag{A9}$$

whose meaning is that, under non-steady state conditions, the oscillation in the total charge trapped at the interface, ΔQ_S , takes place in a very narrow energy range around the steady state value of the quasi-Fermi level at the interface.

We can use these results to explicitly evaluate the time variation of the interface Fermi function itself, hence obtaining a self-consistency argument of the whole formalism. In steady state f_{Fi0} depends upon barrier height Φ_{B0} and (indirectly) upon the quantity V_{1i0} . Therefore we can write:

$$f_{Fi0}(E) \equiv f_{Fi}(E, E_{Fi0}) \equiv f_{Fi}(E, \Phi_{B0}, V_{1i0}). \quad (\text{A10})$$

Under non-steady state we can expand up to first order to obtain:

$$\begin{aligned} f_{Fi}(E, t) &= f_{Fi0}(E) + \Delta f_{Fi}(E, t) \\ &= f_{Fi0}(E) + \left(\frac{\partial f_{Fi}}{\partial \Phi_B} \right)_{V_{1i0}} \Delta \Phi_B \\ &\quad + \left(\frac{\partial f_{Fi}}{\partial V_{1i}} \right)_{\Phi_{B0}} \Delta V_{1i}. \end{aligned} \quad (\text{A11})$$

The derivatives are evaluated to yield:

$$\left(\frac{\partial f_{Fi}}{\partial \Phi_B} \right) = \left(\frac{\partial f_{Fi}}{\partial V_{1i}} \right) = -\frac{q_e}{k_B T} f_{Fi} (1 - f_{Fi}), \quad (\text{A12})$$

which, introduced in (A11), yields:

$$\Delta f_{Fi}(E, t) = \frac{\Delta q_S(E, t)}{q_e N_S(E)} \quad (\text{A13})$$

which is the expected expression for the variation of the trapped charge as a function of the variation of the Fermi distribution [see Eq. (77)]

APPENDIX B: INTERFACE TRAPPED CHARGE DYNAMICS

The capture/emission dynamics at the interface is obtained by writing and solving a kinetic equation for the variation of the charge per unit area trapped at the interface, ΔQ_S . We incorporate to the equations the energy-distributed capture cross-section, and we essentially follow the Pike's idea of solving the equation by means of the Laplace transform technique.³² The charge balance equation is

$$\begin{aligned} \dot{q}_S(E, t)dE &= dJ_{capt} - dJ_{emis} \\ &= A\sigma_S(E)N_S(E) (1 - f_{Fi}(E, E_{Fi})) \\ &\quad \times \exp(-(\xi + q_e\Phi_B)/k_B T) \\ &\quad \times \left\{ 1 + e^{-q_e V/k_B T} - 2e^{-q_e V_{1i}/k_B T} \right\} dE \end{aligned} \quad (\text{B1})$$

We have to integrate Eq. (B1) both over energies and time [see Eq. (A8)]. The integration over the t variable is simplified by expanding all the quantities around their steady-state

values to first order. Therefore, we expand Φ_B , V_{1i} , and $f_{Fi}(E, E_{Fi})$ and, following the method introduced by Pike,³² we Laplace-transform the resulting equation and perform the integral over energies. The result is that $\Delta Q_S(t) = C_Q(\omega)\Delta V(t)$, with:

$$C_Q(\omega) = \lim_{s \rightarrow i\omega} \frac{K_{V_0} I(s)}{(C_{L0} + C_{R0})k_B T/q_e^2 + I(s)}, \quad (\text{B2})$$

with the time and energy dependent relaxation time

$$\tau \equiv \tau(E, V_0, \Phi_{B0}) = \frac{q_e}{2A\sigma_S(E)} \exp\{(\xi + q_e \Phi_{B0} + q_e V_{1i0})/k_B T\}. \quad (\text{B3})$$

and with

$$I(s) = \int_{E_V}^{E_C} \frac{N_S(E) f_{Fi0}(E) (1 - f_{Fi0}(E))}{1 + s\tau(E) f_{Fi0}(E)} dE, \quad (\text{B4})$$

and

$$K_{V_0} \equiv C_{R0} - f_{V_0} \times (C_{L0} + C_{R0}) = C_{R0} - \frac{C_{L0} + C_{R0}}{1 + e^{q_e V_0/k_B T}}. \quad (\text{B5})$$

The result described by Eqs. (B2)-(B5) introduces a characteristic time-scale for capture/emission processes at the interface, given by the quantity τ from Eq. (B3). Note that $\tau \equiv \tau(V_0)$, as it depends on Φ_{B0} and $q_e V_{1i0}$, both function of V . Were it be $\tau = 0$, i.e., were it be instantaneous the reaction of interface states to changes in the local position of the quasi-Fermi level, then Eq. (B2) would present no imaginary part, and would not introduce any specific effect. It is precisely the retarded dynamics of the interface electronic structure, unable to instantaneously respond to the bias fluctuations, that introduces an out-of-phase modulation in the currents flowing across the system. One of the most clear manifestations of this characteristic field and energy dependent interface response time is the appearance of excess capacitances at low frequencies, which is illustrated in Figs. 2 and 3. From Eq. (B3), we see that the relaxation time exponentially decreases when the bias increases. For a given barrier height, at a fixed frequency ω and for a small bias, the quantity $1/\tau$ will be small, so that $\omega\tau_2 \ll 1$ and the interface will be unable to follow the measuring signal (much in the same way as it happens with the deep levels, as discussed in Ref. 37). Upon increasing bias, τ decreases, so there is a point where $\omega\tau_2 \approx 1$ and, at this point, the interface enters into a resonance situation with the applied signal, hence given rise to a sudden and pronounced increase in the capacitance. This kind of behaviour is a nitid clue for the presence of electrically active interfaces in the system. For example, Figs. 2 and 3 correspond to ceramic $ZnO : Bi_2O_3$ samples with highly active interfaces, and we can see how they clearly follow the kind of behavior predicted by Eqs. (B2)-(B5).

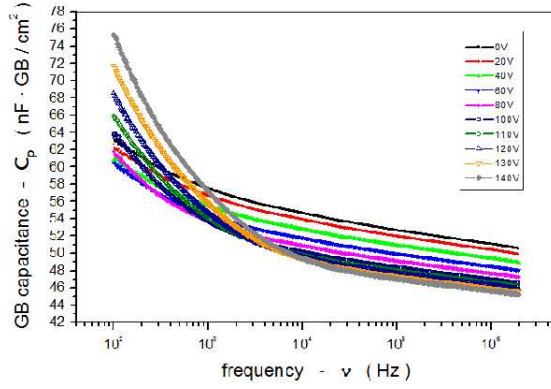


FIG. 2: Spectral behavior of capacitance $Im\{Y(\omega)/\omega\}$ for a sample of ceramic $ZnO : Bi_2O_3$ material

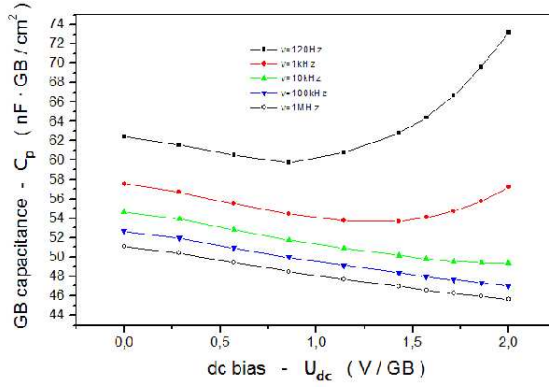


FIG. 3: Capacitance response under an external applied field for the same sample as above. The resonance due to the activation of interface is clearly seen and it constitutes a clear sign of the presence of electrically active interfaces.

APPENDIX C: ELECTRICAL RESPONSE WITH EXPLICIT CONSIDERATION OF INTERFACE CHARGE DYNAMICS

We start from Eqs. (30) and (35), where the E – *dependent* nature of the interface capture cross-section has already been introduced. We rewrite these equations as $J = J_R^{transp} + J_R^{desp} = J_R^{trav} + J_R^{ce} + \dot{Q}_R$, where $J_R^{trav} = J_{inc,LR} - J_{inc,RL}$ [see Eq. (30)], while

$$\begin{aligned} J_R^{ce} &= \frac{1}{2} \int dJ_{emis} dE - \int dJ_{capt,LR} dE \\ &= A \times \exp[-(\xi + q_e \Phi_B)/k_B T] \end{aligned}$$

$$\begin{aligned} & \times \int \sigma_S(E) N_S(E) [1 - f_{Fi}(E, E_{Fi})] \\ & [\exp(-q_e V_{1i}/k_B T) - 1] dE. \end{aligned} \quad (C1)$$

The expansions of J_R^{trav} and J_R^{desp} are straightforward.³² We will therefore deal with the expansion of J_R^{ce} . By using Eqs. (40), (42), (44), (A8), and (A13), we can write Eq. (C1) up to first order as:

$$\begin{aligned} J_R^{ce} \approx & \Lambda \left(1 - \frac{\beta}{k_B T} \Delta Q_S + \frac{\alpha}{k_B T} \Delta V \right) \\ & \times \int_{E_V}^{E_C} \sigma_S(E) N_S(E) \left(1 - f_{Fi0} - \frac{\Delta q_S(E)}{q_e N_S(E)} \right) \left[(e^{-q_e V_{1i0}/k_B T} - 1) \right. \\ & \left. - \frac{\alpha}{k_B T} \Delta V e^{-q_e V_{1i0}/k_B T} + \frac{\beta}{k_B T} \Delta Q_S e^{-q_e V_{1i0}/k_B T} - \frac{\mu(E)}{k_B T} \Delta q_S(E) e^{-q_e V_{1i0}/k_B T} \right] dE, \end{aligned} \quad (C2)$$

where $\Lambda \equiv A^* T^2 \times \exp[-(\xi + q_e \Phi_{B0})/k_B T]$, $\alpha \equiv q_e C_{R0}/(C_{L0} + C_{R0})$, $\beta \equiv q_e/(C_{L0} + C_{R0})$, and $\mu(E) \equiv -k_B T/[q_e N_S(E) f_{Fi0}(E)(1 - f_{Fi0}(E))]$. We also define:

$$N_{T1}(E_{Fi0}) = \frac{1}{k_B T} \int_{E_V}^{E_C} \frac{N_S(E)(1 - f_{Fi0}(E, E_{Fi0}))}{\tau(E)} dE, \quad (C3)$$

and [see Eq. (B3)]

$$\tau_{Fi0} = \tau(E, V_0, \Phi_{B0})|_{E=E_{Fi0}}. \quad (C4)$$

With all these definitions, and using Eq. (A9), we can write Eq. (C2) retaining only first order terms. Then, we evaluate the admittance and we finally obtain the results in Eqs. (45)-(39). Please, note that these equations yield a relevant, yet systematically neglected contribution to the DSB conductance in equilibrium. We can see that

$$\begin{aligned} G_0^{(0)} \equiv G_0(V_0)|_{V_0=0} = & \frac{q_e A}{k_B T} e^{-(\xi + q_e \Phi_{B0})/k_B T} \\ & - \frac{q_e^2 N_{T1}^{(0)}(E_{Fi0}^{(0)})}{4}, \end{aligned} \quad (C5)$$

where

$$E_{Fi0}^{(0)} = E_{Fg} - q_e \Phi_{B0}^{(0)} = E_G - \xi - q_e \Phi_{B0}^{(0)}, \quad (C6)$$

$$\Phi_{B0}^{(0)} \equiv \Phi_{B0}(V_0, Q_{S0})|_{V_0=0} = \frac{(Q_{S0}^{(0)})^2}{8 q_e \epsilon_0 \epsilon_r N_D}, \quad (C7)$$

and

$$N_{T1}^{(0)} \equiv N_{T1}^{(0)}(E_{Fi0}^{(0)}) = \frac{1}{k_B T} \int_{E_V}^{E_C} \frac{N_S(E)(1 - f_{Fi0}(E, E_{Fi0}^{(0)}))}{\tau^{(0)}(E)} dE, \quad (C8)$$

with

$$\tau^{(0)}(E) \equiv \tau(E, V_0)|_{V_0=0} = \left(\frac{q_e}{2A\sigma_S(E)} \right) \times \exp [(\xi + q_e\Phi_{B0})/k_B T], \quad (C9)$$

which we can also write, with the aid of Eq. (31), as

$$G_0^{(0)} = \left(1 - \frac{\hat{c}}{2} \right) \frac{q_e A}{k_B T} e^{-(\xi + q_e\Phi_{B0})/k_B T}. \quad (C10)$$

to be compared with the usually encountered relation:

$$G_0^{(0)} \equiv G_0(V_0)|_{V_0=0} = \frac{q_e A}{k_B T} e^{-(\xi + q_e\Phi_{B0})/k_B T}, \quad (C11)$$

It is worth to point out that, v.g. for ZnO varistors, IDOS have been measured of about 10^{13}cm^{-2} . For typical values of the capture cross section $\sigma_S \sim 10^{-14} \text{cm}^2$, this IDOS leads to $\hat{c} \approx 0.1$, i.e., the error incurred when neglecting the capture/emission component is about 10%. Even more contradictory situations are found in the attempted applications of previous models to electrocally active interfaces in metal-semiconductor junctions. For example, in Ref. 34, the authors find results that lead $\sigma_S N_S \approx 1$, in whose case the approximation $\hat{c} \approx 0$ is clearly wrong.

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¹ A. P. Sutton and R. W. Balluffi, *Interfaces in crystalline materials* (Clarendon Press, Oxford, 1995).

² S. Lombardo, S. U. Campisano, and F. Baroetto, *Phys. Rev. B* **47**, 13561 (1993).

³ N. H. Nickel, N. M. Johnson, and C. G. V. de Walle, *Phys. Rev. Lett.* **72**, 3393 (1994).

- ⁴ K. Uchida and S. Tsuneyuki, Appl. Surf. Sci. **190**, 129 (2002).
- ⁵ N. Li and C. Tu, J. Crystal Growth **188**, 45 (1998).
- ⁶ M. Imaizumi, M. Adachi, Y. Fujii, Y. Hayashi, T. Soga, T. Jimbo, and M. Umeno, J. Crystal Growth **221**, 688 (2000).
- ⁷ I. Shalish, L. Kronik, G. Segal, Y. Shapira, S. Zamir, B. Meyler, and J. Salzman, Phys. Rev. B **61**, 15573 (2000).
- ⁸ K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tallant, J. A. Voight, and B. E. Gnade, J. Appl. Phys. **79**, 7983 (1996).
- ⁹ F. J. Haug, M. Krejci, H. Zogg, A. N. Tiwari, M. Kirsch, and S. Siebentritt, Thin Solid Films **361-362**, 239 (2000).
- ¹⁰ F. M. Hossain, J. Nishii, S. Takagi, A. Ohtomo, T. Fukumura, H. Fujioka, H. Ohno, H. Koinuma, and M. Kawasaki, J. Appl. Phys. **94**, 7768 (2003).
- ¹¹ P. R. Bueno, M. R. De Cassia-Santos, E. R. Leite, E. Longo, J. Bisquert, G. Garca-Belmonte, and F. Fabregat-Santiago, J. Appl. Phys. **88**, 6545 (2000).
- ¹² M. Sinner-Hettenbach, N. Barsan, U. Weimar, T. Weibeta, H. von Schenck, M. Gothelid, L. Giovanelli, and G. L. Lay, Thin Solid Films **391**, 192 (2001).
- ¹³ A. Amin, Phys. Rev. B **49**, 4611 (1994).
- ¹⁴ Y. G. Li and S. G. Cho, J. Appl. Phys. **91**, 4535 (2002).
- ¹⁵ M. Kim, G. Duscher, N. D. Browning, K. Sohlberg, S. T. Pantelides, and S. J. Pennycook, Phys. Rev. Lett. **86**, 4056 (2001).
- ¹⁶ K. Guth, H. U. Krebs, H. C. Freyhardt, and C. Jooss, Phys. Rev. B **64**, 140508(R) (2001).
- ¹⁷ M. Elfving and E. Olsson, J. Appl. Phys. **92**, 5272 (2002).
- ¹⁸ D. Fernández Hevia, M. Peiteado, J. de Frutos, A. C. Caballero, and J. F. Fernández, J. Europ. Ceram. Soc. **24**, 1205 (2004).
- ¹⁹ J. M. Carlsson, H. S. Domingos, P. D. Bristowe, and B. Hellsing, Phys. Rev. Lett. **91**, 165506 (2003).
- ²⁰ S. V. Kalinin and D. A. Bonnell, J. Appl. Phys. **91**, 832 (2002).
- ²¹ M. Freitag, A. T. Johnson, S. V. Kalinin, and D. A. Bonnell, Phys. Rev. Lett. **89**, 216801 (2002).
- ²² R. Shao, S. V. Kalinin, and D. A. Bonnell, Appl. Phys. Lett. **82**, 1869 (2003).
- ²³ N. Bernstein, M. J. Mehl, and D. A. Papaconstantopoulos, Phys. Rev. B **66**, 075212 (2002).

- ²⁴ R. Tamura, Phys. Rev. B **67**, 121408(R) (2003).
- ²⁵ X. Guo and J. Maier, J. Electrochem. Soc. **148**, E121 (2001).
- ²⁶ D. Fernández Hevia, J. de Frutos, A. C. Caballero, and J. F. Fernández, Appl. Phys. Lett. **83**, 2692 (2003).
- ²⁷ A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, Phys. Rev. B **61**, 15019 (2000).
- ²⁸ C. T. Chao, D. P. Cann, R. B. Gall, and Y. Palaci, J. Phys. D: Appl. Phys. **37**, 416 (2004).
- ²⁹ R. F. Klie, M. Beleggia, Y. Zhu, J. P. Buban, and N. D. Browning, Phys. Rev. B **68**, 214101 (2003).
- ³⁰ C. H. Seager and G. E. Pike, Appl. Phys. Lett. **35**, 709 (1979).
- ³¹ C. H. Seager, G. E. Pike, and D. S. Ginley, Phys. Rev. Lett. **43**, 532 (1979).
- ³² G. E. Pike, Phys. Rev. B **30**, 795 (1984).
- ³³ G. Blatter and F. Greuter, Phys. Rev. B **33**, 3952 (1986).
- ³⁴ J. Werner, K. Ploog, and H. J. Queisser, Phys. Rev. Lett. **57**, 1080 (1986).
- ³⁵ J. Werner, A. F. J. Levi, R. T. Tung, M. Anzlowar, and M. Pinto, Phys. Rev. Lett. **60**, 53 (1988).
- ³⁶ G. E. Pike, Private communication (2003).
- ³⁷ D. Fernández Hevia, J. de Frutos, A. C. Caballero, and J. F. Fernández, J. Appl. Phys. **92**, 2890 (2002).
- ³⁸ D. Fernández Hevia, J. de Frutos, A. C. Caballero, and J. F. Fernández, Appl. Phys. Lett. **82**, 212 (2003).
- ³⁹ G. E. Pike, Phys. Rev. B **30**, 3274 (1984).
- ⁴⁰ G. E. Pike and C. H. Seager, J. Appl. Phys. **50**, 3414 ((1979)).
- ⁴¹ J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B **14**, 3539 (1976).
- ⁴² W. E. Taylor, N. H. Odell, and H. Y. Fan, Phys. Rev. **88**, 867 (1952).
- ⁴³ R. K. Mueller, J. Appl. Phys. **32**, 635 (1961).
- ⁴⁴ W. Heywang, J. Materials Sci. **6**, 1214 (1971).
- ⁴⁵ G. D. Mahan, L. M. Levinson, and H. R. Philipp, J. Appl. Phys. **50**, 2799 (1979).
- ⁴⁶ C. H. Seager and G. E. Pike, Appl. Phys. Lett. **37**, 747 (1980).
- ⁴⁷ G. C. McGonigal, D. J. Thomson, J. G. Shaw, and H. C. Card, Phys. Rev. B **28**, 5908 (1983).
- ⁴⁸ M. Isler and D. Liebig, Phys. Rev. B **61**, 7483 (2000).
- ⁴⁹ F. D. Auret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, and D. C. Look,

- Appl. Phys. Lett. **79**, 3074 (2001).
- ⁵⁰ F. D. Auret, S. A. Goodman, M. J. Legodi, W. E. Meyer, and D. C. Look, Appl. Phys. Lett. **80**, 1340 (2002).
- ⁵¹ C. H. Henry and D. V. Lang, Phys. Rev. B **15**, 989 (1977).
- ⁵² M.-F. Li, *Modern Semiconductor Quantum Physics* (World Scientific, Singapore, 1994).
- ⁵³ D. Goguenheim and M. Lannoo, J. Appl. Phys. **68**, 1059 (1990).
- ⁵⁴ D. Goguenheim and M. Lannoo, Phys. Rev. B **44**, 1724 (1991).
- ⁵⁵ A. Palma, A. Godoy, J. A. Jimnez-Tejada, J. E. Carceller, and J. A. Lpez-Villanueva, Phys. Rev. B **56**, 9565 (1997).
- ⁵⁶ N. M'Gafad, H. Amzil, D. Sayah, D. Ballutaud, and M. Barb, Solid-State Electron. **43**, 857 ((1999)).
- ⁵⁷ G. Blatter and F. Greuter, Phys. Rev. B **34**, 8555 (1986).
- ⁵⁸ G. Blatter and D. Baeriswyl, Phys. Rev. B **36**, 6446 (1987).
- ⁵⁹ A. V. Los and M. S. Mazzola, J. Appl. Phys. **89**, 3999 ((2001)).
- ⁶⁰ P. Blood and J. W. Orton, *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States* (Techniques of Physics, Vol. 14. Academic Press, London, 1992).
- ⁶¹ E. H. Nicollian and A. Goetzberger, Bell Sys. Tech. J. **46**, 1055 (1967).
- ⁶² J.-J. Shiao and R. H. Bube, Solid-State Electronics **29**, 1153 ((1986)).
- ⁶³ J.-J. Shiao, A. L. Fahrenbruch, and R. H. Bube, J. Appl. Phys. **59**, 2879 ((1986)).
- ⁶⁴ H. J. Queisser, Phys. Rev. Lett. **54**, 234 ((1985)).
- ⁶⁵ D. Fernández Hevia, J. de Frutos, A. C. Caballero, and J. F. Fernández, Bol. Soc. Esp. Ceram. y Vidrio ((accepted for publication)).
- ⁶⁶ D. Fernández Hevia, J. de Frutos, A. C. Caballero, and J. F. Fernández, Bol. Soc. Esp. Ceram. y Vidrio ((accepted for publication)).
- ⁶⁷ K. Seeger, *Semiconductor Physics* (Springer Series in Solid-State Sciences Vol. 40, Springer Verlag, Berlin, 1997), sixth ed.
- ⁶⁸ Even when the authors in Ref 15 point out that the surface is definitely non-metallic and, therefore, the term double Schottky barrier would be inadequate, the fact is that the geometrical electronic structure arising around the electrically active interface is well described by this model
- ⁶⁹ This is convenient because this side of the band diagram remains constant, with the full bias appearing in the reverse biased side^{32,40} -see, however Ref. 14 for a critical analysis of this

hypothesis in the case of the ferroelectric perovskites

⁷⁰ Please note that the variations in the barrier and conduction band geometry are the only ones defined with a minus sign