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A General Conductivity Expression for Space-Charge-Limited Conduction in Ferroelectrics and Other Solid Dielectrics

Ho-Kei Chan[1,2]
[1]School of Physics, Trinity College Dublin, College Green, Dublin 2,
[2]Department of Applied Physics, Hong Kong Polytechnic University, Kowloon,
[1]Ireland
[2]Hong Kong, China

1. Introduction

For a current density J and an applied voltage V, the experimentally observable Mott-Gurney law $J \sim V^2$ (Carbone et al., 2005; Coelho, 1979; Laha & Krupanidhi, 2002; Pope & Swemberg, 1998; Suh et al., 2000) for steady-state trap-free space-charge-limited conduction (SCLC) inside a plane-parallel dielectric capacitor is derived from three independent assumptions - (i) the presence of a single free-carrier type (i.e. injection of only p-type or n-type free charge-carriers into the dielectric), (ii) the absence of an intrinsic (Ohmic) conductivity, and (iii) the existence of a constant dielectric permittivity ε (i.e. the material being a linear dielectric). Due to the limited applicability of the Mott-Gurney law, there has been the need to derive a more general SCLC formula that applies to cases (i) with the simultaneous presence of p-type and n-type free charge-carriers, (ii) with the presence of a small but finite intrinsic conductivity σ_{in}, as well as (iii) with any possible field dependence of the dielectric permittivity ε. In 2003, while we were searching for a theoretical explanation to the well-known experimental observation of polarization offsets (Schubring et al., 1992) in compositionally graded ferroelectric films, we employed the law of mass action to derive a general local conductivity expression for double-carrier-type SCLC in solid dielectrics and showed numerically that SCLC is a possible origin of the observation of polarization offsets in those graded ferroelectric films (Chan et al., 2004). In those graded films, there exist gradients of electric displacements and therefore, according to Gauss' law, a corresponding presence of free space-charge. The local electrical conductivity is influenced, or even limited, by the presence of free space-charge and consequently becomes non-Ohmic. An important conclusion from this general local conductivity expression is the *necessary* dominance of a single free-carrier type at the limit of zero intrinsic conductivity, which links two of the three independent assumptions in the original derivation of the Mott-Gurney law. In a later study (Zhou et al., 2005a), we have employed this new conductivity expression to understand the origin of imprint effect in homogeneous ferroelectric films. In this Book Chapter, we will (i) review the original derivation of the Mott-Gurney law (Coelho, 1979; Pope & Swemberg,

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e-mail: epkeiyeah@yahoo.com.hk

1998), (ii) review the original problem of polarization offsets in compositionally graded ferroelectric films (Schubring et al., 1992) and explain why such a new local conductivity expression was needed in our theoretical investigation, (iii) review our original derivation of this general local conductivity expression (Chan et al., 2004), (iv) review our study on the limiting case of zero intrinsic conductivity (Chan et al., 2007; Zhou et al., 2005a), (v) supply the derivation of a general expression, via the mass-action approximation, for the corresponding local diffusion-current density (Chan, unpublished), which incorporates the Einstein relations and takes into account the possible presence of a temperature gradient, (vi) present an alternative derivation of this local conductivity expression (Chan, unpublished) with a detailed theoretical justification of the mass-action approximation, and (vii) discuss, in the concluding section, possible future work as to a better understanding of the mechanism of charge flow in a compositionally graded ferroelectric film as well as of the scope of applicability of the general local conductivity expression.

2. Derivation of the Mott-Gurney law

Space-charge-limited conduction (SCLC) in a solid dielectric occurs when free charge-carriers are injected into the dielectric sample at relatively large electric fields (Carbone et al., 2005; Coelho, 1979; Laha & Krupanidhi, 2002; Pope & Swemberg, 1998; Suh et al., 2000). For the case of SCLC in a trap-free plane-parallel dielectric capacitor (Fig. 1), the current density J and the applied voltage V follow a scaling relation
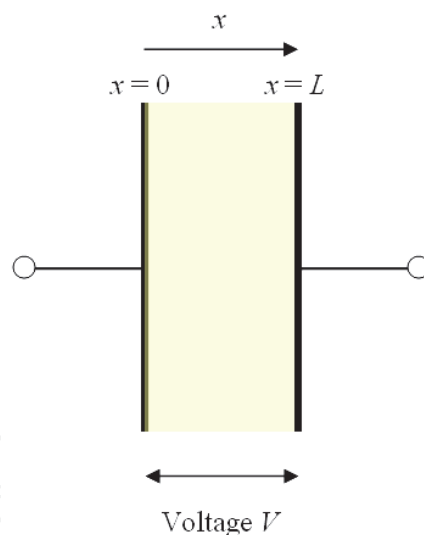

Fig. 1. Schematic diagram of a plane-parallel dielectric capacitor. V is the applied voltage, and x is the position from the electrode where the electric current flows into the dielectric sample. The positive direction of x is the flow direction of the electric current.

$$J \sim V^2 \tag{1}$$

which can be observed experimentally (Carbone et al., 2005; Laha & Krupanidhi, 2002; Suh et al., 2000), and can be derived theoretically (Coelho, 1979) as follows: Consider the case of SCLC by only p-type free charge-carriers, and let this case be denoted by a subscript p in each of the quantities involved. Let the charge mobility $\mu_p > 0$ and the dielectric permittivity

$\varepsilon > 0$ be both independent of the position x from the electrode where the electric current flows into the dielectric sample. The flow direction of the electric current is then given by the positive direction of x. According to Gauss' law, the free-charge density is given by

$$\rho_p(x) = \varepsilon \frac{dE_p(x)}{dx} \geq 0 \tag{2}$$

where $E_p(x)$ is the electric field along the positive direction of x. At steady states, the continuity equation

$$\vec{\nabla} \cdot \vec{J}_p = 0 \tag{3}$$

implies that the current density J_p is independent of the position x. At the absence of both intrinsic (Ohmic) conductivity and diffusion currents, this current density is given by

$$J_p = \mu_p \rho_p(x) E_p(x) = \frac{\mu_p \varepsilon}{2} \frac{dE_p(x)^2}{dx} \tag{4}$$

A spatial integration of Eq. (4) from 0 to x using the boundary condition $E_p(0) = 0$ yields

$$J_p = \frac{\mu_p \varepsilon}{2x} E_p(x)^2 \geq 0 \tag{5}$$

or equivalently

$$E_p(x) = \sqrt{\frac{2J_p x}{\mu_p \varepsilon}} \geq 0 \tag{6}$$

The present justification for the boundary condition $E_p(0) = 0$ is that, at the boundary $x = 0$, any electric field along the positive direction of x, if it ever exists, would be `neutralized' by an electric field in the opposite direction as generated by the injected p-type free carriers (Coelho, 1979). Here we provide a "quantitative explanation" for this: At $x = 0$, the electric field satisfies the inequality $E_p(0) \geq 0$. But since, at this boundary, there is a step change of the free-charge density from zero to some finite positive value, the inequality $E_p(0) \leq 0$ is also satisfied as any finite local electric field is also expected to be pointing along the negative direction of x. The simultaneous inequalities $E_p(0) \geq 0$ and $E_p(0) \leq 0$ together imply $E_p(0) = 0$. Using Kirchoff's loop law (i.e. Kirchoff's voltage law) and Eq. (6), we obtain

$$V = \int_0^L E_p(x)dx = \left(\frac{8J_p}{9\mu_p \varepsilon} \right)^{1/2} L^{3/2} \tag{7}$$

Hence,

$$J_p = \left(\frac{9\mu_p \varepsilon}{8L^3} \right) V^2 \sim V^2 \tag{8}$$

If *n*-type instead of *p*-type free carriers are injected into the dielectric sample, Eqs. (2) and (4) should be replaced by

$$\rho_n(x) = \varepsilon \frac{dE_n(x)}{dx} \leq 0 \tag{9}$$

and

$$J_n = -\mu_n \rho_n(x) E_n(x) = -\frac{\mu_n \varepsilon}{2} \frac{dE_n(x)^2}{dx} \tag{10}$$

respectively, where $\mu_n > 0$, and the subscript *n* denotes the case of SCLC by only *n*-type free carriers. Following a derivation similar to that for the case of *p*-type SCLC but with a consideration of the boundary condition $E_n(L) = 0$, we obtain

$$J_n = \left(\frac{9\mu_n \varepsilon}{8L^3}\right) V^2 \sim V^2 \tag{11}$$

It follows that the scaling relation $J \sim V^2$ holds regardless of whether the injected free carriers are *p*-type or *n*-type.

3. Polarization offsets in graded ferroelectrics and the need for a general local conductivity expression

Our theoretical investigation of SCLC began with a study of the well-known phenomenon of polarization offsets in compositionally graded ferroelectric films (Bao et al. 2000a, 2000b, 2000c, 2001a, 2001b; Bouregba et al., 2003; Brazier et al., 1998; Chen et al., 1999; Mantese et al., 1997; Matsuzaki & Funakubo, 1999; Schubring et al., 1992). Ferroelectric materials are materials that generally exhibit nonlinear, hysteretic *D-E* or *P-E* relations, where *D* is the electric displacement, *P* is the polarization and *E* is the electric field. In contrast to the "normal" hysteresis loops, i.e. loops that are centred at the origin of the *D-E* or *P-E* plot, as observed for homogeneous ferroelectric films, it was first reported in *Physical Review Letters* (Schubring et al., 1992) that compositionally graded ferroelectric films can exhibit vertical displacements of their hysteresis loops along the polarization axis, i.e. polarization offsets, when driven by an alternating applied electric field and placed inside a Sawyer-Tower circuit (Chan et al., 2004; Sawyer & Tower, 1930) for typical *D-E* measurements of ferroelectric materials. This intriguing phenomenon, believed to have potential device applications in infrared detection, actuation and energy storage (Mantese & Alpay, 2005), has triggered much subsequent research in the ferroelectrics community into a theoretical understanding of its origin (Alpay et al., 2003; Bouregba et al., 2003; Brazier et al., 1999; Chan et al., 2004; Fellberg et al., 2001; Mantese & Alpay, 2005; Mantese et al., 1997; Okatan et al., 2010; Poullain et al., 2002).

Such a phenomenon of polarization offsets in compositionally graded ferroelectric films is characterized by three key experimental observations: (i) The shift magnitude exhibits a strong dependence on electric field and temperature (Schubring et al., 1992). In particular, it typically exhibits a power 3 to 5 dependence on the magnitude of the applied electric field (Bao et al., 2000a, 2000b, 2000c, 2001b; Bouregba et al., 2003; Brazier et al., 1998; Mantese et al., 1997); (ii) The vertical hysteresis shift changes from upward to downward, or vice versa,

when the compositional gradient is inverted (Bouregba et al., 2003; Brazier et al., 1998; Mantese et al., 1997). (iii) A vertical polarization offset typically develops like the charging up of a capacitor, where the "time constant" is of the order of magnitude as the product of the capacitance and input impedance of the reference capacitor in the Sawyer-Tower circuit. In the past two decades, various theoretical ideas and models have been proposed to account for the origin of this phenomenon: Originally, the vertical hysteresis shift, or "polarization offset", was thought of as a static polarization developed across the graded ferroelectric film (Mantese et al., 1997), upon excitation by an alternating applied electric field. However, the experimental values of those "offsets" are at least an order of magnitude larger than the typical spontaneous polarization of the ferroelectric material, and therefore such a large static polarization component is deemed unlikely, if not impossible (Brazier et al., 1999). Other theoretical considerations include an interpretation of the vertical hysteresis shift as the result of a static voltage developed across the ferroelectric film (Brazier et al., 1999), as a result of asymmetric electrical conduction by leakage currents in the film (Bouregba et al., 2003), and as an effect of space charge in a perfectly insulating ferroelectric film (Okatan et al., 2010).

In our theoretical investigation where all of the key experimental observations mentioned above were reproduced theoretically (Chan et al., 2004), we proposed that the observation of polarization offsets in a compositionally graded ferroelectric film is a result of "time-dependent" space-charge-limited conduction inside the graded film, where the term "time-dependent" was used because the ferroelectric film was excited by an alternating applied electric field, in contrast to the abovementioned case of steady-state SCLC, in the absence of displacement currents, as described by the Mott-Gurney law. This central assumption was based on the following considerations: A similar phenomenon of polarization offsets was observed for homogeneous ferroelectric films in the presence of a temperature gradient (Fellberg et al., 2001), where the vertical hysteresis shift disappeared when the applied temperature gradient was removed. This suggests that, for this particular case, the shift is a result of thermally induced gradients in the polarization P (Alpay et al., 2003; Fellberg et al., 2001), or more generally in the electric displacement D, where the latter implies the presence of free space-charge according to Gauss' law. If the vertical hysteresis shifts that arise from compositional and thermal gradients are of the same origin, the observation of polarization offsets in compositionally graded ferroelectric films might be mainly a result of electrical conduction by free space-charge, i.e. SCLC. Here, we have deliberately aborted the assumption of a perfectly insulating ferroelectric film, as adopted by some other schools of thought (Alpay et al., 2003; Mantese & Alpay, 2005; Okatan et al., 2010), because experimental observations of small but finite leakage currents, as well as of SCLC currents, have been widely reported in the literature for ferroelectrics and other solid dielectrics (Bouregba et al., 2003; Carbone et al., 2005; Coelho, 1979; Laha & Krupanidhi, 2002; Pope & Swemberg, 1998; Poullain et al., 2002; Suh et al., 2000) and they form a subject of their own (Pope & Swemberg, 1998).

For our consideration of SCLC in compositionally graded ferroelectric films, the Mott-Gurney law $J \sim V^2$ does not apply, due to the following reasons: (i) In the case of a time-varying applied voltage, there is also the presence of displacement currents so that the conduction current J, which now does not necessarily equal the total current, could be varying with position, i.e. Eq. (3) no longer holds. (ii) In many ferroelectric and dielectric materials, there exist two opposite types of free charge-carriers, p-type and n-type, with

the system behaving like a wide bandgap semiconductor. Such double-carrier cases are not considered by the Mott-Gurney law. (iii) The Mott-Gurney law offers no way to take into account any small but finite intrinsic conductivity of a ferroelectric or dielectric material. (iv) For non-linear dielectric materials, the dielectric permittivity ε is not a constant, usually field-dependent, and for ferroelectrics it is even time- or history-dependent. And for inhomogeneous materials, e.g. compositionally graded ferroelectrics, ε typically exhibits a spatial variation. In view of these limitations, we have derived a new local conductivity expression (Chan et al., 2004) that is applicable to cases with the presence of both p-type and n-type free carriers, with a small but finite local conductivity, and with any possible dependence of the local dielectric permittivity ε on the system parameters. It is worth pointing out that a corresponding global conductivity expression, e.g. the Mott-Gurney law, must be obtained via the continuity condition in Eq. (3) and can only be derived with knowledge of the relation of ε with other system parameters. For example, in the derivation of the Mott-Gurney law, ε is a known quantity – it is taken as a constant, independent of any system parameter. In the following Section, we will review our original derivation (Chan et al., 2004) of this local conductivity expression, where the law of mass action was employed as an *ad hoc* approximation to describe the interactions between the two opposite types of free charge-carriers. A detailed justification of this mass-action approximation is provided in subsequent Sections.

4. Original derivation of the general local conductivity expression

For a time-varying applied voltage $V(t)$, the local conduction-current density $J_c(x,t)$, the local electric field $E(x,t)$ as well as the local electric displacement $D(x,t)$ are generally functions of the position x and the time t. The local conduction-current density is related to the local electric field via a generally time-dependent local conductivity $\sigma(x,t)$:

$$J_c(x,t) = \sigma(x,t)E(x,t) \tag{12}$$

Consider the simultaneous presence of p-type and n-type free charge-carriers with the position-dependent mobilities $\mu_p(x)$ and $-\mu_n(x)$, and of electric charges q and $-q$, respectively. Here we have chosen $\mu_p(x)$, $\mu_n(x)$ and q to all be positive quantities. Due to charge neutrality, the intrinsic number concentrations of the two opposite types of free carriers are equal, and they are here both denoted by the symbol $C_{in}(x)$. The time-dependent conductivity can then be expressed as

$$\sigma(x,t) = q\mu_p(x)[C_{in}(x) + \Delta p(x,t)] \\ + [-q][-\mu_n(x)][C_{in}(x) + \Delta n(x,t)] \tag{13}$$

where $\Delta p(x,t)$ and $\Delta n(x,t)$ are respectively the differences between the intrinsic and total number concentrations for each type of free carriers. Here we define a generally position-dependent local intrinsic conductivity

$$\sigma_{in}(x) \equiv q[\mu_p(x) + \mu_n(x)]C_{in}(x) \tag{14}$$

such that the time-dependent conductivity in Eq. (13) can be expressed as

$$\sigma(x,t) = \sigma_{in}(x) + q[\mu_p(x)\Delta p(x,t) + \mu_n(x)\Delta n(x,t)] \tag{15}$$

According to Gauss' law, the density of free space-charge is given by

$$\frac{\partial D(x,t)}{\partial x} = q[C_{in}(x) + \Delta p(x,t)] + [-q][C_{in}(x) + \Delta n(x,t)]$$
$$= q[\Delta p(x,t) - \Delta n(x,t)] \tag{16}$$

Since there generally exist interactions, i.e. generation and recombination, between the two opposite types of free charge-carriers, the free-carrier concentrations $C_{in}(x)+\Delta p(x,t)$ and $C_{in}(x)+\Delta n(x,t)$ are *not* independent of each other, and should be described by an additional physical constraint

$$F[\Delta p(x,t), \Delta n(x,t)] = 0 \tag{17}$$

As an *ah hoc* approximation, we regard any ferroelectric or dielectric material as a wide bandgap semiconductor and then employ the equilibrium law of mass action to be this additional physical constraint:

$$C_{in}(x)^2 = [C_{in}(x) + \Delta p(x,t)][C_{in}(x) + \Delta n(x,t)] \tag{18}$$

The physics described by Eq. (18) is as follows (Chan et al., 2007): In a wide bandgap semiconductor, there are the endothermic generation and exothermic recombination of free charge-carriers. If the energy released by free-carrier recombination is immediately used for free-carrier generation, i.e. a "heat balance" condition, the rates of these endothermic and exothermic processes must be equal, and there would not be any net production of heat nor any net generation of free carriers. On the other hand, the rate of each of these processes can be assumed, as a first approximation, to be proportional to the product of the reactants' concentrations, i.e. *the number of ways per unit volume the different types of reactants can combine to undergo the process*. Since, for a dielectric insulator, the concentration of the source particles for free-carrier generation (e.g. valence electrons or molecules) is by definition orders of magnitude larger than the concentrations of the free carriers, the concentration of source particles, and hence the rate of free-carrier generation, should only have an insignificant time fluctuation and should practically be a material-pertaining property. It follows that any rate of free-carrier recombination, which we have here assumed to be proportional to the product of the concentrations of *p*-type and *n*-type free carriers, can all be taken as equal to the same approximately time-invariant rate of free-carrier generation, hence Eq. (18).
Upon rewriting Eqs. (16) and (18) as

$$\Delta p(x,t) = \frac{1}{q}\frac{\partial D(x,t)}{\partial x} + \Delta n(x,t) \tag{19}$$

and

$$C_{in}(x)[\Delta p(x,t) + \Delta n(x,t)] + \Delta p(x,t)\Delta n(x,t) = 0 \tag{20}$$

respectively, it can be seen that two quadratic equations, for $\Delta p(x,t)$ and $\Delta n(x,t)$ respectively, can be obtained:

$$\Delta p(x,t)^2 + B_p(x,t)\Delta p(x,t) + C_p(x,t) = 0 \tag{21}$$

and

$$\Delta n(x,t)^2 + B_n(x,t)\Delta n(x,t) + C_n(x,t) = 0 \tag{22}$$

where

$$B_p(x,t) \equiv -\frac{1}{q}\frac{\partial D(x,t)}{\partial x} + 2C_{in}(x) \tag{23}$$

$$C_p(x,t) \equiv -\frac{C_{in}(x)}{q}\frac{\partial D(x,t)}{\partial x} \tag{24}$$

$$B_n(x,t) \equiv \frac{1}{q}\frac{\partial D(x,t)}{\partial x} + 2C_{in}(x) \tag{25}$$

and

$$C_n(x,t) \equiv \frac{C_{in}(x)}{q}\frac{\partial D(x,t)}{\partial x} \tag{26}$$

It follows that

$$
\begin{aligned}
q[\mu_p(x)\Delta p(x,t) &+ \mu_n(x)\Delta n(x,t)] \\
= \frac{q}{2}\{\mu_p(x)&[-B_p(x,t) \pm \sqrt{B_p(x,t)^2 - 4C_p(x,t)}] \\
&+ \mu_n(x)[-B_n(x,t) \pm \sqrt{B_n(x,t)^2 - 4C_n(x,t)}]\}
\end{aligned}
\tag{27}
$$

Using the definitions of the quadratic coefficients $B_p(x,t)$, $C_p(x,t)$, $B_n(x,t)$ and $C_n(x,t)$, as well as the definition of $\sigma_{in}(x)$ in Eq. (14), the following relations can be obtained:

$$
\begin{aligned}
-\frac{q}{2}[\mu_p(x)B_p(x,t) &+ \mu_n(x)B_n(x,t)] \\
&= \frac{[\mu_p(x) - \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x} - \sigma_{in}(x)
\end{aligned}
\tag{28}
$$

and

$$
\begin{aligned}
\frac{q}{2}\sqrt{B_p(x,t)^2 - 4C_p(x,t)} &= \frac{q}{2}\sqrt{B_n(x,t)^2 - 4C_n(x,t)} \\
&= \frac{1}{2}\sqrt{\left[\frac{\partial D(x,t)}{\partial x}\right]^2 + \frac{4\sigma_{in}(x)^2}{[\mu_p(x) + \mu_n(x)]^2}}
\end{aligned}
\tag{29}
$$

Using Eqs. (15), (28) and (29), Eq. (27) can be rewritten as

$$
\begin{aligned}
q[\mu_p(x)\Delta p(x,t) &+ \mu_n(x)\Delta n(x,t)] \\
&= \frac{[\mu_p(x) - \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x} - \sigma_{in}(x) \\
&\quad + \frac{[\pm\mu_p(x) \pm \mu_n(x)]}{2}\sqrt{\left[\frac{\partial D(x,t)}{\partial x}\right]^2 + \frac{4\sigma_{in}(x)^2}{[\mu_p(x) + \mu_n(x)]^2}} \\
&= \sigma(x,t) - \sigma_{in}(x)
\end{aligned}
\tag{30}
$$

so that an expression for the time-dependent local conductivity $\sigma(x,t)$ can be obtained:

$$
\sigma(x,t) = \frac{[\mu_p(x) - \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x} \\
+ \sqrt{\left\{\frac{[\pm\mu_p(x) \pm \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x}\right\}^2 + \frac{[\pm\mu_p(x) \pm \mu_n(x)]^2\sigma_{in}(x)^2}{[\mu_p(x) + \mu_n(x)]^2}}
\tag{31}
$$

According to Eqs. (15), (16) and (31), for the case of $\Delta p(x,t) = \Delta n(x,t) = 0$, we have

$$
\frac{\partial D(x,t)}{\partial x} = 0
\tag{32}
$$

and

$$
\sigma(x,t) = \sigma_{in}(x) = \frac{[\pm\mu_p(x) \pm \mu_n(x)]}{[\mu_p(x) + \mu_n(x)]}\sigma_{in}(x)
\tag{33}
$$

where the latter implies that only the root of all upper positive signs in Eq. (31) is valid. Therefore, the correct expression for the time-dependent conductivity should be:

$$
\sigma(x,t) = \frac{[\mu_p(x) - \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x} \\
+ \sqrt{\left\{\frac{[\mu_p(x) + \mu_n(x)]}{2}\frac{\partial D(x,t)}{\partial x}\right\}^2 + \sigma_{in}(x)^2}
\tag{34}
$$

which describes a nonlinear relation between the space-charge density and the overall local conductivity in the presence of a non-zero intrinsic conductivity.

5. Limiting case of zero intrinsic conductivity

Consider a case where $\sigma_{in}(x) \to 0$ but $\sigma(x,t)$ remains finite. According to Eq. (15), either $\mu_p(x)$ or $\mu_n(x)$ has to be non-zero for $\sigma(x,t)$ to remain finite. From the definition of the intrinsic conductivity in Eq. (14), for $\sigma_{in}(x) \to 0$ we must have $C_{in}(x) \to 0$, because the mobility sum $[\mu_p(x) + \mu_n(x)]$ is finite. For $C_{in}(x) \to 0$, Eq. (20) becomes

$$\Delta p(x,t)\Delta n(x,t) \approx 0 \tag{35}$$

Multiplying both sides of Eq. (19) by $\Delta p(x,t)$ or $\Delta n(x,t)$ and then applying Eq. (35), we obtain

$$\Delta p(x,t)\left[\Delta p(x,t) - \frac{1}{q}\frac{\partial D(x,t)}{\partial x}\right] \approx 0 \tag{36}$$

and

$$\Delta n(x,t)\left[\Delta n(x,t) + \frac{1}{q}\frac{\partial D(x,t)}{\partial x}\right] \approx 0 \tag{37}$$

The solutions to Eqs. (36) and (37) are

$$\Delta p(x,t) \approx 0, \quad \Delta p(x,t) \approx \frac{1}{q}\frac{\partial D(x,t)}{\partial x} \tag{38}$$

and

$$\Delta n(x,t) \approx 0, \quad \Delta n(x,t) \approx -\frac{1}{q}\frac{\partial D(x,t)}{\partial x} \tag{39}$$

respectively. According to Eq. (19), however, only the following combinations of solutions are allowed.

$$\Delta p(x,t) \approx 0 \quad and \quad \Delta n(x,t) \approx -\frac{1}{q}\frac{\partial D(x,t)}{\partial x} \tag{40}$$

and

$$\Delta n(x,t) \approx 0 \quad and \quad \Delta p(x,t) \approx \frac{1}{q}\frac{\partial D(x,t)}{\partial x} \tag{41}$$

Since $C_{in}(x) \rightarrow 0$, the quantities $\Delta p(x,t)$ and $\Delta n(x,t)$ effectively become the total free-carrier concentrations and must therefore be non-negative. Eqs. (40) and (41) thus lead to an important conclusion: *At the limit of zero intrinsic conductivity, either p-type or n-type free charge-carriers become dominant*, with the cases of

$$\frac{\partial D(x,t)}{\partial x} > 0 \tag{42}$$

and

$$\frac{\partial D(x,t)}{\partial x} < 0 \tag{43}$$

corresponding to the dominance of *p*-type and *n*-type free charge-carriers, respectively. This conclusion provides a linkage between two of the three independent assumptions, i.e. the absence of an intrinsic conductivity and the presence of only a single type of free charge-

carriers, in the original derivation of the Mott-Gurney law: Although Eqs. (40) and (41) only conclude that the simultaneous presence of p-type and n-type free carriers is *locally* forbidden, this conclusion also holds *globally* across a dielectric sample for the case of a plane-parallel dielectric capacitor as described by the Mott-Gurney law. In the absence of diffusion currents, the total-current density J is equal to the conduction-current density J_c, and they are both spatially continuous; For any non-zero total-current density J, the space-charge density must be non-zero everywhere, otherwise there would be the case of $J = J_c = 0$ somewhere in the sample. Globally, regions of positive space-charge density and regions of negative space-charge density cannot be present simultaneously in the dielectric sample, otherwise there would exist inter-regional boundaries of zero space-charge density at which $J = J_c = 0$. It follows that the space-charge density must be of the same sign across the dielectric sample as well, which implies that the simultaneous presence of p-type and n-type free charge-carriers is also globally forbidden.

For $\sigma_{in}(x) \rightarrow 0$, Eq. (34) becomes

$$\sigma(x,t) \approx \frac{[\mu_p(x) - \mu_n(x)]}{2} \frac{\partial D(x,t)}{\partial x} + \frac{[\mu_p(x) + \mu_n(x)]}{2} \left| \frac{\partial D(x,t)}{\partial x} \right| \tag{44}$$

If Eq. (42) holds, we have

$$\begin{aligned}
\sigma(x,t) &\approx \frac{[\mu_p(x) - \mu_n(x)]}{2} \frac{\partial D(x,t)}{\partial x} \\
&+ \frac{[\mu_p(x) + \mu_n(x)]}{2} \frac{\partial D(x,t)}{\partial x} \\
&\approx \mu_p(x) \frac{\partial D(x,t)}{\partial x}
\end{aligned} \tag{45}$$

Else if Eq. (43) holds, we have

$$\begin{aligned}
\sigma(x,t) &\approx \frac{[\mu_p(x) - \mu_n(x)]}{2} \frac{\partial D(x,t)}{\partial x} \\
&+ \frac{[\mu_p(x) + \mu_n(x)]}{2} \left[-\frac{\partial D(x,t)}{\partial x} \right] \\
&\approx -\mu_n(x) \frac{\partial D(x,t)}{\partial x}
\end{aligned} \tag{46}$$

Eqs. (45) and (46) together verify that, in the case of $\sigma_{in}(x) \rightarrow 0$, the charge mobility in the expression for the generally time-dependent local conductivity $\sigma(x,t)$ is correctly equal to that of the dominant type of free carriers.

6. Derivation of a general expression for the local diffusion-current density

Apart from electrical conduction, i.e. the electric-field-driven flow of free charge-carriers, there also exists the possibility of charge diffusion due to the presence of a charge-density

gradient or a temperature gradient, where the latter is often being referred to as the thermoelectric effect. For any bulk dielectric sample, consider the ith infinitesimal volume with dimensions Δx, Δy and Δz. Along the x-direction, for example, the net force acting on the p-type free carriers within this infinitesimal volume is given by

$$F_{p,i} = (P_{p,i-1} - P_{p,i+1})\Delta y \Delta z \tag{47}$$

where P and the subscript p denote the local pressure and p-type free charge-carriers, respectively. The total amount of charge carried by the p-type free carriers in this infinitesimal volume is

$$Q_{p,i} = qC_p \Delta x \Delta y \Delta z \tag{48}$$

where

$$C_p \equiv C_{in} + \Delta p \tag{49}$$

is the total concentration of p-type free carriers for this infinitesimal volume. The corresponding force per unit charge, i.e. the mechanical counterpart of the electric field, is then given by

$$\tilde{E}_{p,i} \equiv \frac{F_{p,i}}{Q_{p,i}} = -\frac{(P_{p,i+1} - P_{p,i-1})}{qC_p\Delta x} \tag{50}$$

And for the case of conduction by n-type free carriers, we have

$$\tilde{E}_{n,i} \equiv \frac{F_{n,i}}{Q_{n,i}} = -\frac{(P_{n,i+1} - P_{n,i-1})}{(-qC_n)\Delta x} \tag{51}$$

where

$$C_n \equiv C_{in} + \Delta n \tag{52}$$

is the total concentration of n-type free carriers. In the continuum limit, Eqs. (50) and (51) can be replaced by

$$\tilde{E}_p(x,t) = -\frac{1}{qC_p(x,t)}\frac{\partial P_p(x,t)}{\partial x} \tag{53}$$

and

$$\tilde{E}_n(x,t) = -\frac{1}{[-qC_n(x,t)]}\frac{\partial P_n(x,t)}{\partial x} \tag{54}$$

respectively. The diffusion-current density is then given by

$$\begin{aligned}
J_d(x,t) &= q[\mu_p(x)C_p(x,t)\tilde{E}_p(x,t) \\
&\quad + \mu_n(x)C_n(x,t)\tilde{E}_n(x,t)] \\
&= -\left[\mu_p(x)\frac{\partial P_p(x,t)}{\partial x} + [-\mu_n(x)]\frac{\partial P_n(x,t)}{\partial x}\right]
\end{aligned} \tag{55}$$

Using an ideal-gas approximation for each of the two types of free charge-carriers, i.e.

$$P_p(x,t) = k_B T(x,t) C_p(x,t) \tag{56}$$

and

$$P_n(x,t) = k_B T(x,t) C_n(x,t) \tag{57}$$

where k_B is the Boltzmann constant and $T(x,t)$ is a generally position- and time-dependent local temperature, the diffusion-current density can be expressed as

$$J_d(x,t) = -k_B T(x,t) \left[\begin{array}{c} \mu_p(x) \dfrac{\partial C_p(x,t)}{\partial x} \\ + [-\mu_n(x)] \dfrac{\partial C_n(x,t)}{\partial x} \end{array} \right] \\ - k_B \dfrac{\partial T(x,t)}{\partial x} \left[\mu_p(x) C_p(x,t) + [-\mu_n(x)] C_n(x,t) \right] \tag{58}$$

where

$$D_{o,p}(x,t) \equiv \dfrac{\mu_p(x) k_B T(x,t)}{q} \tag{59}$$

and

$$D_{o,n}(x,t) \equiv \dfrac{[-\mu_n(x)] k_B T(x,t)}{(-q)} \tag{60}$$

are the Einstein relations for the local diffusion coefficients of p-type and n-type free charge-carriers, respectively. Using the definitions in Eqs. (49) and (52), Eq. (58) can be rewritten as

$$J_d(x,t) = -k_B T(x,t) \left[\begin{array}{c} [\mu_p(x) - \mu_n(x)] \dfrac{dC_{in}(x)}{dx} \\ + \mu_p(x) \dfrac{\partial \Delta p(x,t)}{\partial x} - \mu_n(x) \dfrac{\partial \Delta n(x,t)}{\partial x} \end{array} \right] \\ - k_B \dfrac{\partial T(x,t)}{\partial x} \left[\begin{array}{c} [\mu_p(x) - \mu_n(x)] C_{in}(x) \\ + \mu_p(x) \Delta p(x,t) - \mu_n(x) \Delta n(x,t) \end{array} \right] \tag{61}$$

From Eqs. (21) and (22), we obtain

$$\Delta p(x,t) = \dfrac{1}{2q} \dfrac{\partial D(x,t)}{\partial x} - C_{in}(x) \\ + \sqrt{\left[\dfrac{1}{2q} \dfrac{\partial D(x,t)}{\partial x} \right]^2 + C_{in}(x)^2} \tag{62}$$

and

$$\Delta n(x,t) = -\frac{1}{2q}\frac{\partial D(x,t)}{\partial x} - C_{in}(x)$$
$$+ \sqrt{\left[\frac{1}{2q}\frac{\partial D(x,t)}{\partial x}\right]^2 + C_{in}(x)^2} \tag{63}$$

Differentiating Eqs. (62) and (63) with respect to x yields

$$\frac{\partial \Delta p(x,t)}{\partial x} = \frac{1}{2q}\frac{\partial^2 D(x,t)}{\partial x^2} - \frac{dC_{in}(x)}{dx}$$
$$+ \left\{\sqrt{\left[\frac{1}{2q}\frac{\partial D(x,t)}{\partial x}\right]^2 + C_{in}(x)^2}\right\}^{-1} \tag{64}$$
$$\times \left[\frac{1}{4q^2}\frac{\partial D(x,t)}{\partial x}\frac{\partial^2 D(x,t)}{\partial x^2} + C_{in}(x)\frac{dC_{in}(x)}{dx}\right]$$

and

$$\frac{\partial \Delta n(x,t)}{\partial x} = -\frac{1}{2q}\frac{\partial^2 D(x,t)}{\partial x^2} - \frac{dC_{in}(x)}{dx}$$
$$+ \left\{\sqrt{\left[\frac{1}{2q}\frac{\partial D(x,t)}{\partial x}\right]^2 + C_{in}(x)^2}\right\}^{-1} \tag{65}$$
$$\times \left[\frac{1}{4q^2}\frac{\partial D(x,t)}{\partial x}\frac{\partial^2 D(x,t)}{\partial x^2} + C_{in}(x)\frac{dC_{in}(x)}{dx}\right]$$

respectively. Putting Eqs. (62) to (65) into Eq. (61), we obtain a general expression for the local diffusion-current density:

$$J_d(x,t) = J_{d1}(x,t) + J_{d2}(x,t) \tag{66}$$

where

$$J_{d1}(x,t) \equiv -\frac{k_B T(x,t)[\mu_p(x) + \mu_n(x)]}{2q}\frac{\partial^2 D(x,t)}{\partial x^2}$$
$$- [\mu_p(x) - \mu_n(x)]k_B T(x,t) \times \left\{\sqrt{\left[\frac{1}{2q}\frac{\partial D(x,t)}{\partial x}\right]^2 + C_{in}(x)^2}\right\}^{-1} \tag{67}$$
$$\times \left[\frac{1}{4q^2}\frac{\partial D(x,t)}{\partial x}\frac{\partial^2 D(x,t)}{\partial x^2} + C_{in}(x)\frac{dC_{in}(x)}{dx}\right]$$

and

$$J_{d2}(x,t) \equiv -k_B \frac{\partial T(x,t)}{\partial x} \left[\begin{array}{c} \dfrac{[\mu_p(x)+\mu_n(x)]}{2q} \dfrac{\partial D(x,t)}{\partial x} \\ +[\mu_p(x)-\mu_n(x)] \\ \times \sqrt{\left[\dfrac{1}{2q}\dfrac{\partial D(x,t)}{\partial x}\right]^2 + C_{in}(x)^2} \end{array} \right] \tag{68}$$

Eq. (67) denotes a contribution to the diffusion current from the presence of a gradient in the space-charge density or in the intrinsic free-carrier concentration, while Eq. (68) denotes a contribution from the presence of a temperature gradient. At the limit of zero intrinsic conductivity, we have $C_{in}(x) \rightarrow 0$ as explained in the beginning of the previous section. Eqs. (67) and (68) are then reduced to

$$J_{d1}(x,t) \approx -\frac{[\mu_p(x)+\mu_n(x)]k_B T(x,t)}{2q} \frac{\partial^2 D(x,t)}{\partial x^2}$$
$$-\frac{[\mu_p(x)-\mu_n(x)]k_B T(x,t)}{2q} \frac{\dfrac{\partial D(x,t)}{\partial x}\dfrac{\partial^2 D(x,t)}{\partial x^2}}{\left|\dfrac{\partial D(x,t)}{\partial x}\right|} \tag{69}$$

and

$$J_{d2}(x,t) \approx -k_B \frac{\partial T(x,t)}{\partial x} \left[\dfrac{[\mu_p(x)+\mu_n(x)]}{2q}\dfrac{\partial D(x,t)}{\partial x} + \dfrac{[\mu_p(x)-\mu_n(x)]}{2q}\left|\dfrac{\partial D(x,t)}{\partial x}\right| \right] \tag{70}$$

respectively. Similar to the case of Eq. (44), for Eqs. (69) and (70) we can also verify that in the case of $\sigma_{in}(x) \rightarrow 0$ the charge mobility is correctly equal to that of the dominant type of free carriers. Following Eqs. (69) and (70), if Eq. (42) is satisfied, we have

$$J_{d1}(x,t) \approx -\frac{[\mu_p(x)+\mu_n(x)]k_B T(x,t)}{2q} \frac{\partial^2 D(x,t)}{\partial x^2}$$
$$-\frac{[\mu_p(x)-\mu_n(x)]k_B T(x,t)}{2q} \frac{\dfrac{\partial D(x,t)}{\partial x}\dfrac{\partial^2 D(x,t)}{\partial x^2}}{\left[+\dfrac{\partial D(x,t)}{\partial x}\right]} \tag{71}$$
$$\approx -\frac{\mu_p(x)k_B T(x,t)}{q} \frac{\partial^2 D(x,t)}{\partial x^2}$$

and

$$J_{d2}(x,t) \approx -k_B \frac{\partial T(x,t)}{\partial x} \left[\frac{[\mu_p(x)+\mu_n(x)]}{2q} \frac{\partial D(x,t)}{\partial x} + \frac{[\mu_p(x)-\mu_n(x)]}{2q} \left[+ \frac{\partial D(x,t)}{\partial x} \right] \right]$$

$$\approx -\frac{\mu_p(x)k_B}{q} \frac{\partial D(x,t)}{\partial x} \frac{\partial T(x,t)}{\partial x} \tag{72}$$

Else if Eq. (43) is satisfied, we have

$$J_{d1}(x,t) \approx -\frac{[\mu_p(x)+\mu_n(x)]k_B T(x,t)}{2q} \frac{\partial^2 D(x,t)}{\partial x^2}$$

$$-\frac{[\mu_p(x)-\mu_n(x)]k_B T(x,t)}{2q} \frac{\frac{\partial D(x,t)}{\partial x} \frac{\partial^2 D(x,t)}{\partial x^2}}{\left[-\frac{\partial D(x,t)}{\partial x} \right]} \tag{73}$$

$$\approx -\frac{\mu_n(x)k_B T(x,t)}{q} \frac{\partial^2 D(x,t)}{\partial x^2}$$

and

$$J_{d2}(x,t) \approx -k_B \frac{\partial T(x,t)}{\partial x} \left[\frac{[\mu_p(x)+\mu_n(x)]}{2q} \frac{\partial D(x,t)}{\partial x} + \frac{[\mu_p(x)-\mu_n(x)]}{2q} \left[- \frac{\partial D(x,t)}{\partial x} \right] \right]$$

$$\approx -\frac{\mu_n(x)k_B}{q} \frac{\partial D(x,t)}{\partial x} \frac{\partial T(x,t)}{\partial x} \tag{74}$$

7. Alternative derivation of the general local conductivity expression

We begin our alternative derivation of the general local conductivity expression in Eq. (34) by identifying the following quantities that appear in the conductivity expression:

$$\mu'(x) \equiv \frac{\mu_p(x)-\mu_n(x)}{2} \tag{75}$$

and

$$\mu''(x) \equiv \frac{\mu_p(x)+\mu_n(x)}{2} \tag{76}$$

The drift velocities of p-type and n-type free carriers can then be expressed as

$$v_p(x,t) = \mu_p(x)E(x,t) = \mu'(x)E(x,t) + \mu''(x)E(x,t) \tag{77}$$

and

$$v_n(x,t) = -\mu_n(x)E(x,t) = \mu'(x)E(x,t) - \mu''(x)E(x,t) \tag{78}$$

where

$$\mu''(x) \geq |\mu'(x)| \geq 0 \tag{79}$$

and $\mu'(x)$ can be positive or negative. In this description, both p-type and n-type free carriers share the same velocity component $\mu'(x)E(x,t)$, with the presence of the additional velocity components $\mu''(x)E(x,t)$ and $-\mu''(x)E(x,t)$ for p-type and n-type free carriers, respectively. The generally time-dependent local electrical conductivity can then be expressed as a sum of contributions from the velocity components $\mu'(x)E(x,t)$ and $\pm\mu''(x)E(x,t)$:

$$\begin{aligned}
\sigma(x,t) = {} & q\mu'(x)[C_p(x,t) - C_n(x,t)] \\
& + q\mu''(x)[C_p(x,t) + C_n(x,t)]
\end{aligned} \tag{80}$$

According to Gauss' law, the density of free space-charge is given by

$$\rho_q(x,t) = \frac{\partial D(x,t)}{\partial x} = q[C_p(x,t) - C_n(x,t)] \tag{81}$$

In the absence of free space-charge, i.e. $\rho_q(x,t) = 0$, both $C_p(x,t)$ and $C_n(x,t)$ are by definition equal to the intrinsic free-carrier concentration $C_{in}(x)$, and the electrical conductivity $\sigma(x,t)$ would then be equal to the intrinsic conductivity

$$\sigma_{in}(x) \equiv 2q\mu''(x)C_{in}(x) \tag{82}$$

according to Eq. (80).

Consider the reversible generation and recombination of p-type and n-type free carriers:

$$\text{1 source particle} \quad \longleftrightarrow \quad \text{1 } p\text{-type free carrier} \quad + \quad \text{1 } n\text{-type free carrier}$$
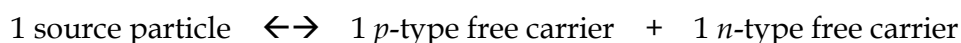
As described right below Eq. (18), the rate of free-carrier generation is assumed to be equal to the rate of free-carrier recombination due to a "heat balance" condition, and the rate of each of these processes is assumed to be proportional to the product of the "reactants". Following these, for $C_s(x,t)$ being the concentration of the source particles for free-carrier generation (e.g. valence electrons or molecules) we have

$$K_g C_s(x,t) = K_r C_p(x,t)C_n(x,t) \tag{83}$$

where K_g and K_r are, respectively, the rate constants for the generation and recombination of free carriers. If the conditions

$$C_p(x,t) \ll C_s(x,t) \tag{84}$$

and

$$C_n(x,t) \ll C_s(x,t) \tag{85}$$

hold for a dielectric insulator such that

$$C_s(x,t) \approx C_s(x) \tag{86}$$

i.e. the concentration of source particles for free-carrier generation has an insignificant fluctuation with time and is practically a material-pertaining property, we have

$$K_g C_s(x) \approx K_r C_p(x,t)C_n(x,t) \approx K_r C_{in}(x)^2 \tag{87}$$

which implies

$$C_p(x,t)C_n(x,t) \approx C_{in}(x)^2 \tag{88}$$

As an example, we show that this mass-action approximation is valid for a dielectric insulator which has holes and free electrons as its p-type and n-type free charge-carriers, respectively, and which has valence electrons as its source particles: A hole is by definition equivalent to a missing valence electron. At anywhere inside the dielectric sample, the generation and annihilation of a hole correspond, by definition, to the annihilation and generation of a valence electron, respectively, and the flow-in and flow-out of a hole are, respectively, by definition equivalent to the flow-out and flow-in of a valence electron in the opposite directions. Therefore,

$$\frac{\partial C_p(x,t)}{\partial t} = -\frac{\partial C_s(x,t)}{\partial t} \tag{89}$$

so that the total concentration of holes and valence electrons is given by

$$C_{p+s}(x) \equiv C_p(x,t) + C_s(x,t) \tag{90}$$

Eq. (83) can then be written as

$$K_g[C_{p+s}(x) - C_p(x,t)] = K_r C_p(x,t)C_n(x,t) \tag{91}$$

For the case of zero space charge where $C_p(x,t) = C_n(x,t) = C_{in}(x)$, we have

$$K_g[C_{p+s}(x) - C_{in}(x)] = K_r C_{in}(x)^2 \tag{92}$$

Define a material paramter

$$\alpha(x) \equiv \frac{C_{in}(x)}{C_{p+s}(x)} \leq 1 \tag{93}$$

and consider the limit of $\alpha(x) \to 0$ for the case of a dielectric insulator. Combining Eqs. (91) to (93), we obtain the mass-action relation in Eq. (88):

$$\begin{aligned} & C_p(x,t)C_n(x,t) \\ &= \underset{\alpha(x)\to 0}{limit} \frac{C_{in}(x)[C_{in}(x) - \alpha(x)C_p(x,t)]}{[1-\alpha(x)]} = C_{in}(x)^2 \end{aligned} \tag{94}$$

Going back to our derivation of the conductivity expression, we notice that Eqs. (81) and (88) together imply

$$C_p(x,t)^2 - \frac{\rho_q(x,t)}{q}C_p(x,t) - C_{in}(x)^2 \approx 0 \tag{95}$$

and

$$C_n(x,t)^2 + \frac{\rho_q(x,t)}{q}C_n(x,t) - C_{in}(x)^2 \approx 0 \tag{96}$$

from which we obtain

$$C_p(x,t) \approx \frac{1}{2}\left[\frac{\rho_q(x,t)}{q} + \sqrt{\left[\frac{\rho_q(x,t)}{q}\right]^2 + 4C_{in}(x)^2}\right] \geq 0 \tag{97}$$

$$C_n(x,t) \approx \frac{1}{2}\left[-\frac{\rho_q(x,t)}{q} + \sqrt{\left[\frac{\rho_q(x,t)}{q}\right]^2 + 4C_{in}(x)^2}\right] \geq 0 \tag{98}$$

and

$$C_p(x,t) + C_n(x,t) \approx \sqrt{\left[\frac{\rho_q(x,t)}{q}\right]^2 + 4C_{in}(x)^2} \tag{99}$$

Using Eqs. (80) to (82) as well as Eq. (99), we obtain the following expression for the generally time-dependent local electrical conductivity:

$$\sigma(x,t) \approx \mu'(x)\rho_q(x,t) + \sqrt{[\mu''(x)\rho_q(x,t)]^2 + \sigma_{in}(x)^2} \tag{100}$$

By defining the reduced paramters

$$\sigma^*(x,t) \equiv \frac{\sigma(x,t)}{\sigma_{in}(x)} \tag{101}$$

$$\mu^*(x) \equiv \frac{\mu'(x)}{\mu''(x)} \in \{-1,+1\} \tag{102}$$

and

$$\rho_q^*(x,t) \equiv \frac{\rho_q(x,t)}{2qC_{in}(x)} \tag{103}$$

Eq. (100) can be expressed in a simpler form:

$$\sigma^*(x,t) \approx \mu^*(x)\rho_q^*(x,t) + \sqrt{[\rho_q^*(x,t)]^2 + 1} \tag{104}$$

For the limiting case of zero intrinsic conductivity with $C_{in}(x) \to 0$, Eqs. (97) and (98) can be rewritten as

$$C_p(x,t) \approx \frac{1}{2}\left[\frac{\rho_q(x,t)}{q} + \left|\frac{\rho_q(x,t)}{q}\right|\right] \tag{105}$$

and

$$C_n(x,t) \approx \frac{1}{2}\left[-\frac{\rho_q(x,t)}{q} + \left|\frac{\rho_q(x,t)}{q}\right|\right] \tag{106}$$

respectively, which imply the dominance of either type of free carriers: If $\rho_q(x,t) > 0$, we have

$$C_p(x,t) \approx \frac{\rho_q(x,t)}{q} \quad and \quad C_n(x,t) \approx 0 \tag{107}$$

Else if $\rho_q(x,t) < 0$, we have

$$C_p(x,t) \approx 0 \quad and \quad C_n(x,t) \approx -\frac{\rho_q(x,t)}{q} \tag{108}$$

8. Conclusions and future work

In this Chapter, a generalized theory for space-charge-limited conduction (SCLC) in ferroelectrics and other solid dielectrics, which we have originally developed to account for the peculiar observation of polarization offsets in compositionally graded ferroelectric films, is presented in full. The theory is a generalization of the conventional *steady-state* trap-free SCLC model, as described by the Mott-Gurney law, to include (i) the presence of two opposite types of free carriers: *p*-type and *n*-type, (ii) the presence of a finite intrinsic (Ohmic) conductivity, (iii) any possible field- and time-dependence of the dielectric permittivity, and (iv) any possible time dependence of the dielectric system under study. Expressions for the local conductivity as well as for the local diffusion-current density were derived through a mass-action approximation for which a detailed theoretical justification is provided in this Chapter. It was found that, in the presence of a finite intrinsic conductivity, both the local conductivity and the local diffusion-current density are related to the space-charge density in a nonlinear fashion, as described by Eqs. (34), (66), (67) and (68), where the local diffusion-current density is generally described as a sum of contributions from the presence of a charge-density gradient and of a temperature gradient. At the limit of zero intrinsic conductivity, it was found that either *p*-type or *n*-type free carriers are dominant. This conclusion provides a linkage between the independent assumptions of (i) a single carrier type and (ii) a negligible intrinsic conductivity in the conventional steady-state SCLC model. For any given space-charge density, it was also verified that the expressions we have derived correctly predict the dominant type of free carriers at the limit of zero intrinsic conductivity.

Future work should be carried out along at least three possible directions: (i) As a further application of this general local conductivity expression, further numerical investigations should be carried out on how charge actually flows inside a compositionally graded ferroelectric film. This would provide answers to interesting questions like: Does a graded ferroelectric system exhibit any kind of charge-density waves upon excitation by an

alternating electric field? What are the physical factors (dielectric permittivity, carrier mobility, etc.) that could limit or enhance the degree of asymmetry in the SCLC currents of a graded ferroelectric film? The latter question has been partially answered by ourselves (Zhou et al., 2005b), where we have theoretically found that the observation of polarization offsets, i.e. the onset of asymmetric SCLC, in a compositionally graded ferroelectric film is conditional upon the presence of relatively large gradients in the polarization and in the dielectric permittivity. Certainly, a detailed understanding of the mechanism of asymmetric electrical conduction in such a graded ferroelectric film would also provide insights into the designing of new types of electrical diodes or rectifiers. The recently derived expression for the local diffusion-current density, as first presented in this Book Chapter (Eqs. (66) to (68)), has also opened up a new dimension for further theoretical investigations: Using this expression, the effect of charge diffusion in the presence of a charge-density gradient or a temperature gradient can be taken into account as well, and a whole new range of problems can be studied. For example, it would be interesting to know whether asymmetric electrical conduction would also occur if a compositionally graded ferroelectric film is driven by a sinusoidal applied temperature difference instead of a sinusoidal applied voltage. In this case, one also needs to take into account the temperature dependence of the various system parameters like the remanent polarization and the dielectric permittivity. The theoretical predictions should then be compared against any available experimental results. (ii) Going back to the generalized SCLC theory itself, it would be important to look for possible experimental verifications of the general local conductivity expression, and to establish a set of physical conditions under which the conductivity expression and the corresponding mass-action approximation are valid. Theoretical predictions from the conductivity expression should be made for real experimental systems and then be compared with available experimental results. It would also be worthwhile to generalize the mass-action approximation, and hence the corresponding local conductivity expression, to other cases where the charge of the free carriers, or the stoichiometric ratio between the concentrations of p-type and n-type free carriers in the generation-recombination processes, is different. (iii) In the derivation of the Mott-Gurney law $J \sim V^2$, the boundary conditions $E_p(0) = 0$ and $E_n(L) = 0$ were employed to describe the cases of conduction by p-type and n-type free carriers, respectively. If we keep $E_p(0)$ or $E_n(L)$ as a variable throughout the derivation, an expression of J as a function of $E_p(0)$ or $E_n(L)$ can be obtained and it can be shown that both the boundary conditions $E_p(0) = 0$ and $E_n(L) = 0$ correspond to a state of maximum current density. As an example, for the case of conduction by p-type free carriers, we have (Fig. 2)

$$j_p \equiv \frac{J_p L^3}{\mu_p \varepsilon V^2} = \frac{\left[\dfrac{9 - 12 e_p(0)^2}{16}\right]}{+ \sqrt{\left[\dfrac{9 - 12 e_p(0)^2}{16}\right]^2 + \dfrac{3}{4} e_p(0)^3 [1 - e_p(0)]}} \tag{109}$$

where $e_p(0) \equiv E_p(0)L/V$. If we consider our general local conductivity expression which takes into account the presence of a finite intrinsic conductivity and the simultaneous presence of

p-type and *n*-type free carriers, it would be important to know whether this maximum-current principle can be generally applied to obtain the system's boundary conditions.
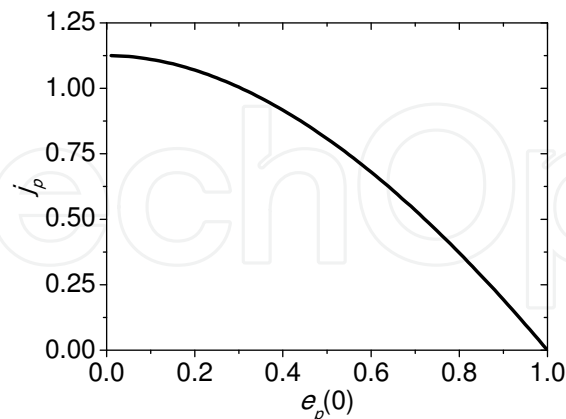

Fig. 2. Plot of j_p against $e_p(0)$, showing a maximum of j_p at $e_p(0) = 0$.

9. Acknowledgments

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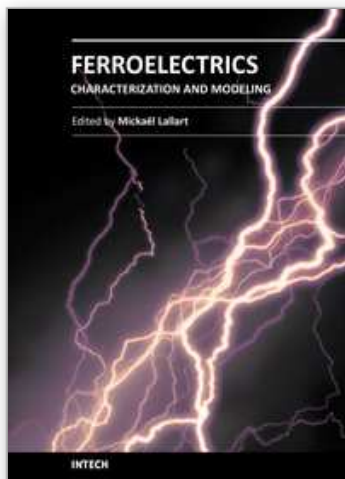
Ferroelectrics - Characterization and Modeling

Edited by Dr. Mickaël Lallart

Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the characterization of ferroelectric materials, including structural, electrical and multiphysic aspects, as well as innovative techniques for modeling and predicting the performance of these devices using phenomenological approaches and nonlinear methods. Hence, the aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric system characterization and modeling, allowing a deep understanding of ferroelectricity.

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