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Fully macroscopic description of bounded semiconductors with an application to the Si-SiO$_2$ interface

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A fully macroscopic description of semiconductors is presented which includes the boundary conditions at the surface of the semiconductor that are required for consistency with the usual diffusion-drift current equations. As in all field theories, e.g., electromagnetism, both the boundary conditions and the differential equations are obtained from the same governing integral forms. The new boundary conditions relate the jump discontinuities in the chemical potentials across the interface to the forces exerted by the lattice on the charge carriers which prevent the carriers from leaving the solid. The expressions for the forces in the static case are found and the values of the material surface coefficients appearing therein are obtained from quasistatic metal-oxide-semiconductor capacitance-voltage measurements for some particular Si-SiO$_2$ interfaces.

I. INTRODUCTION

The basic understanding of the behavior of semiconductors arises from the semiclassical description of the motion of electrons in a periodic potential.[1-3] This model of the semiconductor has proven invaluable in interpreting a host of phenomena in the infinite lattice. Nevertheless, when the electron number density varies appreciably,[4] as it often does near boundary surfaces, or in cases of inhomogeneous doping, a macroscopic description, which is not related in a precise quantitative way to the above-mentioned microscopic model, is employed.[5-7] This standard macroscopic description,[8] consisting of diffusion-drift current equations, the charge balance equations, and the electrostatic constitutive equations, is a continuum field theory, i.e., a system of partial differential equations containing dependent macroscopic field variables as a function of space and time. However, a complete field theory must also have a set of consistent boundary conditions. These are obtained from integral forms of the governing equations just as in electromagnetism, where electromagnetic boundary conditions are obtained from the integral forms of Maxwell's equations.[9,10] In contrast to electromagnetism, however, the integral forms and the associated boundary conditions have never been obtained for the standard macroscopic theory of semiconductors.[5-7]

A well-defined *macroscopic* model of a semiconductor has been presented in the literature[11] along with the integral forms obtained from that model. The integral forms have been shown to yield the conventional diffusion-drift current differential equations plus the associated boundary conditions across the surface of the semiconductor, which are missing in the existing macroscopic semiconductor theory. However, since the equations appearing in Ref. 11 are unduly complicated by the inclusion of mechanical deformations in the description and, for other reasons, are not in a convenient form, we rederive the equations and obtain the more useful form here. The macroscopic model from which the field theory follows[12] is chosen to permit electronic and hole conduction in interaction with the electrostatic field. Although the model can readily be extended to incorporate electric polarization,[11] we do not bother with this refinement and include polarization in the usual linear way. Also, in the interest of clarity all resonance phenomena are expressly excluded from the treatment by ignoring the macroscopic mass of all moving components in the model. Accordingly, the model consists of three suitably defined interpenetrating continua, which are called the lattice continuum, the conduction-electronic continuum, and the hole continuum. The lattice continuum does not move and contains a charge density representative of the fixed ionized impurities responsible for extrinsic semiconduction. The conduction-electronic and hole continua are inertialess charged fluids which move through the lattice continuum while experiencing a force of resistance. In addition, each conducting fluid interacts with neighboring elements of the same fluid by means of defined fluid pressure forces. Furthermore, charge exchange is permitted between all three continua in order to allow for recombination-generation phenomena.

As in all such descriptions the application of the laws of balance of charge and momentum yields the equations of motion of the matter, which, with the equations of electrostatics, constitute an underdetermined system. The system is completed by the addition of various materially descriptive constitutive relations[13] whose allowed functional forms are determined from thermodynamic arguments.[14] The differential forms of the equations of motion for the conduction electronic and hole fluids along with linear constitutive assumptions yield precisely the usual diffusion-drift current equations containing the material coefficients of mobility and diffusivity.

The boundary conditions at the surface of the semiconductor, which are required for the solution of semiconduction problems involving bounded media, are obtained from integral forms of the semiconduction equations. As with all the other differential equations and their associated boundary conditions, this procedure ensures consistency between the semiconduction differential equations and the semiconduction boundary conditions. These boundary conditions, which do not appear in any of the existing literature on semiconductors,[1-3,5-7] relate the jump discontinuities in the electronic and hole chemical potentials across the surface to the forces per unit area per unit charge densities exerted by the lattice continuum on the respective fluids that keep the electrons from leaving the solid.[15] The thermodynamic arguments in Appendix A indicate that the forces per unit area per unit charge densities are functions of the electric field on each side of the surface of the semiconductor and the respective charge densities and velocities of each fluid at the surface. The expressions for the forces per unit area per unit charge densities contain material surface coefficients which are to be determined from measurements just as the mobility and diffusivity coefficients in the differential equations for the semiconductor are often measured. Presumably, the material surface coefficients could be calculated from a more fundamental quantum-mechanical model by means of electronic surface structure calculations,[16,17] but the available results seem to indicate that for quantitative detail such calculations would be prohibitively complicated.[18,19]

The missing boundary conditions have not deterred workers from treating problems concerning semiconductors with boundaries analytically.[20] To be sure, many authors have circumvented the difficulty by imposing various boundary conditions in order to provide the additional condition required for the solution of the boundary-value problem. For example, some have simply disregarded the existence of surface charge on the semiconductor surface.[21] Others, especially those interested in computer-aided design[22] have assumed *a priori* the value of the surface charge.[23-25] Another attack has been that of Kroemer,[26,27] who used the concept of a "control characteristic" in treating certain aspects of Gunn-effect phenomena. Many additional examples may be cited.[28] Although some of these procedures are based on reasonable assumptions over certain ranges,[29] in a number of cases results have been obtained which are clearly at variance with experiment.[30] In addition, none of the previous approaches have formulated the boundary-value problem without assuming boundary conditions not deduced from fundamental principles. In the procedure presented here, when the newly defined material surface coefficients have been found from measurements of a particular material surface, the new boundary conditions enable the solution of semiconduction boundary-value problems.

In the final section of this paper an illustration of this purely macroscopic description of surfaces of semiconductors is presented by treating the often analyzed semiconductor-insulator interface. Much work[31-33] has been done with the purpose of understanding and describing the semiconductor-insulator junction, especially in the case of the Si-SiO_2 interface.[34] Microscopically, this boundary is an immensely complex structure. Even in the case of the much simpler semiconductor-vacuum interface electronic surface structure calculations have yet to yield good quantitative agreement with microscopic measurements.[35] Undoubtedly, the connection of the microscopic calculations with the essentially macroscopic measurements of capacitance and conductance, which are frequently made in studying semiconductor-insulator interfaces using the metal-oxide-semiconductor (MOS) structure, is even further away. Although these measurements are usually expressed in terms of quasimicroscopic entities, such as interface state densities, it is clear that there is actually no real correspondence between such measurements and microscopic quantities. We believe that the approach presented in this paper, which depends crucially on the new (missing) semiconduction boundary conditions, affords a purely macroscopic quantitative description of semiconductor interfaces that can be used to advantage in categorizing semiconductor interfaces. More specifically, as already noted, in this approach the semiconductor interface is characterized by a set of macroscopic material surface coefficients which are to be measured. In the case of the semiconductor-insulator junction MOS quasistatic capacitance-voltage (C-V) measurements provide a means of evaluating the relevant static coefficients, as is exhibited in the last section for the Si-SiO_2 interface. Among other things, a knowledge of the values of these material surface coefficients can provide a detailed quantitative understanding of the influence of the surface on the performance characteristics of devices. For example, in the case of a metal-oxide-semiconductor field-effect transistor (MOSFET) the range in which the values of the surface coefficients must remain with aging in order to satisfy some circuit performance criterion can be established.[36]

II. THE MACROSCOPIC MODEL OF THE SEMICONDUCTOR

As indicated in the Introduction the macroscopic model of the semiconductor consists of three well-defined interacting continua, which are present at each point of space and time. The three continua are defined as follows.

(1) The (combined) lattice continuum, denoted by the superscript i, may have either a positive or negative charge density corresponding to the ionized impurity density.[37] This continuum does not move and contains the macroscopic elements that account for polarization.[38]

(2) The conduction-electronic continuum, denoted by the superscript e, corresponds to the conduction-band electrons and is, of course, negatively charged. This continuum is a macroscopically inertialess, conducting, compressible fluid that experiences a force of resistance from its motion with respect to the lattice continuum.

(3) The hole continuum, denoted by the superscript h, corresponds to the absence of valence-band electrons and is positively charged. This continuum also is a macroscopically inertialess, conducting, compressible fluid that experiences a force of resistance from its motion with respect to the lattice continuum.

The Cartesian components of points in the lattice continuum are denoted by x_i $(i = 1, 2, 3)$, which, of course, denotes the components of the same point in the conduction-electronic and hole fluids also. The charge densities[39] associated with the three continua are denoted ρ^i, ρ^e, and ρ^h, respectively, and are functions of space x_i and time t in general. The three continua are permitted to exchange charge with one another through defined charge source densities labeled γ^i, γ^e, and γ^h. These allow for the possibilities of bulk generation and/or recombination of carriers by means of either changes in the degree of ionization of impurities or electron-hole pair generation or recombination. Then, in order to satisfy the conservation of total macroscopic charge at each macroscopic point, we must have

$$\gamma^e + \gamma^h + \gamma^i = 0 . \tag{2.1}$$

Now, each conducting fluid interacts with the lattice continuum at the macroscopic point x_i by means of defined material electric fields designated $\vec{E}^e$ and $\vec{E}^h$, respectively. These cause equal and opposite forces $\pm\rho^e\vec{E}^e$ and $\pm\rho^h\vec{E}^h$ to be exerted between the lattice continuum and each of the respective conducting fluids. The macroscopic forces $-\rho^e\vec{E}^e$ and $-\rho^h\vec{E}^h$ exerted on the lattice continuum by the fluids are assumed to be sufficiently small that any motion they tend to produce may be ignored for our purposes.[40] Each conducting fluid interacts with neighboring elements of the same fluid by means of pressure forces labeled p^e and p^h, respectively, which act on the surfaces of separation between elements of the respective fluids. The quasistatic Maxwell electric field $\vec{E}$ exerts forces on all elements of charge, but we note that since the lattice continuum does not move, only those forces exerted on the conduction-electronic and hole fluids are of any importance in this work.

III. THE MACROSCOPIC EQUATIONS FOR THE SEMICONDUCTOR

Since the two conducting fluids have different velocities yet occupy the same region of space as the lattice continuum which does not move, it is advantageous to write the integral forms of the balance equations with respect to a stationary element of volume. Accordingly, we write the charge balance equations for the lattice (impurity), the conduction-electronic and the hole continua in the respective integral forms

$$\frac{\partial}{\partial t}\int_V \rho^i dV = \int_V \gamma^i dV , \tag{3.1}$$

$$\frac{\partial}{\partial t}\int_V \rho^e dV + \int_S \vec{n}\cdot\vec{v}^e\rho^e dS = \int_V \gamma^e dV , \tag{3.2}$$

$$\frac{\partial}{\partial t}\int_V \rho^h dV + \int_S \vec{n}\cdot\vec{v}^h\rho^h dS = \int_V \gamma^h dV , \tag{3.3}$$

where $\vec{n}$ is the outwardly directed unit normal to the surface S enclosing the arbitrary volume V fixed in space. The vectors $\vec{v}^e$ and $\vec{v}^h$ denote the velocities of the conduction-electronic and hole continua, respectively. The local differential forms resulting from (3.1)–(3.3) are obtained in the usual way by employing the divergence theorem to convert the surface integrals to volume integrals and by employing the fact that the volume V is fixed in space and is arbitrary, with the result

$$\frac{\partial\rho^i}{\partial t} = \gamma^i , \tag{3.4}$$

$$\frac{\partial\rho^e}{\partial t} + \vec{\nabla}\cdot(\rho^e\vec{v}^e) = \gamma^e , \tag{3.5}$$

$$\frac{\partial\rho^h}{\partial t} + \vec{\nabla}\cdot(\rho^h\vec{v}^h) = \gamma^h . \tag{3.6}$$

Clearly, the total charge ρ and the actual current density $\vec{J}$ at any point are given by

$$\rho = \rho^e + \rho^h + \rho^i\,, \tag{3.7}$$

$$\vec{J} = \rho^e \vec{v}^e + \rho^h \vec{v}^h = \vec{J}^e + \vec{J}^h\,, \tag{3.8}$$

where $\vec{J}^e$ and $\vec{J}^h$ are the conduction-electronic and hole current densities, respectively. Adding (3.1)–(3.3) and employing (2.1), (3.7), and (3.8), we obtain

$$\frac{\partial}{\partial t}\int_V \rho\, dV + \int_S \vec{n}\cdot\vec{J}\, dS = 0\,, \tag{3.9}$$

which is the usual integral form of the conservation of total electric charge. From (3.9), with the aid of the divergence theorem and the arbitrariness of V, we obtain

$$\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0\,, \tag{3.10}$$

which is the usual local differential form of the total charge balance equation. Note that Eq. (3.10) may equally readily have been obtained by adding (3.4)–(3.6) and employing (2.1), (3.7), and (3.8).

In this work we need the usual charge and circulation equations of electrostatics, which take the respective integral forms

$$\int_S \vec{n}\cdot\vec{D}\, dS = \int_V \rho\, dV\,, \tag{3.11}$$

$$\oint_C \vec{E}\cdot d\vec{r} = 0\,, \tag{3.12}$$

where $\vec{D}$ is the electric displacement vector, $\vec{E}$ is the Maxwell electric-field vector, S is an arbitrary surface enclosing the volume V, and C is an arbitrary closed curve. From (3.11), with the aid of the divergence theorem and the arbitrariness of V, we obtain

$$\vec{\nabla}\cdot\vec{D} = \rho\,, \tag{3.13}$$

which is the local differential form of the charge equation of electrostatics. Furthermore, Eq. (3.12), with the aid of Stokes theorem and the arbitrariness of the area enclosed by C, enables us to define the usual scalar electric potential φ such that

$$\vec{E} = -\vec{\nabla}\varphi\,. \tag{3.14}$$

We now note that since the lattice continuum does not move the balances of linear momentum and mass of the lattice continuum may be ignored in this work in which the lattice continuum simply serves as the entity that provides the reactions to the actions of the two conducting fluids. Furthermore, since the conducting fluids have been defined as being massless, the balance of mass of these constituents is not needed. The equations of the balance of linear momentum for the conduction-electronic and hole continua take the respective integral forms

$$-\int_S \vec{n} p^e\, dS + \int_V \rho^e(\vec{E} + \vec{E}^e)\, dV = 0\,, \tag{3.15}$$

$$-\int_S \vec{n} p^h\, dS + \int_V \rho^h(\vec{E} + \vec{E}^h)\, dV = 0\,. \tag{3.16}$$

From (3.15) and (3.16), with the aid of the divergence theorem, the arbitrariness of V, and (3.14), we obtain the local differential forms of the semiconduction field equations for the respective continua:

$$-\vec{\nabla} p^e - \rho^e \vec{\nabla}\varphi + \rho^e \vec{E}^e = 0\,, \tag{3.17}$$

$$-\vec{\nabla} p^h - \rho^h \vec{\nabla}\varphi + \rho^h \vec{E}^h = 0\,. \tag{3.18}$$

At this point we note that the governing differential equations consisting of (3.10), (3.13), any two of (3.4)–(3.6), (3.17), and (3.18), with (2.1), (3.7), (3.8), and (3.14), constitute an underdetermined system, i.e., there are more dependent variables [31 (10 scalars and 7 vectors)] than equations (18). As usual in any macroscopic description of this nature, materially descriptive constitutive equations are required in order to obtain a determinate system. Constitutive equations consistent with the model are obtained by writing the equation of the conservation of energy for the combined material continuum, from which the first law of thermodynamics is obtained, and employing the second law of thermodynamics. However, in order not to obscure the main purpose of this work, which is to indicate the importance of the boundary conditions as well as the differential equations in the macroscopic description of semiconductors, we give the derivation of consistent constitutive equations from the thermodynamics in Appendix A and simply present the resulting constitutive relations here. In accordance with Appendix A the constitutive equations must take the following functional forms:

$$p^e = p^e(\rho^e, T)\,,\quad p^h = p^h(\rho^h, T)\,, \tag{3.19}$$

$$\vec{E}^e = \vec{E}^e(\rho^e, \vec{v}^e, \vec{E}, T)\,, \tag{3.20a}$$

$$\vec{E}^h = \vec{E}^h(\rho^h, \vec{v}^h, \vec{E}, T)\,, \tag{3.20b}$$

$$\vec{D} = \vec{D}(\vec{E}, T)\,, \tag{3.21}$$

$$\begin{aligned} \gamma^e &= \gamma^e(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, \vec{E}, T)\,,\\ \gamma^h &= \gamma^h(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, \vec{E}, T)\,, \end{aligned} \tag{3.22}$$

where T is the (here uniform) absolute temperature. As in all macroscopic theories, e.g., electromagnetism and elasticity, the functional forms and the values of the material coefficients (dielectric constants, elastic constants, etc.) are to be determined from experiment. Any functional form depending on the variables shown in (3.19)–(3.22) will be consistent with the model provided that (A7) is satisfied. For example, the important forms usually chosen for (3.20a) and (3.20b) are

$$\vec{E}^e = \vec{v}^e/\mu^e , \tag{3.23a}$$

$$\vec{E}^h = -\vec{v}^h/\mu^h , \tag{3.23b}$$

where μ^e and μ^h are the measured mobilities of the conduction-electronic and hole fluids, respectively. At high electric fields, it is well known that $\vec{E}$-dependent terms become necessary.[41] Similarly, the form usually chosen for (3.21) is

$$\vec{D} = \epsilon_s \vec{E} , \tag{3.24}$$

where ϵ_s is the permittivity for the semiconductor.

Before proceeding, we note that a significant simplification in (3.17) and (3.18) may be achieved by employing certain relations between the gradients of the pressures p^e and p^h and the gradients of the well-defined chemical potentials $\varphi^e = \varphi^e(\rho^e, T)$ and $\varphi^h = \varphi^h(\rho^h, T)$,[42] which are derived in Appendix A and are of the form

$$(1/\rho^e)\vec{\nabla} p^e = \vec{\nabla}\varphi^e , \quad (1/\rho^h)\vec{\nabla} p^h = \vec{\nabla}\varphi^h . \tag{3.25}$$

The substitution of (3.25) into (3.17) and (3.18) yields

$$-\vec{\nabla}(\varphi^e + \varphi) + \vec{E}^e = 0 , \tag{3.26}$$

$$-\vec{\nabla}(\varphi^h + \varphi) + \vec{E}^h = 0 , \tag{3.27}$$

which, as we shall see, are very useful forms of the differential equations for the semiconducting fluids. Substituting from (3.23) for the respective fluids into (3.26) and (3.27), respectively, and employing (3.14), the definitions in (3.8), the fact that $\varphi^e = \varphi^e(\rho^e, T)$ and $\varphi^h = \varphi^h(\rho^h, T)$ and the assumption of uniform temperature, we obtain

$$\vec{J}^e = -\mu^e \rho^e \vec{E} - D^e \vec{\nabla}\rho^e , \tag{3.28}$$

$$\vec{J}^h = \mu^h \rho^h \vec{E} - D^h \vec{\nabla}\rho^h , \tag{3.29}$$

where

$$D^e = -\mu^e \rho^e \frac{\partial \varphi^e}{\partial \rho^e} , \quad D^h = +\mu^h \rho^h \frac{\partial \varphi^h}{\partial \rho^h} , \tag{3.30}$$

are the diffusion coefficients. Equations (3.28) and (3.29) are the standard[43] diffusion-drift current equations for the conduction-electronic and hole fluids, respectively, and (3.30) contains familiar expressions also.[44] Appropriate forms for (3.22) are well known.[45]

At this point we note that we now have a determinate theory, which by appropriate substitution can readily be reduced to ten equations in the ten dependent variables, φ, ρ, ρ^e, ρ^h, $\vec{J}$, and $\vec{J}^e$ or $\vec{J}^h$. The ten equations are any two of (3.4)–(3.6), (3.10), (3.13), and three each of either (3.26) and (3.27) or (3.28) and (3.29).[46,47] In order to have a complete field theory the boundary (or jump) conditions across surfaces have to be adjoined to the system of differential equations. However, before we discuss the boundary conditions we note that the particularly useful differential forms, (3.26) and (3.27), for the semiconducting fluids are equivalent to the integral forms

$$-\int_S \vec{n}(\varphi^e + \varphi)dS + \int_V \vec{E}^e dV = 0 , \tag{3.31}$$

$$-\int_S \vec{n}(\varphi^h + \varphi)dS + \int_V \vec{E}^h dV = 0 , \tag{3.32}$$

because the local differential forms in (3.26) and (3.27) can readily be obtained from the respective integral forms in (3.31) and (3.32) when the field variables are differentiable. Moreover, we now take (3.31) and (3.32) to be valid even when the field variables are not differentiable and (3.26) and (3.27) cannot be obtained, such as across surfaces of discontinuity. Of course, all the other integral forms are taken to hold across surfaces of discontinuity also. For purposes of obtaining boundary conditions in this work, the integral forms (3.31) and (3.32) replace (3.15) and (3.16), respectively, because they are considerably simpler forms that result in more convenient boundary conditions.

The pertinent boundary (or jump) conditions are obtained by applying the integral forms (3.9), (3.11), (3.31), (3.32), and any two of (3.1)–(3.3) to an arbitrary pill-box region encompassing a portion of the surface of discontinuity and taking the limit of the region as the volume shrinks to zero faster than the area in the usual way,[48] while assuming that the volumetric densities either remain bounded or become unbounded in a specified way. The boundary (or jump) condition obtained from (3.12), which contains a circulation integral, is determined instead by taking the circulation around an arbitrary area normal to and intersecting a portion of the surface of discontinuity and taking the limit as the area enclosed by the circuit collapses to the surface of discontinuity in the usual way.[48] The jump conditions obtained from any of (3.1)–(3.3) are not of interest in the present work (because only total surface charge is of interest) and consequently, are not obtained here. From (3.11) in the above-mentioned way we obtain the well-known condition

$$\vec{n} \cdot [\vec{D}] = \sigma , \tag{3.33}$$

where we have introduced the conventional notation $[\vec{C}]$ for $\vec{C}^+ - \vec{C}^-$, $\vec{n}$ denotes the unit normal directed from the minus to the plus side of the surface of discontinuity, and σ is the surface charge density, which is defined by

$$\int_S \sigma dS = \lim_{V\to 0} \int_V \rho dV . \tag{3.34}$$

Similarly, from (3.9) with the aid of the time derivatives of (3.33) and (3.34), we obtain

$$\vec{n}\cdot\left[\frac{\partial \vec{D}}{\partial t} + \vec{J}\right] = 0 . \tag{3.35}$$

From the circulation integral (3.12) in the abovementioned usual way, we obtain the well-known condition of electrostatics

$$\vec{n}\times[\vec{E}] = 0 , \tag{3.36}$$

which, with the aid of (3.14), enables us to obtain the boundary condition[49]

$$[\varphi] = 0 . \tag{3.37}$$

The application of (3.31) to the arbitrary limiting pill-box region in the aforementioned manner yields

$$\vec{n}[\varphi^e + \varphi] = f^e \vec{n} , \tag{3.38}$$

where

$$\int_S f^e \vec{n} dS = \lim_{V\to 0} \int_V \vec{E}^e dV , \tag{3.39}$$

and we note that the force per unit charge $\vec{E}^e$ exerted by the lattice continuum on the conduction-electronic fluid at the interface must be permitted to become unbounded in the manner indicated in (3.39) because there must be a force exerted by the lattice continuum on the conduction-electronic fluid at the boundary which prevents the electrons from leaving the semiconductor. Substituting from (3.37) into (3.38) and omitting the $\vec{n}$, which is unnecessary, we obtain

$$[\varphi^e] = f^e , \tag{3.40}$$

which states that the jump in the chemical potential of the conduction-electronic fluid across a surface of discontinuity is equal to the restraining surface interaction force exerted by the lattice. In view of (3.20a) and (3.39), the constitutive equation for f^e is taken in the form

$$f^e = f^e(\rho^e, \vec{v}^e, \vec{E}, T) . \tag{3.41}$$

In a similar way, from (3.32) and (3.37), we obtain

$$[\varphi^h] = f^h , \tag{3.42}$$

where

$$\int_S f^h \vec{n} dS = \lim_{V\to 0} \int_V \vec{E}^h dV , \tag{3.43}$$

and from (3.20b) and (3.43) we must have

$$f^h = f^h(\rho^h, \vec{v}^h, \vec{E}, T) . \tag{3.44}$$

Equations (3.40) and (3.42), with (3.41), (3.44), and the functional dependences of φ^e and φ^h, respectively, on ρ^e and ρ^h are the previously discussed required semiconduction boundary conditions, the existence of which along with the application in the next section constitute the main point of this work. Appropriate specific forms for (3.41) and (3.44) are discussed in the application in the next section and expressions for

$$\varphi^e = \varphi^e(\rho^e, T) , \quad \varphi^h = \varphi^h(\rho^h, T) \tag{3.45}$$

are discussed in Appendix B.

IV. APPLICATION TO Si-SiO$_2$ INTERFACES

As noted in the Introduction, the purely macroscopic equations for the semiconductor, which have been developed here, are particularly well suited for the description of the influence of the properties of the surface of the semiconductor on gross sample behavior. The MOS quasistatic C-V experiment provides a convenient means of demonstrating some of the advantages of the purely macroscopic description. As already mentioned, this experiment provides a means of evaluating some of the macroscopic material surface coefficients that occur in expressions to be written for f^e and f^h. The values of these coefficients for a particular semiconductor surface are obtained by solving a straightforward one-dimensional problem corresponding to the experimental setup and deriving an expression for an observable consequence in terms of the unknown material surface coefficients, from which the values of the coefficients are determined by comparison with measurements. In order that our model of the actual MOS quasistatic C-V experiment be valid, the following requirements must be satisfied[50]:

(1) The geometry should be such that the assumption of one-dimensional dependence holds.[51]

(2) The thickness of the semiconductor should be sufficiently large that one end can be assumed (in the problem) to be at infinity.

(3) There should be no fixed or mobile oxide charges.

(4) The static form of the equations should be applicable.[52]

(5) The semiconductor properties should be macroscopically uniform.

(6) The oxide capacitance should not be much smaller than other capacitances in order that the surface behavior be detectable by a total capacitance measurement.[53]

A schematic of the modeled MOS structure with associated coordinate system is shown in Fig. 1.

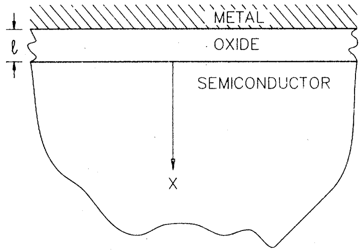

FIG. 1. Schematic diagram of the MOS structure.

Under the assumed static conditions we have

$$\vec{v}^e = \vec{v}^h = 0, \quad \gamma^e = \gamma^h = \gamma^i = 0, \tag{4.1}$$

and the dynamic equations consisting of (3.5), (3.6), and (3.10) are satisfied identically. The nontrivial equations remaining are (3.13), (3.28), and (3.29) in the absence of $\vec{J}^e$ and $\vec{J}^h$. Since in the problem under consideration we have one-dimensional-, i.e., x-, dependence only, from (3.13), with (3.7), (3.14), and (3.24), we have

$$\frac{d^2\varphi}{dx^2} = -\left(\frac{1}{\epsilon_s}\right)(\rho^e + \rho^h + \rho^i), \quad 0 \leq x \tag{4.2}$$

and (3.28) and (3.29) take the respective forms

$$\rho^e \frac{d\varphi}{dx} = \left(\frac{D^e}{\mu^e}\right)\frac{d\rho^e}{dx}, \quad 0 \leq x \tag{4.3}$$

$$\rho^h \frac{d\varphi}{dx} = -\left(\frac{D^h}{\mu^h}\right)\frac{d\rho^h}{dx}, \quad 0 \leq x. \tag{4.4}$$

Since the charge density vanishes in the oxide, we have

$$\frac{d^2\varphi}{dx^2} = 0, \quad -l \leq x \leq 0. \tag{4.5}$$

As a consequence of condition 2 above, we have

$$\rho \to 0, \tag{4.6a}$$

$$\varphi \to 0, \tag{4.6b}$$

$$\frac{d\varphi}{dx} \to 0 \text{ as } x \to \infty. \tag{4.6c}$$

The boundary condition to be satisfied at the interface between the oxide and the metal is

$$\varphi = \varphi_0 - \varphi_{\text{MOS}} \text{ at } x = -l, \tag{4.7}$$

where φ_{MOS} is due to the potential jumps arising from possible double layers at the metal-oxide interface and the metal-semiconductor interface and φ_0 is the applied (gate) voltage relative to a metal "ground" plate. From (3.37), (3.40), and (3.42) we see that the additional boundary conditions to be satisfied at the interface between the oxide and the semiconductor are

$$\varphi_{\text{ox}} = \varphi_{\text{sem}} \text{ at } x = 0, \tag{4.8}$$

$$[\varphi^e] = f^e\left(\rho^e, \left.\frac{d\varphi}{dx}\right|_{\text{ox}}, \left.\frac{d\varphi}{dx}\right|_{\text{sem}}, T\right) \text{ at } x = 0, \tag{4.9}$$

$$[\varphi^h] = f^h\left(\rho^h, \left.\frac{d\varphi}{dx}\right|_{\text{ox}}, \left.\frac{d\varphi}{dx}\right|_{\text{sem}}, T\right) \text{ at } x = 0, \tag{4.10}$$

where the electric-field terms are evaluated on either side of and immediately adjacent to the oxide-semiconductor interface, and we note that

$$\varphi_{\text{ox}}(0) = \varphi_{\text{sem}}(0) \equiv \varphi_s, \tag{4.11}$$

where φ_s is the surface potential of the semiconductor.[54] Integrating (4.3) and (4.4) and employing the boundary conditions (4.6), we obtain

$$\varphi = \frac{D^e}{\mu^e}\ln\frac{\rho^e}{\rho^e_\infty} = -\frac{D^h}{\mu^h}\ln\frac{\rho^h}{\rho^h_\infty}, \quad 0 \leq x \tag{4.12}$$

where ρ^e_∞ and ρ^h_∞ are the constant charge densities of the respective fluids at infinity. From (4.6a), condition 5, and (3.7) we have

$$\rho^e_\infty + \rho^h_\infty + \rho^i = 0. \tag{4.13}$$

Solving (4.12) for ρ^e and ρ^h in terms of φ, substituting in (4.2), and employing (4.13), we obtain a single nonlinear differential equation in the single dependent variable φ, a first integral of which may be written[7] in the form

$$\frac{d\varphi}{dx} = \pm\left(\frac{2}{\epsilon_s}\right)^{1/2}\left[-\rho^e_\infty\frac{D^e}{\mu^e}\left(e^{\mu^e\varphi/D^e} - \frac{\mu^e\varphi}{D^e} - 1\right) + \rho^h_\infty\frac{D^h}{\mu^h}\left(e^{-\mu^h\varphi/D^h} + \frac{\mu^h\varphi}{D^h} - 1\right)\right]^{1/2}, \tag{4.14}$$

where the integration constant has been found from the boundary condition at infinity given in (4.6b) and (4.6c). The sign of $d\varphi/dx$ is undetermined at this stage. Equation (4.14) may be reduced to a quadrature immediately. In order to evaluate the integration constant and fix the presently unknown sign in (4.14), we must employ the heretofore unknown (missing) boundary conditions in (4.9) and (4.10). Since these boundary conditions involve the chemical potentials φ^e and φ^h, we digress with a derivation of some simple expressions for φ^e and φ^h in the static case. By virtue of (3.30), (4.3) and (4.4) can be written in the form

$$\frac{d\varphi}{dx} + \frac{d\varphi^e}{dx} = 0, \quad 0 \leq x \tag{4.15}$$

$$\frac{d\varphi}{dx} + \frac{d\varphi^h}{dx} = 0, \quad 0 \leq x \tag{4.16}$$

which are just the one-dimensional versions of (3.26) and (3.27) in the absence of $\vec{E}^e$ and $\vec{E}^h$, which vanish when the velocities of the conduction-electronic and hole fluids vanish.

Clearly, Eqs. (4.15) and (4.16), which are the same as (4.3) and (4.4), can be integrated immediately to obtain

$$\varphi + \varphi^e = \varphi^e_\infty, \quad 0 \leq x \tag{4.17}$$

$$\varphi + \varphi^h = \varphi^h_\infty, \quad 0 \leq x \tag{4.18}$$

where φ^e_∞ and φ^h_∞ are the constant values of the chemical potentials away from the space charge region, and we have employed (4.6b).[55] Now, the left-hand sides of (4.9) and (4.10) are

$$[\varphi^e] = \varphi^e_{\text{sem}} - \varphi^e_{\text{ox}}, \quad [\varphi^h] = \varphi^h_{\text{sem}} - \varphi^h_{\text{ox}}, \tag{4.19}$$

into which we can substitute from (4.17) and (4.18) for φ^e_{sem} and φ^h_{sem}. Subtracting $[\varphi^h]$ from $[\varphi^e]$, we obtain,

$$[\varphi^e] = \varphi^h_{\text{ox}} - \varphi^e_{\text{ox}} - \varphi^h_\infty + \varphi^e_\infty + [\varphi^h], \tag{4.20}$$

where, of course, φ^e_{ox} and φ^h_{ox} are the constant chemical potentials in the oxide. The four constants appearing in (4.20) are presumed known and, therefore, in the static case $[\varphi^e]$ and $[\varphi^h]$ and, of course, from (4.9) and (4.10), f^e and f^h are not independent quantities. Consequently, in the static case (4.9) and (4.10) are not independent boundary conditions, which is not surprising since only one integration constant remains undetermined. Since f^e and f^h differ only by a constant and the functional dependences for f^e and f^h are of the forms shown in (4.9) and (4.10), it is clear from (4.12) that the functional dependences of f^e and f^h on ρ^e and ρ^h must be through the respective variables $\log_{10}\rho^e/\rho^e_\infty$ and $\log_{10}\rho^h/\rho^h_\infty$ because the conditions (4.9), (4.10), and (4.20) hold for *arbitrary* ρ^e and ρ^h. In view of the foregoing, from (4.9), (4.11), (4.12), (4.17), and (4.19), the one required boundary condition at the semiconductor-oxide interface in the static case must be of the form

$$\varphi^e_\infty - \varphi^e_{\text{ox}} - \varphi_s = f^e\left(\varphi_s, \left.\frac{d\varphi}{dx}\right|_{\text{ox}}, \left.\frac{d\varphi}{dx}\right|_{\text{sem}}, T\right). \tag{4.21}$$

Equation (4.21) provides a relation between the surface potential φ_s and the electric fields on either side of the interface and, as noted earlier, contains material surface coefficients, which are to be measured and are characteristic of the particular interface. When the material surface coefficients are known, Eq. (4.21) provides the one independent condition which enables the one remaining integration constant to be found and, thus, the solution to the posed problem to be obtained.

In the case of the static one-dimensional problem being treated here calculations are greatly simplified as a result of (4.14), which may be evaluated at $x = 0$ to obtain $d\varphi/dx|_{\text{sem}}$ explicitly as a function of φ_s. By satisfying (4.5), (4.7), and (4.11) for the oxide portion of the problem, we find

$$\left(\frac{d\varphi}{dx}\right)_{\text{ox}} = \frac{\varphi_s - \varphi_0 + \varphi_{\text{MOS}}}{l}, \tag{4.22}$$

and, hence, (4.21), with (4.14) and (4.22), provides a *direct* relation between φ_0 and φ_s at constant temperature. The aforementioned simplification in the calculations also causes a weakness in our ability to obtain definitive values of the material surface response coefficients from MOS quasistatic one-dimensional C-V measurements and to distinguish conclusively between field and surface-potential (charge-density) terms in the expression for f^e. In this paper, where we intend only to illustrate the completely macroscopic approach to semiconductor interfaces, we are content merely to provide reasonably convincing (but not definitive) evidence for the forms chosen for (4.21).

In establishing a form for f^e and determining the values of the attendant material surface coefficients that arise, experimental data are utilized. In the quasistatic C-V experiment the total capacitance is measured directly as a function of the applied voltage. The Berglund integration[56] of the capacitance may be used to give reasonably accurate values for φ_s vs φ_0 over certain ranges of φ_s.[57] The aforementioned simplification of (4.21) resulting from the existence of (4.14) makes these (φ_s vs φ_0) data preferable.[58] It is also to be recommended by the fact that these data are a direct measure of semiconductor surface response, whereas total capacitance is not. At this point it should perhaps be mentioned that the procedure of using the C-V data to generate $[-(1/q)d\sigma/d\varphi_s]$, which is commonly referred to as N_{ss}, the surface-state density, is unnecessary insofar as the determination of macroscopic surface coefficients is concerned. However, in a number of cases we have used these data since it is the form usually presented in the literature.

Now, an explicit representation of f^e in (4.21) is found by choosing a suitable simple expression in the variables shown and obtaining the material coefficients in the expression from experimental σ vs φ_s or $d\sigma/d\varphi_s$ vs φ_s data. The wide range of variation in measured surface response[59] seems to indicate that the possibility of obtaining one form for f^e for all Si-SiO$_2$ interfaces is unrealistic. However, for annealed MOS structures, interface response is found to be qualitatively similar[59,60] and hence for these interfaces a single form for f^e appears to be appropriate. The expression we choose for f^e is[61]

$$f^e = A_1(T, \varphi_s)\frac{d\varphi}{dx}\bigg|_{\text{ox}} + A_2(T, \varphi_s)\frac{d\varphi}{dx}\bigg|_{\text{sem}} + A_3(T)\varphi_s + A_4(T)\varphi_s^2 + \cdots , \tag{4.23}$$

where all coefficients are functions of temperature, which is constant in the present work. We note that the electric-field terms *must* be present in (4.23) because the dependence of φ_s on φ_0 arises only through the $d\varphi/dx|_{\text{ox}}$ term and unless a dependence on φ_0 appears in (4.23), (4.21) reduces to an equation for φ_s independent of the external conditions. Only terms linear in $d\varphi/dx$ on each side of the interface are retained in (4.23) because the electric field is the force per unit charge. Further specification of (4.23), as to which terms are to be kept and the values of the coefficients A_i, is accomplished by use of a regression analysis (including plots of residuals) of the experimental data. The goal here is to achieve reasonable accuracy in the representation of f^e while employing the minimum number of terms.[62] However, it is important to realize that, ultimately, the level of accuracy required in the representation of f^e is dictated by the particular problem under consideration. It is found that although the surface coefficients A_1 and A_2 can depend on φ_s, no dependence on φ_s is required in order to obtain reasonable agreement with the experimental data considered in this work. However, such a dependence can improve the accuracy of the representation. The remaining terms in the expression for f^e are a power series in φ_s. The number of terms retained in any polynomial approximation depends on the accuracy desired. We have found that typically no more than three terms in the power series are necessary to give adequate agreement.

For the purpose of obtaining the material surface coefficients A_i from experimental data of σ vs φ_s or $d\sigma/d\varphi_s$ vs φ_s, the solution can be put in a particularly useful form by employing the constitutive relation for the oxide

$$D_{\text{ox}} = -\epsilon_{\text{ox}}\frac{d\varphi}{dx} , \tag{4.24}$$

where ϵ_{ox} is the permittivity of the oxide. By substituting from (3.24) and (4.24) into (3.33) we obtain an expression for $d\varphi/dx|_{\text{ox}}$ which is inserted into (4.23). The resulting expression for f^e is substituted into (4.21), from which for $A_1 \neq 0$ we obtain

$$\sigma = B_0 + B_1\frac{d\varphi}{dx}\bigg|_{\text{sem}} + B_2\varphi_s + B_3\varphi_s^2 + \cdots , \tag{4.25}$$

where

$$B_0 = \frac{\epsilon_{\text{ox}}}{A_1}(\varphi_\infty^e - \varphi_{\text{ox}}^e) , \quad B_1 = -\left(\epsilon_s + \frac{A_2\epsilon_{\text{ox}}}{A_1}\right) ,$$
$$B_2 = -\frac{\epsilon_{\text{ox}}}{A_1}(1 + A_3) , \quad B_i = -\frac{A_{i+1}}{A_1}\epsilon_{\text{ox}} , \quad i \geqslant 3 \tag{4.26}$$

and we have taken the liberty of omitting the temperature dependences. Although (4.25) is a particularly convenient form for use in this work, it should be noted that the A_i are to be regarded as fundamental here and not the derived B_i.[63] In existing work on semiconductors interfaces the coefficient B_0 is often called the surface-state charge.[64] We also remark that since N_{ss} data are proportional to $d\sigma/d\varphi_s$ they do not provide a measure of B_0. In Fig. 2 some experimental $d\sigma/d\varphi_s$ vs φ_s data[65] are presented along with a reasonably accurate fit to that data using the φ_s derivative of (4.25). The nonzero B_i and A_i coefficients determined from this fit for this particular Si-SiO$_2$ interface are also shown.[66]

An equation similar to (4.25) has been used elsewhere[23] as the additional boundary condition required for the solution of a boundary-value problem to be obtained. However, as noted in the Introduction, assumed conditions, such as that in Ref. 23, are used simply because something is needed and are not obtained from fundamental physical principles dictated by the field theory as is done here.[67] Furthermore, the assumed condition of Ref. 23 is a static condition and not dynamic (as it is used) as shown by the

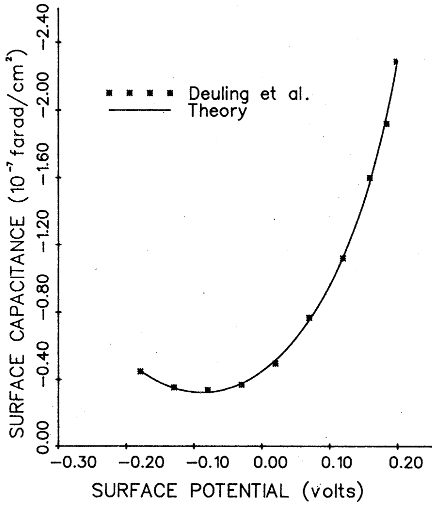

FIG. 2. Comparison of experimental data from Ref. 65 with the theoretical curve obtained using the expression for f^e given in Eq. (4.23). The B_i coefficients are $B_0 = 1.6\times10^{-8}$ C/cm^2 (assumed), $B_1 + 1.2\times10^{-14}$ farad/cm, $B_2 = -4.3\times10^{-8}$ farad/cm^2, $B_3 = -1.4\times10^{-7}$ C/V^2 cm^2, $B_4 = -5.2\times10^{-7}$ C/V^{3}cm^2. The A_i coefficients are $A_1 = -7.6\times10^{-5}$ cm, $A_2 = 2.4\times10^{-4}$ cm, $A_3 = -1.1\times10^1$, $A_4 = -3.3\times10^1$ V^{-1}, $A_5 = -1.2\times10^2$ V^{-2}.

derivation of (4.25). Moreover the condition employed in Ref. 23 does not contain the B_1 term appearing in (4.25). The appearance of the B_1 term in (4.25) is guaranteed by the fact that the terms linear in the electric field must be present in (4.23) as noted earlier. Nevertheless it is entirely possible that the B_1 (field) term could be much smaller than the other terms and, hence, negligible. It is to be expected that if the B_1 term is ever important, it would be when very high fields exist near the surface, which is the case when large voltages are applied or when the semiconductor is heavily doped and subject to moderate voltages. This expectation is also consistent with the fact that high fields tend to cause many quantities to be field dependent, e.g., mobilities. The regression studies appear to support this expectation. However, as already noted, on account of a weakness in the static one-dimensional problem no definitive experimental evidence of the necessity of the B_1 term can be obtained in this way.

Figure 3 presents a comparison of fits of the φ_s derivative of (4.25), both with and without the B_1 (field) term, to a particular data set.[68] As was typically the case for the data considered in this work, inclusion of the field term yielded a better fit with fewer terms needed. In addition in strong accumulation or inversion it is the field term which constitutes the dominant contribution to f^e, whereas for n-type semiconductors if our sole interest is in the surface-potential range $-0.55\text{ V} \leqslant \varphi_s \leqslant 0.0\text{ V}$, the field term may be accurately expanded in a few φ_s polynomial terms. We note that for the particular sample of Fig. 3 the surface field $d\varphi/dx|_{\text{sem}}$ in strong accumulation is ~10^6 volts/cm.[69]

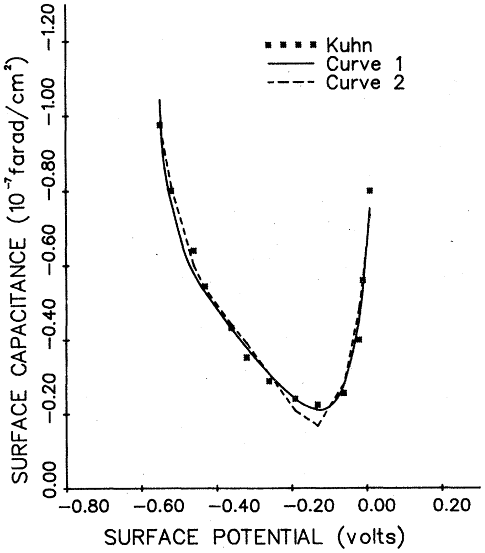

FIG. 3. Comparison of two theoretical curves obtained using Eq. (4.25) with data from Ref. 68. Curve 1 is obtained including the field term while curve 2 is obtained without the field term. The nonzero B_i coefficients are as follows: Curve 1: $B_1 = 1.9\times10^{-12}$ farad/cm, $B_2 = 3.4\times10^{-8}$ farad/cm^2, $B_3 = 8.0\times10^{-8}$ C/V^{2}cm^2. Curve 2: $B_2 = -6.4\times10^{-8}$ farad/cm^2, $B_3 = -4.4\times10^{-7}$ C/V^{2}cm^2, $B_4 = -1.8\times10^{-6}$ C/V^{3}cm^2, $B_5 = -3.1\times10^{-6}$ C/V^{4}cm^2, $B_6 = -2.1\times10^{-6}$ C/V^{5}cm^2.

The findings presented here concerning values of material surface coefficients and of the actual expression used for f^e in (4.23) should be regarded merely as illustrative. Extensive and systematic experimentation would be needed to definitely establish a "best" form for f^e for annealed samples. With the aid of such a form, a catalog of the values of surface coefficients along with the sample-preparation techniques necessary to achieve or alter those values could be obtained and would constitute the complete macroscopic description of the Si-SiO$_2$ interface. As an illustration, Table I gives a tabulation of values for material surface coefficients for a specific Si-SiO$_2$ interface,[70] the $d\sigma/d\varphi_s$ vs φ_s curves of which are shown in Fig. 4, based on the form of f^e in (4.23). Each sample underwent the same preparation technique except that different metals were used for the front contact in each case.

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TABLE I. The material surface coefficients found for the Si-SiO$_2$ interfaces studied in Ref. 70 where different front contact metals were used on otherwise identical samples.

	Contact metals		
	Cr	Al	Mg
A_1 (cm)	-4.1×10^{-5}	-5.0×10^{-5}	-7.0×10^{-5}
A_2 (cm)	1.4×10^{-4}	1.7×10^{-4}	2.4×10^{-4}
A_3	-2.8	-2.5	-3.0
A_4 (volts^{-1})	-2.1	-1.7	-2.8
A_5 (volts^{-2})	-3.6	-2.9	-3.9

APPENDIX A: THERMODYNAMIC CONSIDERATIONS (REF. 71)

The integral form of the conservation of energy for the three-component combined continuum, consisting of the two conducting fluids plus the polarizable lattice, states that the time rate of increase of *total* stored energy in the three continua in any *fixed* volume is equal to the rate at which work is done by the fluid pressure forces minus the rate at which stored energy flows out of the fixed volume plus the rate at which energy is supplied to the combined semiconducting continuum by the electric field, which enables us to write

$$\frac{\partial}{\partial t}\int_V (\epsilon+\rho^e\epsilon^e+\rho^h\epsilon^h)dV=\int_S[-p^e\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^e-p^h\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^h-\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^e\rho^e\epsilon^e-\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^h\rho^h\epsilon^h]dS+\int_V\Sigma\, dV\,, \tag{A1}$$

where ϵ is the stored internal energy per unit volume in the lattice continuum, ϵ^e and ϵ^h are the stored internal energies per unit charge of the conduction-electronic and hole fluids, respectively, $-p^e\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^e$ and $-p^h\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^h$ are the rates at which work is done per unit area by the pressures acting on the two charged fluids, $\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^e\rho^e\epsilon^e$ and $\vec{\mathrm{n}}\cdot\vec{\mathrm{v}}^h\rho^h\epsilon^h$ are the rates of efflux of stored internal energies of the two fluids from the fixed volume, and Σ is the rate of supply of energy per unit volume to the combined semiconducting continuum from the electric field. The quasistatic Maxwell electric field acting on all charged elements in the macroscopic model of Sec. II supplies energy according to

$$\Sigma=\rho^e\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}^e+\rho^h\vec{\mathrm{E}}\cdot\vec{\mathrm{v}}^h+\vec{\mathrm{E}}\cdot\frac{d\vec{\mathrm{P}}}{dt}, \tag{A2}$$

where the third term containing the electric polarization $\vec{\mathrm{P}}$ would arise from a detailed treatment of polarization in the macroscopic model[11] but is here taken merely as a plausible assumption.

Taking the time derivatives in (A1), substituting from (A2), employing the divergence theorem, (3.5), (3.6), (3.17), (3.18), the arbitrariness of V, the defined material derivatives

$$\frac{d}{dt}\equiv\frac{\partial}{\partial t},\quad \frac{d^e}{dt}\equiv\frac{\partial}{\partial t}+\vec{\mathrm{v}}^e\cdot\vec{\nabla},\quad \frac{d^h}{dt}\equiv\frac{\partial}{\partial t}+\vec{\mathrm{v}}^h\cdot\vec{\nabla}, \tag{A3}$$

and in accordance with the model, making the plausible assumptions

$$\epsilon^e=\epsilon^e(\rho^e,T),\quad \epsilon^h=\epsilon^h(\rho^h,T), \tag{A4}$$

we obtain

$$\frac{d\epsilon}{dt}+\left(\rho^e\frac{\partial\epsilon^e}{\partial\rho^e}-\frac{p^e}{\rho^e}\right)\frac{d^e\rho^e}{dt}+\left(\rho^h\frac{\partial\epsilon^h}{\partial\rho^h}-\frac{p^h}{\rho^h}\right)\frac{d^h\rho^h}{dt}+\left(\rho^e\frac{\partial\epsilon^e}{\partial T}+\rho^h\frac{\partial\epsilon^h}{\partial T}\right)\frac{dT}{dt}-\vec{\mathrm{E}}\cdot\frac{d\vec{\mathrm{P}}}{dt}$$
$$=-\rho^e\vec{\mathrm{E}}^e\cdot\vec{\mathrm{v}}^e-\rho^h\vec{\mathrm{E}}^h\cdot\vec{\mathrm{v}}^h-\gamma^e\left(\frac{p^e}{\rho^e}+\epsilon^e\right)-\gamma^h\left(\frac{p^h}{\rho^h}+\epsilon^h\right), \tag{A5}$$

where we have made use of the fact that $\vec{\nabla}T$ is $\equiv 0$ since T is uniform in this work. Equation (A5) is commonly called the first law of thermodynamics for the thermodynamic system under consideration.

Since the first law of thermodynamics for the combined continuum is of the form shown in (A5) and only the terms on the right-hand side are dissipative, the expression of the second law of thermodynamics may be written in the form[72]

$$\frac{d\epsilon}{dt}+\left(\rho^e\frac{\partial\epsilon^e}{\partial\rho^e}-\frac{p^e}{\rho^e}\right)\frac{d^e\rho^e}{dt}+\left(\rho^h\frac{\partial\epsilon^h}{\partial\rho^h}-\frac{p^h}{\rho^h}\right)\frac{d^h\rho^h}{dt}+\left(\rho^e\frac{\partial\epsilon^e}{\partial T}+\rho^h\frac{\partial\epsilon^h}{\partial T}\right)\frac{dT}{dt}-\vec{\mathrm{E}}\cdot\frac{d\vec{\mathrm{P}}}{dt}=T\frac{d\eta}{dt}, \tag{A6}$$

where η is the entropy per unit volume. Then, for a uniform temperature state, the entropy inequality takes the form

$$\frac{d\eta}{dt}=-\frac{1}{T}\left[\rho^e\vec{\mathrm{E}}^e\cdot\vec{\mathrm{v}}^e+\rho^h\vec{\mathrm{E}}^h\cdot\vec{\mathrm{v}}^h+\gamma^e\left(\frac{p^e}{\rho^e}+\epsilon^e\right)+\gamma^h\left(\frac{p^h}{\rho^h}+\epsilon^h\right)\right]\geqslant 0, \tag{A7}$$

and $d\eta/dt$ is the rate of entropy production.

Equations (A6) and (A7), which arise from the laws of thermodynamics as applied to this continuum, are the basis for the generation of two types of constitutive relations: Those from the former are termed recoverable and from the latter, dissipative.

In obtaining the recoverable constitutive equations it turns out to be convenient to define a thermodynamic state function χ by

$$\chi = \epsilon - \vec{E}\cdot\vec{P} - \eta T\,, \tag{A8}$$

the substitution of which in (A6) yields

$$\frac{d\chi}{dt} + \left(\rho^e \frac{\partial\epsilon^e}{\partial\rho^e} - \frac{p^e}{\rho^e}\right)\frac{d^e\rho^e}{dt} + \left(\rho^h\frac{\partial\epsilon^h}{\partial\rho^h} - \frac{p^h}{\rho^h}\right)\frac{d^h\rho^h}{dt} + \vec{P}\cdot\frac{d\vec{E}}{dt} + \left(\eta + \rho^e\frac{\partial\epsilon^e}{\partial T} + \rho^h\frac{\partial\epsilon^h}{\partial T}\right)\frac{dT}{dt} = 0\,. \tag{A9}$$

Since (A9) is a state function equation, we must have

$$\chi = \chi(\vec{E}, T)\,. \tag{A10}$$

Taking the total time derivative of (A10) and substituting it into (A9), we obtain

$$(\vec{\nabla}_{\vec{E}}\chi + \vec{P})\cdot\frac{d\vec{E}}{dt} + \left(\rho^e \frac{\partial\epsilon^e}{\partial\rho^e} - \frac{p^e}{\rho^e}\right)\frac{d^e\rho^e}{dt} + \left(\rho^h\frac{\partial\epsilon^h}{\partial\rho^h} - \frac{p^h}{\rho^h}\right)\frac{d^h\rho^h}{dt} + \left(\frac{\partial\chi}{\partial T} + \eta + \rho^e\frac{\partial\epsilon^e}{\partial T} + \rho^h\frac{\partial\epsilon^h}{\partial T}\right)\frac{dT}{dt} = 0\,. \tag{A11}$$

Since all the time derivatives appearing in (A11) are independent and (A11) holds for arbitrary values of those time derivatives, each coefficient must vanish separately, which yields

$$P = -\vec{\nabla}_{\vec{E}}\,\chi \tag{A12a}$$

$$\eta = -\frac{\partial\chi}{\partial T} - \rho^e\frac{\partial\epsilon^e}{\partial T} - \rho^h\frac{\partial\epsilon^h}{\partial T}\,, \tag{A12b}$$

$$p^e = (\rho^e)^2\frac{\partial\epsilon^e}{\partial\rho^e}\,,\quad p^h = (\rho^h)^2\frac{\partial\epsilon^h}{\partial\rho^h}\,. \tag{A13}$$

Equations (A12) and (A13) are the recoverable constitutive relations for $\vec{P}$, η, p^e, and p^h. The substitution of the functional dependences for χ, ϵ^e, and ϵ^h shown in (A4) and (A10) in (A12a) and (A13), and the appropriate use of the definition of $\vec{D}$ give rise to the functional forms in (3.19) and (3.21).

As usual, chemical potentials are defined in terms of ϵ^e and ϵ^h as[73]

$$\varphi^e \equiv \frac{\partial(\rho^e\epsilon^e)}{\partial\rho^e}\,,\quad \varphi^h \equiv \frac{\partial(\rho^h\epsilon^h)}{\partial\rho^h}\,, \tag{A14}$$

where φ^e and φ^h are the chemical potentials of the conduction-electronic and hole fluids, respectively. These are clearly related to the fluid pressures through (A13).[74] A useful relation between the gradients of the chemical potentials and of the pressures in the respective fluids is readily found by taking the gradients of (A13) and (A14), assuming no material inhomogeneity, with the results

$$\frac{1}{\rho^e}\vec{\nabla}p^e = \vec{\nabla}\varphi^e\,,\quad \frac{1}{\rho^h}\vec{\nabla}p^h = \vec{\nabla}\varphi^h\,, \tag{A15}$$

which have been used in Sec. III.

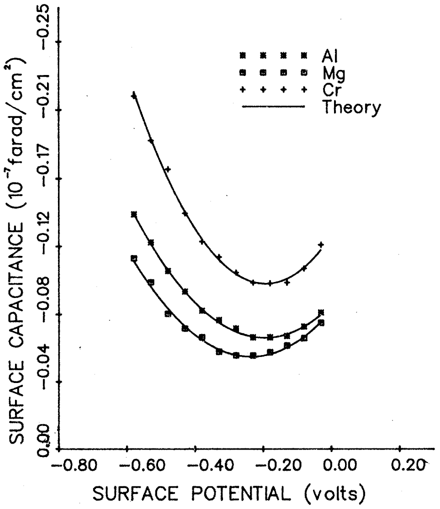

FIG. 4. Comparison of theoretical curves with experimental data from Ref. 70 showing the variation of response with the use of different front contact metals on otherwise identical samples. The nonzero material surface coefficients for each case are given in Table I.

Equations (A13) and (A14) enable us to write Eq. (A7) in the form

$$\rho^e\vec{E}^e\cdot\vec{v}^e + \rho^h\vec{E}^h\cdot\vec{v}^h + \gamma^e\varphi^e + \gamma^h\varphi^h \leqslant 0\,. \tag{A16}$$

Since φ^e is a function only of ρ^e and T, and φ^h only of ρ^h and T, and (A16) must always be true in order that the laws of thermodynamics not be violated, we must have the dissipative constitutive relations

$$\begin{aligned}
\vec{E}^e &= \vec{E}^e(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, T)\,,\\
\vec{E}^h &= \vec{E}^h(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, T)\,,\\
\gamma^e &= \gamma^e(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, T)\,,\\
\gamma^h &= \gamma^h(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, T)\,,
\end{aligned} \tag{A17}$$

along with certain conditions dictated by the inequality in (A16) which are not of particular interest to us here.

However, since the recoverable constitutive equations (A12) and (A13) depend on $\vec{E}$, there is no logical reason to exclude $\vec{E}$ from the dissipative constitutive equations in (A17).[75] Also, since the fluids have been chosen to interact solely through the generation and/or recombination terms γ^e and γ^h, we exclude the dependence of $\vec{E}^e$ on ρ^h and $\vec{v}^h$ and of $\vec{E}^h$ on ρ^e and $\vec{v}^e$. The functional dependence of the dissipative constitutive equations may then be written in the form

$$\vec{E}^e = \vec{E}^e(\rho^e, \vec{v}^e, \vec{E}, T)\,, \quad \vec{E}^h = \vec{E}^h(\rho^h, \vec{v}^h, \vec{E}, T)\,, \tag{A18}$$

$$\gamma^e = \gamma^e(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, \vec{E}, T)\,, \quad \gamma^h = \gamma^h(\rho^e, \rho^h, \vec{v}^e, \vec{v}^h, \vec{E}, T)\,,$$

which were given in (3.20) and (3.22).

APPENDIX B: SOME RELATIONS BETWEEN THE MACROSCOPIC DESCRIPTION AND CONVENTIONAL SEMICONDUCTOR THEORY

The macroscopic theory can be further specified (beyond Sec. IV) by making particular choices for the energy functions ϵ^e and ϵ^h which, as usual, will contain macroscopic material parameters.[76] However, since ϵ^e and ϵ^h are descriptive of the conducting fluids in the *interior* of the semiconductor these parameters may be related to and calculated with reasonable accuracy from the usual quasi microscopic model based on a semiclassical view of the infinite periodic lattice. By making the specific selections

$$\epsilon^e = -\frac{E_c}{q} - \frac{kT}{q}\left[\ln\left(\frac{\rho^e}{-qN_c}\right) - 1\right], \tag{B1}$$

$$\epsilon^h = -\frac{E_v}{q} + \frac{kT}{q}\left[\ln\left(\frac{\rho^h}{qN_v}\right) - 1\right], \tag{B2}$$

where N_c and N_v are the quasimicroscopically defined "effective densities of states" in the conduction and valence bands, respectively, we can deduce the Maxwell gas approximation for the electrons and holes in the semiconductor.[6] Equations (B1) and (B2) give the energies per unit charge for this particular model. The use of (B1) and (B2) in (A13) and (A14), respectively, allows us to obtain[77]

$$p^e = \frac{-kT\rho^e}{q} = kTn\,, \quad p^h = \frac{kT\rho^h}{q} = kTp\,, \tag{B3}$$

$$\varphi^e = -\frac{E_c}{q} - \frac{kT}{q}\ln\left(\frac{\rho^e}{-qN_c}\right) = -\frac{E_c}{q} - \frac{kT}{q}\ln\left(\frac{n}{N_c}\right), \tag{B4a}$$

$$\varphi^h = -\frac{E_v}{q} + \frac{kT}{q}\ln\left(\frac{\rho^h}{qN_v}\right) = -\frac{E_v}{q} + \frac{kT}{q}\ln\left(\frac{p}{N_v}\right), \tag{B4b}$$

where n and p are the electron and hole number densities, respectively. Differentiating (B4) with respect to the charge densities and comparing the result with (3.30), we can obtain the Einstein relations for the Maxwell gas model.

When no electron current is flowing $\vec{E}^e \equiv 0$ and hence (3.26) can be integrated, with the aid of (B4a), to yield[78]

$$\varphi + \hat{\varphi}^e = \hat{\varphi}^e_b = \frac{-kT}{q}\ln\left(\frac{n_b}{N_c}\right), \tag{B5}$$

where n_b is the electron number density in the bulk of the semiconductor and φ has been assumed zero in the bulk. In the conventional quasimicroscopic theory for nondegenerate situations at thermal equilibrium an expression for n_b may be written in terms of the Fermi energy E_F, and the conduction-band energy E_c. The expression is

$$n_b = N_c \exp[(E_F - E_c)/kT]\,. \tag{B6}$$

Consequently, when no electron current flows we may combine (B5) and (B6) to obtain

$$\varphi + \hat{\varphi}^e = \frac{1}{q}(E_c - E_F)\,, \tag{B7}$$

where it is to be noted that when electron current flows the left-hand side of (B7) remains well defined while the right-hand side does not. However, (B7) may be extended to include current flow situations by employing (B7) *to define* a quasi-Fermi level[79] for electrons $E_F^{(n)}$, with

$$\frac{1}{q}E_F^{(n)} = \frac{1}{q}E_c - \varphi - \hat{\varphi}^e\,. \tag{B8}$$

The relations (B7) and (B8) with (B4a) substituted are in agreement with expressions in the literature.[80]

Equation (B7) [or (B8)] may be used to exhibit the connection between the boundary condition (3.40) and the conventional semiconductor nomenclature. For the semiconductor-vacuum boundary (an oxide interface is treated analogously) we have (for the no-current situation),

$$f^e = [\hat{\varphi}^e] = \hat{\varphi}^e_{\text{sem}} - \hat{\varphi}^e_{\text{vac}} = \frac{1}{q}(E_c - E_F) - \varphi_s\,, \tag{B9}$$

where $\hat{\varphi}^e_{\text{vac}}$ has been taken to be identically zero and φ_s is the surface potential. We may rewrite (B9) in the form,

$$f^e = \frac{1}{q}(E_c^* - E_F) = \frac{1}{q}\Psi - \chi \equiv \Gamma\,, \tag{B10}$$

where E_c^* is the "bent" conduction-band energy, Ψ is the work function, and χ is the electron affinity. Equation (B10) provides a ready understanding of f^e in the conventional semiconductor terminology. When an n-type semiconductor is in accumulation Γ is small and, hence, f^e is small. This reflects the fact that in accumulation the energy of the near-surface electrons has been lowered and, hence, less force need be exerted by the lattice to keep those electrons in the crystal. In inversion the reverse is true. The effects of changes in temperature may be argued in a similar manner. It is important to emphasize that while (B9) or (B10) allow the interpretation of f^e within the framework of conventional semiconduction theory, in order to use (3.40) in the solution of semiconductor boundary-value problems it is necessary to provide an expression for f^e in terms of the dependent variables as is done in Sec. IV. For holes expressions analogous to (B5)–(B10) may easily be found and are in agreement with the literature.[80]

We conclude this appendix by utilizing the above expressions to obtain relations for the two constants $\hat{\varphi}^e_\infty$ and $\hat{\varphi}_{\mathrm{ox}}$, which appear in (4.21) and are required for the conversion of the B_i coefficients in (4.25) to the fundamental A_i coefficients in (4.23). Since no current flows (B7) gives immediately

$$\hat{\varphi}^e_\infty = \frac{1}{q}(E_c - E_F^\infty), \tag{B11}$$

which is approximately equal to 0.55 V in intrinsic silicon. Concerning the oxide, we view insulators simply as semiconductors in which $\vec{\mathrm{E}}^e$ is balanced by $\vec{\mathrm{E}}$. As a result of this assumption, with (3.26) we can assume uniformity of $\hat{\varphi}^e$, i.e., $\hat{\varphi}^e = \hat{\varphi}^e_{\mathrm{ox}} = \mathrm{const}$, *even when* a field is applied. Hence

$$\hat{\varphi}^e_{\mathrm{ox}} = \frac{1}{q}(E_c^{\mathrm{ox}} - E_F^{\mathrm{ox}}) \quad , \tag{B12}$$

which is approximately 4.0 in silicon dioxide.[81] Expressions for $\hat{\varphi}^h_\infty$ and $\hat{\varphi}^h_{\mathrm{ox}}$ may be found in a similar manner.

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[1] E. Spenke, *Electronic Semiconductors* (McGraw-Hill, New York, 1958).

[2] A. F. Ioffe, *Physics of Semiconductors* (Academic, New York, 1960).

[3] R. Stratton, IEEE Trans. Electron Devices ED-19, 1288 (1972).

[4] This is subject to the usual restriction that it must vary slowly compared with the spacing of discrete elements.

[5] W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand, Princeton, New Jersey, 1950).

[6] A. C. Smith, J. F. Janak, and R. B. Adler, *Electronic Conduction in Solids* (McGraw-Hill, New York, 1967).

[7] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969).

[8] The conventional macroscopic theory is often termed phenomenological. We prefer the term macroscopic since it is more descriptive of the purpose and limitations of the theory.

[9] J. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).

[10] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).

[11] H. G. de Lorenzi and H. F. Tiersten, J. Math. Phys. 16, 938 (1975).

[12] The procedure of developing the description from a completely macroscopic model is employed because we believe it to be the clearest and simplest procedure for obtaining a consistent system of macroscopic differential equations and boundary conditions.

[13] These equations make the system determinate in the sense that the number of differential equations is equal to the number of dependent variables.

[14] See Appendix A.

[15] For the relation of this description to the conventional quasimicroscopic model see Appendix B.

[16] J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 32, 225 (1974).

[17] J. Pollmann and S. T. Pantelides, Phys. Rev. B 18, 5524 (1978).

[18] The calculation for the material surface coefficients requires that a quantitative prediction of a macroscopically measurable quantity be obtained directly from a microscopic model. We distinguish here between macroscopic measurements and microsopic or particle experiments which also serve as valuable probes of the semiconductor surface. Clearly microscopic measurements on clean surfaces, e.g., LEED, Auger spectroscopy, are more likely to be within the grasp of "first-principle" calculations, but even in these cases problems are encountered in achieving quantitative agreement. See Refs. 16, 17, and 19.

[19] P. Mark, E. So, and M. Bonn, J. Vac. Sci. Technol. 14, 865 (1977).

[20] Strictly speaking, all semiconductor problems involve boundaries since there are no semiconductors of infinite size. We are concerned here only with problems in which the effects of bounding surfaces on overall response is important.

[21] K. M. Lakin and H. J. Shaw, IEEE Trans. Microwave Theory Tech. MTT-17, 912 (1969).

[22] We recognize that in computer-aided design (CAD), where the ultimate goal is the efficient reasonably accurate calculation of the behavior, the fundamentally correct formulation is not always preferable.

[23] D. Vandorpe, J. Borel, G. Merckel, and P. Saintot, Solid-State Electron. 15, 547 (1972), Sec. 4.

[24] P. M. Marcus, IBM J. Res. Dev. 8, 496 (1964).

[25] J. McKenna and N. L. Schryer, Bell Syst. Tech. J. 51, 1471 (1972).

[26] H. Kroemer, IEEE Trans. Electron Devices ED-15, 819 (1968).

[27] In the opinion of the present authors the work of Kroemer in Ref. 26, although argued in a quasimicroscopic way, is in conformity with the spirit of macroscopic modeling.

[28] H. K. Gummel, IEEE Trans. Electron Devices, ED-11, 455 (1964), Sec. III and App. I.

[29] Some assumed conditions may be shown to be correct for specific cases over restricted ranges. See the latter part of Sec. IV.

[30] S. Zemon and E. N. Conwell, Appl. Phys. Lett. 17, 218 (1970).

[31] K. H. Zaininger and G. Warfield, IEEE Trans. Electron Devices 12, 179 (1965).

[32] B. E. Deal, J. Electrochem. Soc. 121, 198 (1974).

[33] K. Ziegler and E. Klausmann, Appl. Phys. Lett. 26, 400 (1975).

[34] Through extensive experimentation, involving the Si-SiO$_2$ interface, an empirical understanding of interfacial mechanisms and a concept of how to manipulate and especially "minimize" boundary effects has, to a great degree, been achieved. See E. H. Nicollian, J. Vac. Sci. Tech. 14, 1112 (1977).

[35] References 18 and 19.

[36] When the *sole* desire is the minimization of boundary effects on some desired bulk phenomenon the main advantages of the purely macroscopic description are somewhat negated (see Ref. 34); however, the example considered here illustrates a possibly important application in a case where boundary effects represent undesired features. When interface behavior is essential to the operation of a device, as in surface-wave devices (see Ref. 30) or in Gunn-effect oscillators (see Ref. 26), the information contained in a macroscopic boundary description may be more important.

[37] The doped semiconductor may entail a weaker continuum assumption because of the comparatively large spacings between impurities.

[38] Polarization is not introduced in a detailed manner here. See Ref. 11 for further discussion.

[39] We choose to speak of charge density rather than number density (though of course, the two are trivially related) because in the macroscopic description the conduction electrons, for example, are represented as a fluid of *continuously* distributed charge *not* as a collection of *individual countable point* charges. The former is a macroscopic view, the latter a microscopic view, and our nomenclature is chosen to reflect this.

[40] This is undoubtedly a reasonable macroscopic assumption.

[41] J. L. Moll, *Physics of Semiconductors* (McGraw-Hill, New York, 1964).

[42] For a particular microscopic model these functions φ^e and φ^h can be shown to be related to the "ideal-gas" chemical potential that is often used. See Appendix B.

[43] Reference 5, Chap. 12.

[44] Reference 1, Chap. 8.

[45] Reference 7, Chap. 2.

[46] The set given here is essentially that originally formulated in Ref. 5.

[47] Clearly numerous other choices for which different equations and variables are basic is possible. For example see J. E. Parrott, Solid State Electron. 17, 707 (1974).

[48] Reference 9, Sec. 1.13.

[49] Although (3.36) implies only that $[\varphi]$ = constant, we assume the constant to be zero. This discounts the possible existence of a double layer at this interface. While such things are quite important for metal surfaces, we feel that for semiconductor-insulator boundaries such a quantity, if not zero, is surely negligible. However, as with metal boundaries, it could be included if desired.

[50] All assumptions except condition (6) may be greatly modified, however, since the experiment is being used to measure coefficients defined by the theory, the experiment can be tailored to best meet the needs of the theory, i.e., to satisfy conditions (1)–(5).

[51] This requires that the ratios of oxide thickness and Debye length to electrode width be small.

[52] This demands that the quasistatic C-V experiment be done at a low enough frequency ($\lesssim 10$ Hz) so that the slowest response—that of the generation of minority carriers in the inversion layer—is capable of following the low frequency. See M. Kuhn and E. H. Nicollian, J. Electrochem. Soc. 118, 370 (1971).

[53] This requires that the oxide thickness not be too great.

[54] The assertion in (3.37) makes (4.11) unambiguous.

[55] In the static problem no specification of φ^e and φ^h is necessary beyond their functional dependences and their values at infinity and in the oxide. In a dynamic situation, where (4.17) and (4.18) do not hold, specific choices for φ^e and φ^h would have to be made, such as those appearing in Appendix B.

[56] C. N. Berglund, IEEE Trans. Electron Devices ED-13, 701 (1966).

[57] We remark that the low-frequency C-V measurement is inadequate for probing semiconductor surface response in the extremes of surface potential, as is well known. The energy-level ranges which correspond to these surface potentials have been explored by the method of P. V. Gray and D. M. Brown, Appl. Phys. Lett. 8, 31 (1966). This method, however, is not relevant to the problem being treated by Sec. IV because, within the macroscopic framework and terminology, it is concerned with the temperature dependence of f^e at zero applied voltage, whereas we are concerned with establishing the functional dependence of f^e at constant temperature. Macroscopically speaking, these are distinct questions.

[58] Any quantities which can be derived from φ_s vs φ_0, such as σ_{sem}, σ_{met}, $-(1/q)d\sigma_{\text{sem}}/d\varphi_s \equiv N_{ss}$ vs. φ_s may, of course, also be used. Another measurement which is perhaps better for the purposes of this paper in that it claims greater accuracy is the direct measurement of the gate surface charge. See J. Koomen, Solid State Electron. 14, 571 (1971).

[59] B. E. Deal and R. R. Razouk, Technical Report—ECOM U. S. Army Electronics Command, Fort Monmouth, New Jersey (unpublished).

[60] We remark that these N_{ss} vs φ_s curves for annealed samples sometimes contain peaks, e.g., see Ref. 33. We treat only those curves without peaks here because the presence of the peaks causes certain difficulties with the expression for f^e.

[61] It should be noted that a term $A_0(T)$ could appear in the expression for f^e in (4.23). However, such a term is not required for the treatment of any static or dynamic electrical problems involving semiconducturs.

[62] The particular form chosen for f^e should be regarded merely as a good representation of some ideal function truly characteristic of surface response. If too many terms in the power series in φ_s had been required, different (better) functional forms with fewer defined material surface coefficients would have been considered.

[63] In obtaining (4.25) additional assumptions, i.e., Eqs. (3.24), (4.24), and the static expressions (4.17) and (4.18) were employed. Therefore the B_i coefficients depend on parameters independent of surface behavior and could change even when the actual surface response remains the same. In contradistinction the A_i are fundamental material parameters descriptive of the surface response alone.

[64] B. E. Deal, M. Sklar, A. S. Grove, and E. H. Snow, J. Electrochem. Soc. 114, 266 (1967).

[65] H. Deuling, E. Klausman, and A. Goetzberger, Solid State Electron. 15, 559 (1972), Fig. 5.

[66] In calculating A_0 from the measured B_0 it is necessary to know φ_∞^e and φ_{ox}^e. Values for these quantities may be found in Appendix B.

[67] And hence it suffers from the deficiency noted in Ref. 63.

[68] M. Kuhn, Solid State Electron. 13, 873 (1970).

[69] Electric fields of this magnitude are well within the regime of field-dependent mobilities in silicon.

[70] S. Kar, Solid State Electron. 18, 723 (1975), Figs. 5 and Table 2. This is a case where data are given only in the central φ_s region and, as previously mentioned, the field term is well represented by power-series terms in φ_s in this range. As a result the coefficients presented here are composites of actual φ_s terms appearing in (4.23) and φ_s terms resulting from a power-series expansion of the field term.

[71] The present macroscopic theory represents a thermodynamic system and hence is subject to the laws of thermodynamics. In this vein, see the introductory sections of C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949).

[72] S. R. DeGroot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).

[73] C. Truesdell and R. A. Toupin, in *Encyclopedia of Physics*, edited by S. Flügge (Springer, Berlin, 1960), Vol. III/1, Sec. 255.

[74] The question arises as to why chemical potentials were not employed from the outset here since much of the existing work on semiconductors is grounded either explicitly or implicitly in the chemical potentials. The reason is that in the fully macroscopic balance law approach used here forces and pressures are fundamental. Only after the governing equations are obtained are the pressures abandoned in favor of more *convenient* variables.

[75] This procedure has been termed the principle of equipresence by Truesdell. See Ref. 73, Sec. 293.

[76] As was pointed out in Ref. 55 detailed specifications of φ^e and φ^h are necessary when dynamic problems are to be treated.

[77] The expressions in (B4) can be found in Ref. 1, Chap. 10. It is noted that if we were to choose expressions for ϵ^e to match those in the conventional theory for degenerate cases then φ^e would be taken as $-(1/q)[E_c + \xi(n/N_c)]$ [where $\xi(n/N_c)$ is defined in Appendix II of Ref. 1].

[78] When spatially inhomogeneous cases are considered it turns out that a $\hat{\varphi}^e$ different from φ^e can be defined such that $(1/\rho^e)\vec{\nabla}p^e = \vec{\nabla}\hat{\varphi}^e$. This $\hat{\varphi}^e$ in the ideal-gas case is related to φ^e by $\hat{\varphi}^e = \varphi^e + E_c/q$. In the event that E_c is constant everywhere except for jumps in value across interfaces, which is the only case considered here, both $\hat{\varphi}^e$ and φ^e satisfy the same differential equation (3.26) on either side of any interface, but the boundary condition (3.40) should be written as $[\hat{\varphi}^e] = f^e$. Since in this appendix we are interested in writing this boundary condition for a situation where E_c suffers a jump in value, we work here in terms of $\hat{\varphi}^e$. Of course, all the corresponding expressions for holes are treated analogously.

[79] Reference 5, Chap. 12. Note that in terms of φ^e, (B8) may be written $\varphi + \varphi^e \equiv (-1/q)E_F^{(n)}$, i.e., $(-1/q)E_F^{(n)}$ defined here is equal to the "electrochemical" potential in accordance with the conventional terminology.

[80] Reference 1, Chap. 10.

[81] Reference 7, p. 468.