Thermally Stimulated Deep-Level Impedance Spectroscopy
Application to an n-GaAs Schottky Diode

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ABSTRACT

Impedance spectroscopy with temperature as a parameter is shown to be sensitive to deep-level states in an n-GaAs Schottky diode. A mathematical model is developed which accounts for the influence of electronic transitions involving deep-level states on the impedance response of the device. Regression of the model to the data is shown to require a weighting strategy that accounts for the variance of the measurements. The parameters obtained are compared to those obtained by deep-level transient spectroscopy and those reported in the literature. Good agreement was seen for the number, concentration, and activation energies of deep-level states, but the reaction cross sections obtained differed from those obtained by deep-level transient spectroscopy by several orders of magnitude. This discrepancy is attributed to the need to refine the process model to account for the influence of recombination pathways on the leakage current observed at low frequencies.

Introduction

Deep-level states play an important role in solid-state devices through their behavior as recombination centers. The electronic states of interest lie within the bandgap of the semiconductor. The goal is to determine that these states exist as well as to determine their concentration distribution and the associated rate constants for electronic transitions. Knowledge of these parameters is essential for the engineering of many electronic devices. For example, deep-level states are undesirable when they facilitate electronic transitions which reduce the efficiency of photovoltaic cells. In other cases, the added reaction pathways for electrons result in desired effects. Electroluminescent panels, for example, rely on electronic transitions that result in emission of photons.

The impact of deep-level states can be significant, even in concentrations that are very low by normal chemical standards. Several states can be associated with a chemical species, and such states may also appear as a result of vacancies or other crystalline defects. Traditional chemical means of detection, therefore, do not provide complete identification of deep-level electronic states. The techniques commonly employed to detect deep-level states tend to be electrical in nature since it is through their electronic behavior that these states influence device performance.

Experimental techniques used to identify deep-level states were summarized in Ref. 1. Deep-level transient spectroscopy (DLTS) is the dominant capacitance-based technique used to detect deep-level electronic states. In DLTS, one monitors the space-charge capacitance of the semiconductor in response to a step in potential. The temperature is changed in the experiment to vary the coefficient of the emission rate. The capacitance is measured at high electrical frequencies, and the technique accounts for the large time constant for deep-level transitions by measuring the capacitance at two times for each square wave cycle. Interpretation of differences between the two values is based on assumption of an Arrhenius form for the rate constants.

While frequency-based techniques such as impedance spectroscopy are often thought to be insensitive to the presence of deep-level states, Orazem et al. 1 have shown that impedance spectroscopy is sensitive to deep-level states if the weighting strategy used to obtain model parameters accounts for the variance of the measurements. In their work, impedance spectra were obtained at fixed temperatures ranging from 300 to 420 K. Regression of a process model yielded only parameters corresponding to a single activation energy controlled process; whereas four activation energy processes were found when the regression was weighted by the inverse of the independently determined experimental variance. This result was consistent with the results obtained through independent DLTS measurements.

The object of this work is to explore the complete range of parameter values that could be obtained from comparison of model to impedance experiments and to compare these values to those obtained by independent DLTS experiments. The system chosen for this comparison was an n-GaAs single-crystal diode with a Ti Schottky contact and a Au, Ge, Ni Schottky contact at the eutectic composition. This material has been well characterized in the literature and, in particular, has a well known EL2 deep-level state that lies 0.83 to 0.85 eV below the conduction band edge. 2 Results for other less well-defined systems will be discussed in subsequent communications.

Theoretical Development

The process model used for this work follows the small signal analysis for electrons, holes, and deep-level states presented by Sah for bulk and surface states. 3, 9, 10

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \mathbf{V} \cdot \mathbf{j}_e - \langle c_e \rangle m_p + \langle c_p \rangle n + G_e
\]  

[1]

\[
\frac{\partial p}{\partial t} = \frac{1}{q} \mathbf{V} \cdot \mathbf{j}_h - \langle c_h \rangle m_e + \langle c_e \rangle p + G_h
\]  

[2]

Governing equations.—Conservation of species for conduction band electrons, valence band holes, and electrons within a deep-level energy state yields

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 摘要：深陷阱能级的等温阻抗谱应用

应用到n-GaAs肖特基二极管

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摘要

等温阻抗谱通过温度作为参数表明对深陷阱能级是敏感的在n-GaAs肖特基二极管。通过开发的数学模型计算了电子和空穴等温阻抗的响应，通过数据回归显示需要考虑流经深陷阱能级的权重策略。获得的参数与通过深陷阱瞬变光谱学和文献中报告的参数进行了比较。对于深陷阱能级的数目、浓度和活化能有良好的一致性，而反应截面的差异从深陷阱瞬变光谱学通过多种方式难以检测到。这种差异被归因于需要改进过程模型以考虑到深陷阱能级对泄漏电流的影响的路径。

引言

深陷阱能级在固体态设备中扮演重要角色，通过行为作为电荷再组合中心。电子状态的需要在于半导体的带隙中。目的是确定这些状态存在以及它们的浓度分布和电子转换的相联率常数。这些参数的知识对电子器件的工程是至关重要的。例如，深陷阱状态是当它们促进电子转换时降低光电转换效率的。在其他情况下，添加的反应路径对电子产生期望的效果。例如，电致发光面板，例如，依赖于电子转换产生光信号。

深陷阱状态的影响可能是显著的，即使在浓度由正常化学标准时很低。状态可以与化学物种相关联，也可以由于空位或其他晶格缺陷而出现。传统的化学方法用于检测，因此，不能提供完整的深陷阱电子状态的鉴定。检测深陷阱状态的技术通常使用等温瞬变光谱学进行。在等温瞬变光谱学中，监控空间电荷电容的半导体响应于电势步变化。温度在实验中被改变以变化发射率的系数。容量在高频测量，此技术考虑到深陷阱转换的长时间常数通过两次测量每个阶跃波周期。通过推断两个值的不同基于假设为Arrhenius形式率常数。

虽然频率技术如等温阻抗谱通常被认为是不敏感到深陷阱状态的，Orazem et al. 1已经显示等温阻抗谱对深陷阱状态是敏感的如果使用的权重策略来获得模型参数考虑变量的测量。在他们的工作，等温阻抗谱被获得在固定温度范围从300到420 K。回归一个过程模型只产生了对应一个活化能控制过程的参数；而有四个活化能过程在独立的检测中被发现。这个结果与通过等温瞬变光谱学获得的结果一致。这将在后续通讯讨论。

理论发展

用于此工作的过程模型遵循Sah的方程用于 bulk和表面状态。3, 9, 10

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \mathbf{V} \cdot \mathbf{j}_e - \langle c_e \rangle m_p + \langle c_p \rangle n + G_e
\]  

[1]

\[
\frac{\partial p}{\partial t} = \frac{1}{q} \mathbf{V} \cdot \mathbf{j}_h - \langle c_h \rangle m_e + \langle c_e \rangle p + G_h
\]  

[2]

控制方程—电荷守恒为导带电子，价带空穴，和电子在低能级能量状态中
and 
\[ \frac{\partial n}{\partial t} = q \left( c_n \mu_p n - \langle e_p \rangle p n - \langle e_p \rangle p - G_n \right) \]  
respectively, where \( q \) is the electronic charge \((1.602 \times 10^{-19} \text{ C})\) and \( G_n \) represents the optical excitation of electrons into the conduction band. The term \( \langle c_n \rangle \) is the mean capture coefficient for conduction band electrons which can be considered to be a rate constant \( c_n \) that is integrated over the energy range of the conduction band \((E_c \rightarrow \infty)\), i.e.,

\[ \langle c_n \rangle = \frac{\int_{E_c}^{\infty} c_n(E) f(E) dE \Delta E}{\int_{E_c}^{\infty} f(E) dE} \]  

Similarly, \( \langle e_p \rangle \) represents the mean emission coefficient for electrons being excited from the deep-level state. Thus

\[ \langle e_p \rangle = \int_{E_c}^{\infty} e_p(E)(1 - f(E)) D(D(E) \Delta E) dE \]  

Similar definitions apply for the corresponding terms for holes and deep-level state electrons. The carrier flux is given in terms of migration and diffusion terms by

\[ j_n = q \mu_p n E + q D_n \n \]  

for electrons and by

\[ j_p = q \mu_p p E - q D_p \n \]  

for holes, where \( \mu_p \) and \( D_p \) are the mobility and diffusivity, respectively, of the species indicated by the subscript \( i \). Poisson's equation is given by

\[ \rho = q(n - n + n_a - N_a) = K \epsilon_0 \n \]  

where \( n_a \) and \( N_a \) are the concentrations of ionized electron donors or acceptors (which can be functions of time), \( K \) is the dielectric constant, \( \epsilon_0 \) is the permittivity of vacuum \((8.85419 \times 10^{-12} \text{ C/V cm})\), and \( \Psi \) is the electrostatic potential.

**Small signal analysis.**—The following development is made under the assumptions that

1. The sinusoidal perturbation to the system has a small amplitude such that the perturbation from equilibrium concentration distributions (where \( np_n = n_n \)) is sufficiently small that the time dependence can be linearized.

2. The shallow-level donors and acceptors are fully ionized.

3. The semiconductor is nondegenerate such that the Nernst-Einstein relation

\[ D_i = \frac{kT}{q} \mu_i \]  

applies. This assumption can be shown to be equivalent to assuming that activity coefficient corrections for electrons and holes can be neglected and allows use of quasi-Fermi energy levels in the Boltzmann expression for electron concentration. Note that a Fermi-Dirac distribution function is still used for the occupation of deep-level states.

4. The systems may be regarded as being one-dimensional.

5. The rate constants \( \langle c_n \rangle, \langle c_p \rangle, \langle e_p \rangle \), and \( \langle c_p \rangle \) are independent of time. An implication of this assumption is that the difference \( E_n - E_p \) is a constant.

Under the above assumptions, the flux of electrons and holes can be given in terms of the gradient of the Fermi energy as

\[ j_n = \mu_n p \frac{\partial E}{\partial x} \]  

and

\[ j_p = \mu_p n \frac{\partial E}{\partial x} \]  

The concentration of conduction band electrons can be expressed by

\[ n = N + \left( \frac{\partial n}{\partial t} \right) \]  

where \( N \) is the steady-state value for the electron concentration. Since

\[ n = n_e \exp \left( \frac{F_n - E_n}{kT} \right) \]  

it can be shown that

\[ n = N + \frac{N_k}{kT} d(F_n - E_n) \]  

Similarly, the concentration of holes can be given in terms of a perturbation to the steady value \( P \) as

\[ p = P - \frac{P}{kT} d(F_p - E_p) \]  

The corresponding expressions for the concentrations of electrons and holes in deep-level states are given as

\[ n_i = N_i + \frac{N_i}{kT} \frac{P}{N_n} d(F_n - E_n) \]  

and

\[ p_i = P_i - \frac{P_i}{kT} \frac{N_i}{N_n} d(F_p - E_p) \]  

where \( N_n \) represents the total concentration of deep-level states.

A semianalytic solution to the above equations was obtained under the assumption that the semiconductor could be divided at a uniform spacing \( \Delta x \) into discrete elements in which, for each element, the quasi-Fermi potentials, the dynamic generation terms, and the steady-state concentrations were independent of position. The resulting set of equations for a given element of width \( W = \Delta x \) yields the electrical response of the equivalent electrical circuit shown in Fig. 1. Here, the potentials represent respective energy levels, i.e.,

\[ V_n = -\frac{1}{q} dF_n \]  

\[ V_p = -\frac{1}{q} dF_p \]  

\[ V_i = -\frac{1}{q} dF_i \]  

and

\[ V_i = -\frac{1}{q} dE_i \]  

The capacitances in this circuit are given in terms of physical properties as

\[ C_n = \frac{q^2 N}{kT} W \]  

\[ C_p = \frac{q^2 P}{kT} W \]  

\[ C_i = \frac{q^2 N_i P}{kTN_n} W \]  

and

\[ C_n = \frac{K \epsilon_0}{\Delta x} \]
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Fig. 1. The electrical circuit suggested by the small-signal analysis for deep-level states in a semiconductor. The definitions of the symbols are given as Eq. 19-22.

where the index \( k \) represents the element number and \( W = \Delta x \). As written above, the capacitances have the customary units of farads per unit area.

The flux terms result in conductance terms given as

\[
G_n = \frac{q\mu_n N}{\Delta x} \tag{20a}
\]

and

\[
G_p = \frac{q\mu_p P}{\Delta x} \tag{20b}
\]

The electronic transitions also yield conductance terms given as

\[
G_{ni} = \frac{1}{R_{ni}} = \frac{q^2(c_n)N_P}{kT}W \tag{21a}
\]

\[
G_{pi} = \frac{1}{R_{pi}} = \frac{q^2(c_p)P_N}{kT}W \tag{21b}
\]

\[
G_{nt} = \frac{q^2P}{kTN_n}W((c_n)N_P - (c_p)N_t) \tag{21c}
\]

and

\[
G_{pt} = \frac{q^2N}{kTN_p}W((c_p)N_P - (c_n)P_t) \tag{21d}
\]

The current densities result from the sinusoidal perturbation \( g \) of band-to-band electronic transitions \( G \) such that

\[
i_n = -qg_n \tag{22a}
\]

\[
i_p = qg_p \tag{22b}
\]

and

\[
i_t = -qg_t \tag{22c}
\]

Surface states can be treated in a manner equivalent to that presented here for bulk states. Since electrons and holes do not cross a pure Schottky contact, the Schottky contact is represented in Fig. 1 by a capacitance \( C_s \) connected to the intrinsic energy line. An ohmic contact can be treated as being a short of all three energy lines because a potential difference cannot be sustained at the metal contact. Note that, as developed here, the circuit does not account for presence of a leakage current across the Schottky contact.

Simplified electrical circuit.—For an n-type semiconductor (as was studied here), the concentration of electrons is many orders of magnitude greater than the concentration of holes. Thus the hole conductance \( G_{pt} \), the hole capacitance \( C_p \), and the hole recombination conductance \( G_{pt} \) terms can be removed from the circuit shown in Fig. 1. It was also assumed that the experiments performed in this work did not perturb the semiconductor far from equilibrium such that the steady-state quasi-Fermi levels equal the equilibrium Fermi level, \( E_F \). The steady-state concentrations are equal to their equilibrium concentrations with this assumption. As a direct result of this equilibrium assumption, the transconductance term, \( G_{nt} \), is equal to zero (rate of emission equals rate of capture) and can be removed from the circuit.

The equivalent circuit can be further simplified if there is only a surface state and no bulk states or only a bulk state and no surface state. A general feature becomes apparent in both situations: a trap conductance-capacitance series is in parallel to a capacitance. The trap conductance-capacitance series can be thought of as a recombination arm and the capacitance as a space-charge capacitance. The space-charge capacitance is composed of either the dielectric capacitance and the electron capacitance in series for the surface state case, or, only the electron capacitance for a bulk state. This space-charge capacitance will remain constant in either case so long as the concentration of deep-level states is several orders of magnitude smaller than the concentration of electrons due to shallow-level states.

The governing equations in this section have been developed for the case of one bulk deep-level state and one surface state. There is one additional governing equation that resembles the kinetic trap equation for each additional state present. These appear as additional recombination arms in parallel to those discussed above. Multiple energy level states were also treated by Sah.\(^5\)

The simplified equivalent circuit used to regress the experimental data is given in Fig. 2. This circuit has all the essential features that were mentioned above, namely, the equivalent circuit for a surface state is identical to that of a bulk state. It is possible to distinguish the two types of states by means of a Mott-Schottky plot as discussed earlier. A leakage resistor has been added to the equivalent circuit of Fig. 2 to account for the nonideal behavior of the Schottky contact (dc leakage current). This term is expected to be proportional to the exponential of an activation energy. The activation energy can be the barrier height of the Schottky barrier or the energy difference between the conduction band and a surface state energy level.

Fig. 2. The simplified electrical circuit for multiple deep-level states in an n-type semiconductor.
Leakage resistance was addressed for a p-n junction in the literature.11,12

A similar circuit was derived by van der Ziel in 1959 to account for generation-recombination noise due to traps in semiconductors.13 Van der Ziel also determined trap activation energies by measuring recombination noise as a function of frequency and temperature (similar to admittance spectroscopy).14 Dare-Edwards et al.15 developed a similar circuit by eliminating terms from the governing equations before developing an equivalent circuit. Nicollian and Goetzberger developed this circuit (without leakage resistance) to analyze interface states of metal insulator semiconductor (MIS) capacitors.16

Analysis of circuit components.—Physical properties can be obtained from the temperature dependence of the circuit parameters given in Fig. 2.

The steady-state concentration of conduction band electrons for a nondegenerate semiconductor is given by (see, e.g., Ref. 17)

\[ N = N_o \exp \left( \frac{E_o - E_f}{kT} \right) \]  

[23]

where

\[ N_o = 2^{\frac{2\pi m^* kT}{\hbar^2}} \frac{e^{M_c}}{h^2} \]  

[24]

and \( m^* \) is the effective mass of the electron, \( h \) is the Planck constant, and \( M_c \) is the number of equivalent conduction band minima. The product \( N P_i \) can be represented as

\[ N P_i = N_o N_n \frac{1}{g} \exp \left( \frac{E_f - E_c}{kT} \right) \]  

[25]

where \( g \) is the spin degeneracy of the trap state. The electron capture cross section is defined to be the capture coefficient divided by the thermal velocity of the electron, i.e.

\[ \sigma_n = \frac{1}{\nu_e} = \frac{\langle c_o \rangle}{\sqrt{3kT/m_c}} \]  

[26]

Therefore, the resistance term in Fig. 2 for deep-level state \( j \) can be expressed as

\[ R_{nj} = k \frac{q^2 \gamma_n \gamma_c N_{ni} W}{g} \frac{1 + \exp \left( \frac{E_{fj} - E_c}{kT} \right)}{\exp \left( \frac{E_f - E_c}{kT} \right)} \exp \left( \frac{E_c - E_{fj}}{kT} \right) \]  

[27]

where

\[ \gamma_c = 2 \frac{2\pi m^* k T}{\hbar^2} M_C \sqrt{3kT/m_c} \]  

[28]

The corresponding recombination or trap capacitance can be expressed as

\[ C_{nj} = \frac{q^2 N_{ni} W}{g kT} \left[ 1 + \exp \left( \frac{E_{fj} - E_f}{kT} \right) \right] \left[ 1 - \exp \left( \frac{E_{fj} - E_f}{kT} \right) \right] \]  

[29]

The product of the recombination resistance and the recombination capacitance is the time constant of the recombination arm. The inverse of this time constant can be thought of as a characteristic frequency. The equivalent circuit characteristic frequency can be expressed as

\[ \frac{1}{R_{nj} C_{nj}} = \sigma_n \gamma_c T^2 \left[ \exp \left( \frac{E_f - E_c}{kT} \right) + \frac{1}{g_j} \exp \left( \frac{E_{fj} - E_f}{kT} \right) \right] \]  

[30]

The temperature dependence explicit in Eq. 27, 29, and 30 can be used to assess values for physical parameters associated with electronic properties of the material.

Equations 27, 29, and 30 can be further simplified following the observation that deep-level states influence the impedance response only if they are partially occupied. States that are completely full or completely empty will not emit or capture electrons in response to the sinusoidal perturbation. Thus, under thermal excitation, only the states that are close to the Fermi energy level, or brought close to the Fermi energy level through biasing, will influence the impedance response. (Optical excitation is a way these states can influence the impedance response without being close to the Fermi level.) In the portion of the space-charge region that influences the impedance, the energy of the deep-level state approximately equals the Fermi level. Thus, \( E_f \approx E_y \), and Eq. 27, 29, and 30 yield

\[ TR_{nj} = \frac{k}{q^2 \sigma_n \gamma_c N_{ni} W} \left( g_j + 1 \right) \exp \left( \frac{E_f - E_c}{kT} \right) \]  

[31]

\[ TC_{nj} = \frac{q^2 N_{ni} W}{k} \frac{1 + g_j}{\left( g_j + 1 \right)^2} \]  

[32]

and

\[ \frac{1}{T R_{nj} C_{nj}} = \sigma_n \gamma_c \left( 1 + \frac{1}{g_j} \right) \frac{E_j - E_f}{E_c - E_f} \]  

[33]

respectively. Equations 31, 32, and 33 were used in the present work to extract values for physical parameters from impedance spectra.

Experimental

Two independent techniques were used to evaluate the \( n \)-GaAs sample. In the first, impedance spectroscopy was conducted at fixed temperatures. Deep-level transient spectroscopy (DLTS) was used to provide independent values for physical parameters.

Gallium arsenide sample.—An \( n \)-type gallium arsenide sample was used to calibrate the technique presented here against the well-known deep-level transient spectroscopy (DLTS) technique. Other samples analyzed had large bandgaps and will be discussed in a later paper. The interest in single-crystal gallium arsenide in the past couple of decades has led to the generation of vast amounts of literature on its properties. A good source on GaAs is the collection of reprints edited by Blakemore.4

Several characteristic deep-level states were reported to exist. The state referred to as EL2 is of particular interest to this work because its energy band lies approximately 0.83 eV below the conduction band, and it is a majority trap. Thus, an \( n \)-type single gallium arsenide crystal with a Schottky barrier on one side and an Ohmic contact on the bottom and a gold Ohmic contact (Au, Ge, Ni) on the bottom. The Schottky contacts were circular dots with a diameter of 1 mm.
Impedance spectroscopy.—A scheme of the experimental setup is presented in Fig. 2 and 3 of Ref. 1. The temperature control system was taken from the deep-level transient spectrometer provided by Sula Technologies, described in the subsequent section. The temperature was held constant during measurement of each impedance scan to within 0.1°C by resistive heating using a Lake Shore 805 controller. Liquid nitrogen was used to cool the samples during experiments at or below ambient temperatures. The sample housing acted as a Faraday cage to reduce noise in the 60 Hz range. The impedance measurements were made with a Solartron 1250 frequency response analyzer (FRA) with a Solartron 1286 electrochemical interface. Replicate scans were taken at temperatures ranging from 300 to 420 K, and the frequency range for the impedance measurement was 1 to 65,000 Hz. The potential bias was 0 V and the applied sinusoidal perturbation was 3 mV. The Solartron 1286 potentiostat was used with bandwidth C. The long-integration feature of the FRA was used on the current channel.

The experimental data are presented in Fig. 3a and b for the real and imaginary parts of the impedance, respectively, for data collected at temperatures ranging from 400 to 320 K. The logarithmic scale used emphasizes the scatter seen in the imaginary impedance at low frequencies. The impedance response is seen to be a strong function of temperature. The impedance plane plots, e.g., Fig. 4, show the classic semicircle associated with a single relaxation process.

DLTS.—The DLTS equipment consisted of a cryostatic chamber, a Sula Technologies deep level spectrometer, a Lake Shore Model 805 temperature controller, a 7 liter Dewar flask to hold liquid nitrogen, and a variable-speed circulation pump used to draw liquid nitrogen through the cryostatic chamber. A roughing pump was used to evacuate the cryostatic chamber to prevent condensation from forming on the semiconductor sample at low temperatures and to minimize heat loss to the environment due to convection.

Inside the cryostatic chamber, a thermal block was connected to a heater element, controlled by the temperature controller, and a stainless steel tube through which liquid nitrogen is drawn. The combination provided a wide range of controllable temperatures. The lowest temperature possible was 78 to 84 K and the highest practical temperature was around 420 K.

A Teflon sheet was placed between a small stainless steel plate and the thermal block. One of the voltage leads was attached to the steel plate. The other voltage lead was connected to a blunted needle. Vacuum grease was used on both sides of the Teflon spacer to improve the thermal contact. A small copper shell was riveted to the stainless steel plate to house a 100 Ω platinum temperature sensor used to measure the sample temperature.

A Hewlett Packard 7090A x-y plotter, capable of analog-to-digital data acquisition with 12 bit resolution, was used to interface the Sula Technologies deep level spectrometer with an IBM-compatible personal computer. The temperature controller has an IEEE-488 interface, which was used to control and monitor the cryostat temperature.

The ratio of times $t_1$ and $t_2$ was designed to be constant in the spectrometer as recommended by Lang. For this spectrometer, the rate window, or time constant, at the peak capacitance difference is

$$\tau = \frac{1}{e_{n}} = 4.3t_1$$

where $t_1$ is also referred to as the initial delay. Another important relationship used to estimate the state concentration is the capacitance difference at the start of the reverse bias

$$\Delta C(t = 0) = 3(C(t_1) - C(t_2))$$

which is evaluated at its peak value.

The steady-state or background capacitance $C_0$ was determined with a 150 mV peak to peak voltage sinusoid at a frequency of 1 MHz applied across the semiconductor sample. Deep-level states are not expected to influence the signal at such a high frequency. The steady-state capacitance was also used in Mott-Schottky plots to assess the doping level.

Results

The model corresponding to the equivalent circuit given in Fig. 2 was regressed to the impedance data at each temper-
perature. A complex nonlinear regression was used based on a modified Levenberg-Marquardt algorithm and using the independently measured frequency-dependent variance to weight the regression. Parameters corresponding to deep-level states were added sequentially to the model until the confidence interval for one of the regressed parameters included zero. Four resistor-capacitor pairs were regressed to the impedance data taken at 300, 320, and 340 K; three pairs at 360, 380, and 400 K; and two pairs at 420 K.

Use of other more standard weighting strategies such as proportional, modulus, or no-weighting approaches yielded a smaller number of parameters. The reduced presentation of the data given in Fig. 5 illustrates that the impedance data collected at different temperatures were normalized by the maximum mean value of the real part of the impedance and plotted against a normalized frequency defined by

$$\omega^* = \frac{\omega}{B} \exp\left(\frac{E}{kT}\right)$$

where $E$ was given a value of 0.827 eV, and the characteristic frequency $B$ was given a value of $2.964 \times 10^{11}$ Hz such that the imaginary part of the normalized impedance values reached a peak value near $\omega^* = 1$. The data collected at different temperatures were reduced to a single line. An optimal weighting strategy was therefore required to extract parameters for the less dominant electron transitions. While Macdonald has suggested that models based on distributed relaxation processes could provide nearly the same quality of fits as were obtained for the discrete energy levels implicit in Fig. 2, the independent DLTS measurements and results reported in the literature show the presence of discrete energy levels. Thus, the discrete energy level model used in the present work is the most appropriate for extracting meaningful physical parameters.

As suggested by Eq. 31, the product of temperature and resistance obeys an Arrhenius relationship as shown in Fig. 6. The lines in Fig. 6 represent regression results. The resulting activation energy (proportional to the slope) for each line is shown. Following Eq. 32, the product of temperature and the recombination arm capacitances have a weak Arrhenius relationship with temperature (see Fig. 7). The time constants show a strong Arrhenius dependence following Eq. 33 (see Fig. 8), but the energies obtained differ slightly from those obtained from Fig. 6.

The space-charge capacitance term $C_s$ is expected to have a slight Arrhenius dependence on temperature with an activation energy of $E_s - E_F$, i.e.

$$C_s T = \frac{q^2N_W}{k} \exp\left(\frac{E_s - E_F}{kT}\right)$$

The assumption that $E_s = E_F$ was not necessary here because $C_s$ does not depend on the concentration of deep-level states. The regressed space-charge capacitance exhibited a slight Arrhenius relationship with temperature as can be seen from inspection of Fig. 7. A value of 0.041 eV below the conduction band was obtained from the slope, and a donor concentration of $8 \times 10^{15}$ cm$^{-3}$ was found from the intercept. The Arrhenius relationship is
Deep-level transient spectroscopy (DLTS) performed on this sample provided a check on the parameter values obtained by impedance spectroscopy. The emission rate divided by the square of the peak temperature is plotted as a function of the inverse temperature in Fig. 9. Three states were found with activation energies of 0.83, 0.48, and 0.32 eV. The state at an energy below the band gap was not tabulated in the literature. However, Weber et al. point out that a group V atom on a group III site (proposed for EL2) is expected to be a double donor. They also observed from photo-EPR (electron paramagnetic resonance) that the EL2 state was a double donor with an energy level at $E_d + 0.78$ eV and another at $E_d + 0.52$ eV.

As shown in Table I, the activation energies from DLTS are in fair agreement with those determined from numerical regression of the impedance data. The capture cross sections, determined from the intercepts of the curves in Fig. 8, differ by several orders of magnitude from the DLTS values. The difference could be due to the narrow range of temperatures used (300 to 420 K) which necessitates extrapolation over a very large temperature range. The intercept would be strongly influenced by small deviations in the regressed slope. These intercepts are not dependent on the parameter $W$, unlike the intercept of Fig. 6. Trap concentrations and the shallow-level dopant concentration (from the space-charge capacitance) were determined from the intercepts of the curves in Fig. 6.

The appropriate value of $eV$ below the calculation of shallow and deep-level concentrations was assumed to be the volume near or within the Schottky depletion region where the concentration of holes and electrons fluctuate with the perturbing signal. Bonham and Orazem used a numerical model to determine the width of this region. They obtained a value of approximately six to eight times the Debye length. The Debye length for a GaAs sample with $N_d = 1.1 \times 10^{17}$ cm$^{-3}$ at room temperature is $1.2 \times 10^{-4}$ cm. The volume used to obtain the values given in Table I was six times the Debye length multiplied by the surface area of the Ti contact (1 mm diam), i.e., $5.6 \times 10^{-4}$ cm$^2$.

The capacitance was measured as a function of reverse bias with the DLTS spectrometer. These data were plotted in the form of a Mott-Schottky plot (Fig. 10). The shallow-level dopant concentration was determined from the slope to be $N_d = 1.1 \times 10^{17}$ cm$^{-3}$. This value was one order of magnitude greater than the value determined from the regressed space-charge capacitance. The Mott-Schottky value for the donor concentration was used to calculate the Fermi level according to $E_F - E_d = \frac{kT}{\pi} \ln \left( \frac{N_d}{N_i} \right)$. The Fermi level was calculated to be $0.038$ eV below the conduction band (as compared to $0.041$ eV which was determined from Fig. 7 and Eq. 37.

**Discussion and Conclusions**

Impedance spectroscopy is sensitive to deep-level electronic transitions in semiconductors when the regression procedure uses a weighting strategy that accounts for the

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**Table I. Comparison of values obtained by impedance spectroscopy (DLTS) and deep-level transient spectroscopy (DLTS) to literature values.**

<table>
<thead>
<tr>
<th></th>
<th>Impedance</th>
<th>DLTS</th>
<th>Literature$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy</td>
<td>$0.77 \pm 0.03$ eV</td>
<td>$0.83 \pm 0.04$ eV</td>
<td>$0.83$ to $0.85$ eV (ET1 = ES1 = EL2)</td>
</tr>
<tr>
<td>Capture cross section</td>
<td>(from leakage resistance)</td>
<td>$2.7 \pm 0.3 \times 10^{13}$ cm$^2$</td>
<td>$1$ to $6.5 \times 10^{13}$ cm$^2$</td>
</tr>
<tr>
<td>Concentration</td>
<td>$7.8 \times 10^{13}$ cm$^3$</td>
<td>$0.48 \pm 0.05$ eV</td>
<td></td>
</tr>
<tr>
<td>Activation energy</td>
<td>$0.45 \pm 0.4$ eV</td>
<td>$8.1 \pm 0.5 \times 10^{13}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>Capture cross section</td>
<td>$1.3 \pm 0.6 \times 10^{14}$ cm$^2$</td>
<td>$8.4 \times 10^{13}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>$1 \times 10^{14}$ cm$^{-3}$</td>
<td>$0.32 \pm 0.01$ eV</td>
<td></td>
</tr>
<tr>
<td>Activation energy</td>
<td>$0.25 \pm 0.03$ eV</td>
<td>$3.0 \pm 0.2 \times 10^{14}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>Capture cross section</td>
<td>$9.8 \pm 0.6 \times 10^{14}$ cm$^2$</td>
<td>$8.7 \times 10^{14}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td>$1 \times 10^{14}$ cm$^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$^a$ Values for the donor concentration were obtained from literature.$^b$ ESR(DLTS) and ESR(EPR).
The comparison of the results obtained through DLTS and impedance spectroscopy reveals the power of the error analysis approach for interpretation of impedance spectra. The number of line shapes or relaxation processes identified by regressing a model to impedance spectra with a weighting strategy that accounted for the independently obtained error structure was greater than that obtained when standard weighting strategies were employed, and this number was consistent with the result of DLTS measurements. One consequence of the equivalence of mathematical models constructed from passive elements is that the number of parameters obtained is independent of the model structure. Thus, when used in conjunction with an independent assessment of the stochastic and bias errors, a model such as developed here can be used to identify the maximum number of relaxation processes that can be resolved from impedance data. The number of relaxation processes resolved will be independent of the model structure so long as only passive elements are used. For example, the Voigt model, used as a measurement model by Agarwal et al., yielded the same number of line shapes for the data presented here as did the circuit presented in Fig. 2. The regression approach can therefore be used to identify the maximum number of relaxation processes resolvable from impedance data, even when the appropriate model structure is unknown. Changes in the number of resolved relaxation processes were used, for example, to reveal the influence of monochromatic illumination on electronic transitions.

Acknowledgments
The authors thank Professor Chih-Tang Sah for his valuable discussions and reprints on semiconductor physics and Darwin Thusius of Sula Technologies for the GaAs sample and discussions on the DLTS instrumentation. This work was supported by DARPA under the Optoelectronics Program of the Florida Initiative in Advanced Microelectronics and Materials.

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REFERENCES
Optically Stimulated Deep-Level Impedance Spectroscopy
Application to an n-GaAs Schottky Diode

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ABSTRACT

Optically stimulated deep-level impedance spectroscopy (OS-DLZS) is a light-enhanced form of electrochemical impedance spectroscopy. The effect of photonic excitation on electronic transitions is detected by impedance spectroscopy applied over a broad frequency range. The photonic energy of the light used is less than the bandgap energy; therefore, any changes in the frequency spectrum with illumination can be attributed to transitions involving energy levels within the bandgap. OS-DLZS is distinguished from the more commonly used deep-level transient spectroscopy (DLTS) in that the wavelength of monochromatic sub-bandgap light is varied to excite electronic transitions at a fixed temperature, whereas, in DLTS, temperature is varied to change the occupancy of the states. A broad range of frequency (with emphasis on lower frequencies) for the impedance measurements is used instead of measuring an effective capacitance at a single high frequency. The measurement of complex impedance over a broad frequency range is the essential distinction between this approach and photocapacitance spectroscopy. The experimental part of OS-DLZS here is similar to optical admittance spectroscopy (OAS). The major difference is that the complex impedance response is analyzed in DLZS, whereas, the complex admittance response is treated in OAS. Analysis in terms of impedance emphasizes the system response to deep-level states at low frequencies. Experimental and modeling work has shown that deep-level states have the largest influence on the impedance response at low frequencies, whereas the space-charge capacitance is obtained most easily from high frequency measurements where the influence of leakage currents is minimized.

Orazem et al. and Jansen et al. have shown that the application of impedance spectroscopy at different temperatures (thermally stimulated deep-level impedance spectroscopy (TS-DLZS)) could be used to identify the influence of deep-level states in an n-GaAs Schottky diode. The required sensitivity was achieved only when the regression procedure used to extract physical parameters employed a weighting strategy that accounted for the variance of the measurement. The measurement model approach described by Agarwal et al. was used to obtain the error structure for the impedance measurements. Jansen and Orazem have demonstrated the application of impedance spectroscopy under monochromatic optical excitation to large bandgap materials. The object of the present work was to explore the information that can be obtained by OS-DLZS for an n-type GaAs diode and to compare this information to that obtained by TS-DLZS and DLTS.

Introduction

Optically stimulated deep-level impedance spectroscopy (OS-DLZS) is a light-enhanced form of electrochemical impedance spectroscopy. The effect of photonic excitation on electronic transitions is detected by impedance spectroscopy applied over a broad frequency range. The photonic energy of the light used is less than the bandgap energy; therefore, any changes in the frequency spectrum with illumination can be attributed to transitions involving energy levels within the bandgap. OS-DLZS is distinguished from the more commonly used deep-level transient spectroscopy (DLTS) in that the wavelength of monochromatic sub-bandgap light is varied to excite electronic transitions at a fixed temperature, whereas, in DLTS, temperature is varied to change the occupancy of the states. A broad range of frequency (with emphasis on lower frequencies) for the impedance measurements is used instead of measuring an effective capacitance at a single high frequency. The measurement of complex impedance over a broad frequency range is the essential distinction between this approach and photocapacitance spectroscopy. The experimental part of OS-DLZS here is similar to optical admittance spectroscopy (OAS). The major difference is that the complex impedance response is analyzed in DLZS, whereas, the complex admittance response is treated in OAS. Analysis in terms of impedance emphasizes the system response to deep-level states at low frequencies. Experimental and modeling work has shown that deep-level states have the largest influence on the impedance response at low frequencies, whereas the space-charge capacitance is obtained most easily from high frequency measurements where the influence of leakage currents is minimized.

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Experimental

Coupled optical/impedance system.—A scheme of the experimental setup is given in Fig. 1 of Ref. 1. The setup can be divided into two sections, one responsible for the optical frequency and the other for the electrical frequency. The light source was a 450 W xenon lamp capable of emitting wavelengths of light greater than 300 nm. This light was diffracted in a SPEX Model 1681B spectrometer to produce monochromatic light in accordance with Bragg's law. The spectrometer was chosen over laser