A Mathematical Model for the Influence of Deep-Level Electronic States on Photoelectrochemical Impedance Spectroscopy

II. Assessment of Characterization Methods Based on Mott-Schottky Theory

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ABSTRACT

The impact of the assumptions inherent in using the Mott-Schottky theory to identify deep-level electronic states in semiconductors was assessed by comparison to the results of a less restrictive mathematical model. The model, developed in another paper, treated the transport and recombination reactions involving electrons, holes, and electronic states located within the bandgap. The capacitive component used in standard Mott-Schottky theory was found to be insensitive to bulk electronic states within the bandgap for concentrations significantly less than the doping level. The resistive component measured at low frequencies was much more sensitive to deep-level states and may be used to determine their distribution. For high concentrations of deep-level states, the model results were in agreement with the current practice of attributing changes in the slope of the Mott-Schottky curve to partial ionization of single-energy deep-level states with applied potential. In the absence of frequency dispersion, these changes in slope could be attributed instead to nonuniform dopant distribution.

Mott-Schottky theory is commonly used to evaluate the dopant level and flatband potential of semiconductors [see, e.g., Ref. (1, 2)]. The technique is based on the equation

\[ \frac{1}{C_{sc}^2} = \frac{2(V + RT/F)}{eF(N_d - N_a)} \]  \[ \text{(1)} \]

which provides the relationship between the applied potential and the capacitance of the semiconductor space-charge region for an evenly doped, ideally polarizable electrode under reverse bias potentials. Following this relationship, a plot of \( 1/C^2 \) for an evenly doped semiconductor in the absence of deep-level electronic states is linear over a range of potentials where a depletion layer is formed. A depletion layer is formed near the polarized interface at potentials such that the semiconductor is reverse-biased \( (V < 0 \) for an n-type semiconductor) and such that the electron and hole concentrations are significantly less than the dopant concentration. This requirement is violated at low and high reverse biases when the potential drop across the semiconductor reaches a value that allows either the electron or hole concentration to be of the same magnitude as the doping concentration.

Mott-Schottky analysis of uniformly doped semiconductors is subject to the assumption that deep-level states are not present in significant concentration. Deviations from straight lines in Mott-Schottky plots, therefore, are frequently attributed to the influence of potential dependent charging of surface or bulk states. This interpretation is supported by analytic calculations of the contribution of deep-level states to the space charge as a function of applied potential (3-5). It should be noted that this approach treats only the high-frequency asymptotic limit to the imaginary part of the impedance.

Deviations from linearity of Mott-Schottky plots could also be attributed to a nonuniform dopant distribution. The local dopant concentration is obtained through Eq. [1] from the slope of the Mott-Schottky plot at a given potential. This potential is related to a probing depth through an expression for the depletion layer width \( W \) (6) where

\[ W = \sqrt{\frac{-2e(V + RT/F)}{F(N_d - N_a)}} \]  \[ \text{(2)} \]

A further simplification can be made by noting that

\[ W = \frac{\varepsilon}{C_{sc}} \]  \[ \text{(3)} \]

where \( C_{sc} \) is given by Eq. [1]. These relationships are the basis of C-V profiling, although C-V profiling generally involves etching to change the position used in the measurement. A major assumption forming the basis of C-V profiling is that the Mott-Schottky slope at a given potential is a reflection of the semiconductor conditions at a specific depth, and that this depth is the depletion layer width.

The object of this work was to examine the influence of bulk and surface states on Mott-Schottky plots through the use of a comprehensive numerical model which is not subject to the restrictions required in the derivation of Mott-Schottky theory. The model, which provides explicit treatment of the influence of deep-level states on the impedance response of semiconductors, is described in Ref. (7) and (9). This model was used to explore the deviations from linear Mott-Schottky theory that occur when the semiconductor is nonuniformly doped or when deep-level states are present. A final objective was to propose other methods for interpretation of impedance data to obtain the distribution of deep-level states in a manner independent of Mott-Schottky theory.

Results and Discussion

Mott-Schottky theory is commonly employed to determine the doping concentration and flatband potential of uniformly doped semiconductors. In this analysis, a space-charge capacitance \( C_{sc} \) is obtained from the impedance data (consisting of real and imaginary portions of the complex impedance as a function of frequency and potential). In the absence of deep-level states, the space charge capacitance is assumed to be a function of potential only. The space-charge capacitance was calculated here by assuming that the semiconductor system can be represented at high frequency and in the absence of faradaic reactions by a simple R-C series electrical circuit (10, 11). The capacity is therefore given by

\[ C_{sc} = \frac{-1}{\omega Z_i} \]  \[ \text{(4)} \]

Computer-generated values are presented in Fig. 1 for an n-type semiconductor with a uniform doping value of \( 10^{16} \text{ cm}^{-3} \). These calculated results were analyzed in accordance with Eq. [1], and the result of this analysis was in agreement with the input values of \( 10^{16} \text{ cm}^{-3} \) for the dop-
Effect of a nonuniform distribution of doping species.—The mathematical model was used to investigate the effects of a nonuniform distribution of shallow-level donor species on Mott-Schottky plots. The shallow-level donor distribution was in the form of a step change where the concentration of these species was equal to \(2 \times 10^{16} \text{ cm}^{-3}\) between the semiconductor surface and a depth of 2000 Å and \(1 \times 10^{16} \text{ cm}^{-3}\) throughout the remaining semiconductor. A value of 2000 Å was chosen for the step change since the potential associated with this distance (see Eq. [2]) is well within the 0.8 V range investigated. One might expect that the Mott-Schottky curve corresponding to this case would show an abrupt change in slope at the potential corresponding to a depletion width of 2000 Å. The Mott-Schottky plot calculated for this system reveals a gradual change in slope. The apparent dopant distribution, calculated from Eq. [1], is presented in Fig. 3 as a function of potential. Comparison of the input ionized donor distribution, obtained by calculating the potential associated with the corresponding input depth through Eq. [2], shows that abrupt changes in the doping level and 0.0 V for the flatband potential. A flatband potential of 0.0 V was obtained since the calculated potentials were referenced to the flatband potential. This agreement between Mott-Schottky theory and the transport-based mathematical model is to be expected since the model parameters were consistent with the assumptions made in developing the Mott-Schottky theory.

Effect of deep-level states.—Application of Mott-Schottky theory is not strictly valid in the presence of high concentrations of deep-level states since these species also contribute to the space charge as a function of applied potential. The mathematical model was employed to investigate the influence of uniform and nonuniform distributions of deep-level states on Mott-Schottky plots.

Uniform distribution of deep-level states.—The effect of deep-level states was explored in this work by modeling a dopant profiles deep within the depletion region are seen as gradual changes through application of Mott-Schottky theory. The apparent error in the calculated dopant concentration near the surface is due to violation of the depletion layer assumption near the flatband potential.

The use of Eq. [1] and [2] yields a “smoothed” concentration profile. The averaging region for the profile is centered about the depletion layer thickness. To illustrate this point, a step change in dopant concentration at a depth of 1000 Å was explored. The results, presented in Fig. 4, demonstrate similar behavior to the previous case. The “local” doping level calculated from the Mott-Schottky slope shows good agreement with the input dopant concentration far from the surface, but the apparent transition is not sharp. These results show that the probing region is in the form of a band which, at large potentials, does not encompass the surface.

Uniform distribution of deep-level states.—The effect of deep-level states was explored in this work by modeling a
semiconductor with a uniform distribution of both shallow- and deep-level donor species. The Mott-Schottky plot for this case is presented in Fig. 6 for an n-type semiconductor with a uniform doping level of $10^{16}$ cm$^{-3}$ and with uniformly distributed deep-level donor sites with energy $1.1$ eV, referenced to the valence band. The slope of curve a, obtained with a deep-level donor concentration of $10^{14}$ cm$^{-3}$, can be used to calculate a total donor concentration of $10^{16}$ cm$^{-3}$ (see Eq. 1). In this instance, the deep-level donor states are nearly obscured by the dopant species. This can be contrasted to curve b, where the influence of a deep-level donor concentration of $10^{16}$ cm$^{-3}$ is readily apparent through changes in the Mott-Schottky slope with increasing potential. The slope of this line at large potentials (where the deep-level species near the surface are completely charged) might be expected to yield a total donor concentration of $2 \times 10^{14}$ cm$^{-2}$, corresponding to the sum of the ionized deep-level donor and dopant concentrations. The total donor concentrations calculated from Eq. 1, however, range from $1 \times 10^{14}$ cm$^{-3}$ to $1.38 \times 10^{16}$ cm$^{-3}$, and these values are significantly smaller than the sum of the deep-level donor and dopant concentrations.

This apparently anomalous behavior was explored by examining plots of the calculated total donor concentration as a function of semiconductor depth, given in Fig. 7. In this case, the minimum total donor concentration (made dimensionless with respect to doping level) is 1.0 due to the doping species, which are always completely ionized. The presence of deep-level states is not apparent until a potential is applied. Larger applied potentials result in an increase in the dimensionless total donor concentration to a maximum of 2.0 near the surface. In cases where sufficient potential is applied, there is a transition region or “ionization wave,” which is seen to extend to greater depths with increasing potential. The previous examples with shallow-level donors indicated that the capacity associated with C-V profiling reflects the conditions over a region of the semiconductor, rather than at a specific point. This effect may also be responsible for the calculated values of the donor concentration which are apparently averaged over a region encompassing the “ionization wave.”

Nonuniform distribution of deep-level states.—Deep-level species are often localized near the surface as opposed to being uniformly distributed throughout the semiconductor crystal. In this instance, these species become completely charged at high potentials and there is no “ionization wave” movement like that described in the previous example. The model generated results for n-type GaAs with a uniform doping level of $10^{16}$ cm$^{-3}$ are presented in Fig. 8 for cases both with and without near surface deep-

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**Fig. 5.** Local donor concentration as a function of potential calculated using the Mott-Schottky theory for the results of Fig. 4. Symbols represent calculated results. Lines represent the input ionized donor distribution which has been expressed as a function of potential using Eq. [2].

**Fig. 6.** Calculated Mott-Schottky plots for an n-type semiconductor at equilibrium with even distribution of deep-level donors and with deep-level donor concentration as a parameter. The doping level was $10^{16}$ cm$^{-3}$, and the deep-level energy was $1.1$ eV referenced to the valence band. Curve a, $10^{14}$ cm$^{-2}$; curve b, $10^{16}$ cm$^{-2}$. Symbols represent calculated results.

**Fig. 7.** Total donor concentration (including deep-level and dopant species) as a function of depth for curve (b) in Fig. 6 with applied potential as a parameter.

**Fig. 8.** Calculated Mott-Schottky plots for an n-type semiconductor at equilibrium with deep-level donor distribution as a parameter. The doping level was $10^{14}$ cm$^{-3}$ and the deep-level energy was $1.1$ eV referenced to the valence band for both curves. Curve a, no deep-level states; curve b, concentration of deep-level states was $10^{16}$ cm$^{-3}$ at the surface, decaying to 1% of this value at 500 Å. Symbols represent calculated results.
level donor states. Curve b represents Mott-Schottky behavior typical of a semiconductor in the absence of deep-level states. Curve b was obtained for an arbitrary near-surface distribution given by

\[ c_d = c_d' \exp(-m y) \]  

where \( c_d \) is the surface concentration, \( m = 3.638 \), and \( y \) is the distance from the interface measured in Debye lengths. The deep-level state energy level was 1.1 eV, referenced to the valence band. In curve b, the influence of the near-surface states is reflected by a decrease in the Mott-Schottky slope in the potential range of 0.2 to 0.4 V. At higher potentials, however, the slope of the curve returns to a value associated with the absence of deep-level species. The potential at which these changes in slope occur reflects the energy level of the deep-level states. Mott-Schottky curves of this type have been reported under illumination [see, e.g., Ref. (12-14)] and have been attributed to the presence of surface states.

The manner in which the near-surface states become charged with increasing potential is illustrated in Fig. 9 where the model-generated total charged donor concentration from curve b in Fig. 8 is plotted as a function of semiconductor depth at several potentials. At flatband, the great majority of the deep-level states are not ionized. The degree of ionization increases with increasing potential to a value of about 0.4 V, where all states are completely ionized. The total donor distribution is unaffected by further increases in potential and, since the C-V probing region simultaneously extends deeper into the semiconductor, application of Eq. [1] yields only the bulk donor concentration of \( 10^{14} \) cm\(^{-3} \).

**Determination of the distribution of deep-level states.**

The distribution of deep-level species, in addition to that of the doping species, is of interest to the experimentalist. Analysis of the real part of the impedance response may be useful in this regard [see, e.g., Ref. (15-18)]. For example, Nagasubramanian et al. (16) report that, at low frequencies, the real part of the impedance goes through a maximum when the potential is increased from the flatband potential. This maximum was not observed when surface treatment was said to prevent formation of surface states. Similar effects have been observed for numerically generated, low-frequency real impedance data for a system where the distribution of electronic states is highly localized near the surface (7).

One advantage of emphasizing the real part of the impedance response is that effects due to completely ionized dopant species can be distinguished from those due to partially ionized deep-level states. Prior work (7) indicated that the contribution of deep-level states to the real impedance was greatest where the Fermi level within the semiconductor was coincident with the energy level of these species. These effects were observed to be several orders of magnitude stronger than the corresponding effect due to the completely charged shallow-level donor species. Since changes in the applied potential shift the spatial location in the semiconductor where deep-level states are partially filled, resolution of the distribution of electronic states within the bandgap should be possible.

A normal distribution of species with a deep-level energy of 1.1 eV with respect to the valence band was chosen to explore the use of real impedance data to resolve the spatial distribution of deep-level states. This distribution was given by

\[ c_d' = c_d'' \exp \left(\frac{y - 2.53^2}{1.39}\right) \]  

where \( c_d' \) is the maximum concentration and \( y \) is in Debye lengths. The curve parameters were chosen such that a maximum concentration of \( 10^{14} \) cm\(^{-3} \) occurred at a depth 1000 Å, with the concentration of donors falling to 1% of the maximum 1000 Å in either direction perpendicular to the interface. The real part of the impedance \( Z_r \) calculated for this distribution is presented in Fig. 10 as a function of potential with frequency as a parameter. A maximum is observed for frequencies lower than 10 Hz. As was previously observed, \( Z_r \) was not sensitive to deep-level species at high frequencies.

The real part of the calculated impedance presented in Fig. 10 for a frequency of \( 10^{-2} \) Hz can be plotted in terms of the depletion width (presented as curve a in Fig. 11). The depletion width is given in Eq. [2] and provides a means by which the potential (referenced to flatband) can be expressed in terms of a probing depth. The transformation from potential to depletion width results in a very good representation of the deep-level state distribution with the exception that the depth of the calculated spatial distribution of the deep-level states is incorrect. The difficulty associated with the profiling depth is not too surprising since the depletion width is a measure of the depth of the space-charge region. The depletion layer width, therefore, is an inappropriate characteristic distance for ionization of deep-level species. The presence of deep-level states has the greatest effect upon the impedance response when the probability of occupancy of that state is roughly one-half.

The appropriate characteristic length for ionization of deep-level states is, therefore, the position where Fermi level and the species energy coincide. This position is much smaller than the depletion width under the conditions chosen and is given by

\[ W_r = \sqrt{\frac{-2e}{F N_d} \left( V + \frac{RT}{F} \right)} \sqrt{\frac{-2e}{F N_d} \left( \Phi_v + \frac{RT}{F} \right)} \]  

where \( \Phi_v \) is the value of the electrostatic potential, referenced to the semiconductor bulk, that applies at the posi-
Fig. 11. Real part of the calculated impedance as a function of position. Curve a, the position scale (W) is calculated from the applied potential through Eq. [2], curve b, the position scale (W) is calculated from the applied potential through Eq. [7], and curve c, the input distribution, scaled to the maximum value of the real impedance. Symbols represent calculated results.

The approach presented here does not yield the magnitude of deep-level states, and other techniques are needed to extract this information from the real part of the impedance response measured at low frequencies. The method proposed here may be most applicable to semi-insulating semiconductors or to semiconductors with large bandgaps (for ideal blocking interfaces are more easily fabricated).

Conclusions

Transport-based models of ac impedance provide a useful tool in the interpretation of experimental impedance results. The capacitive component, used in standard Mott-Schottky theory, was found to be insensitive to bulk electronic states within the bandgap if the concentration of these states is significantly less than the doping level. In contrast, the resistive component is much more sensitive to deep-level states at low frequencies. For high concentrations of deep-level states, changes in the slope of the Mott-Schottky curve can be interpreted in terms of partial ionization of deep-level states with applied potential. These effects, however, could also be attributed to a nonuniform dopant distribution. Subbandgap photoexcitation of electronic states or observation of a frequency-dependent capacity could be used to distinguish between the possible causes of this behavior. The work presented here also illustrates the limitations of C-V profiling for identifying abrupt spatial changes of doping concentration, even in the absence of deep-level states.

The results of the model indicate that the real part of the impedance response measured at low frequencies, coupled with an appropriate expression relating potential to depth, may be useful for determining the distribution of deep-level states. This approach may be appropriate for large bandgap materials since leakage currents will also influence the impedance response at low frequencies. In the work presented here, deep-level states were assumed to have a single energy referenced to the valence band. Future work will examine methods to interpret the impedance response influenced by multiple deep-level states.

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