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Evidence of the Meyer-Neldel Rule in InGaAsN Alloys: Consequences for Photovoltaic Materials

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S.W. Johnston and R.S. Crandall

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Evidence of the Meyer-Neldel Rule in InGaAsN Alloys: Consequences for Photovoltaic Materials

Steven W. Johnston and Richard S. Crandall
National Renewable Energy Laboratory,
Golden, CO 80401, U.S.A.

ABSTRACT

We present data showing the potential adverse effects on photovoltaic device performance of all traps in InGaAsN. Deep-level transient spectroscopy measurements were performed on InGaAsN samples grown by both metal-organic chemical vapor deposition and RF plasma-assisted molecular-beam epitaxy. For each growth technique, we studied samples with varying nitrogen composition ranging from 0% to 2.2%. A deep hole trap with activation energy ranging between 0.5 and 0.8 eV is observed in all samples. These data clearly obey the Meyer-Neldel rule, which states that all traps have the same emission rate at the isokinetic temperature. A fit of our trap data gives an isokinetic temperature of 350 K. We find that the emission time for all deep hole traps is on the order of milliseconds at room temperature. This means that both deep and shallow traps emit slowly at the operating temperature of solar cells—thus, the traps can be recombination centers.

INTRODUCTION

Adding nitrogen to GaAs initially reduces the bandgap [1-3]. This alloy can be grown epitaxially on GaAs, and lattice-matching can be improved by also adding In [4]. With about 2% N and 6% In, a 1-eV bandgap material lattice-matched to GaAs can be grown [4,5]. These properties are advantageous for developing a four-junction high-efficiency solar cell, consisting of GaInP, GaAs, InGaAsN, and Ge. Such a structure has an ideal AM0 efficiency of 41% [6], but to date, poor minority-carrier properties have limited the material's usefulness in multijunction cells [5,7].

Deep-level transient spectroscopy (DLTS) is a powerful technique for characterizing material defects and providing information to identify lifetime-killing defects that degrade device performance. DLTS data have been reported on both metal-organic chemical-vapor-deposited (MOCVD) and RF plasma-assisted molecular-beam epitaxy (MBE) InGaAsN alloys. Krispin et al. report several hole traps in MBE-grown material having activation energies of 0.16 to 0.17, 0.35 to 0.36, 0.39, 0.55, and 0.69 eV [8]. The larger activation-energy traps (0.55 and 0.69 eV) appear in the largest concentrations. They assign the 0.55-eV level to an Fe_{Ga} (Fe on a Ga site) substitutional defect, and the 0.69-eV level to a $Ga_{As}^{-/2-}$ (charge-state change) anti-site defect [9]. Chen et al. [10] report a hole trap in N-implanted GaAs and suggest that this level at 0.545 eV is a nitrogen-related acceptor defect. Kwon et al. [11] and Kaplar et al. [12] have reported hole traps with activation energies of 0.10, 0.23, and 0.48 eV, along with a broad peak corresponding to ~0.5 eV in MOCVD-grown material. Kaplar et al. [13] also report activation energies of 0.37, 0.51, and 0.71 eV in MBE material. Johnston [14] reported a deep hole-trap ranging in activation energy from 0.61 to 0.79 eV in MOCVD samples of varying In and N composition; using these data plus data from similar MBE-grown samples, we will show evidence of the Meyer-Neldel-rule behavior.

EXPERIMENTAL DETAILS

A series of p-type samples with varying N and In composition were grown by MOCVD and MBE on conductive GaAs substrates. Details about the growth processes are published elsewhere [5,15,16]. An ohmic contact was deposited on the back surface, and Schottky contacts formed by sputtered Au were deposited on the top surfaces. Estimates of N content were obtained from a combination of measured photoluminescence bandgap and X-ray diffraction [5]. The samples were then characterized by measuring room-temperature carrier concentration using the capacitance-voltage (C-V) technique [17] at a frequency of 1 MHz.

DLTS data were collected using a SULA Technologies [18] instrument, which provides up to 12 rate-windows and measures capacitance at a frequency of 1 MHz. Temperature was scanned at a rate of 10 K per minute, and data for each rate window were collected during both upward and downward temperature sweeps. These data were then averaged to account for any temperature lag between the temperature sensor and the sample.

DISCUSSION

DLTS data were collected at an applied reverse bias of 1 V, a pulse amplitude of 1 V (to 0 V), and a pulse width of 10 ms. The data for the 0.2-ms rate window during the heating cycle are shown in figure 1. The values of ΔC, the capacitance changes during the rate windows, are converted to trap density by using the relation [19] $N_T = 2N_a\Delta C/C$, with N_T the trap concentration, N_a the acceptor density determined from room-temperature C-V curves, and C the reverse bias capacitance.

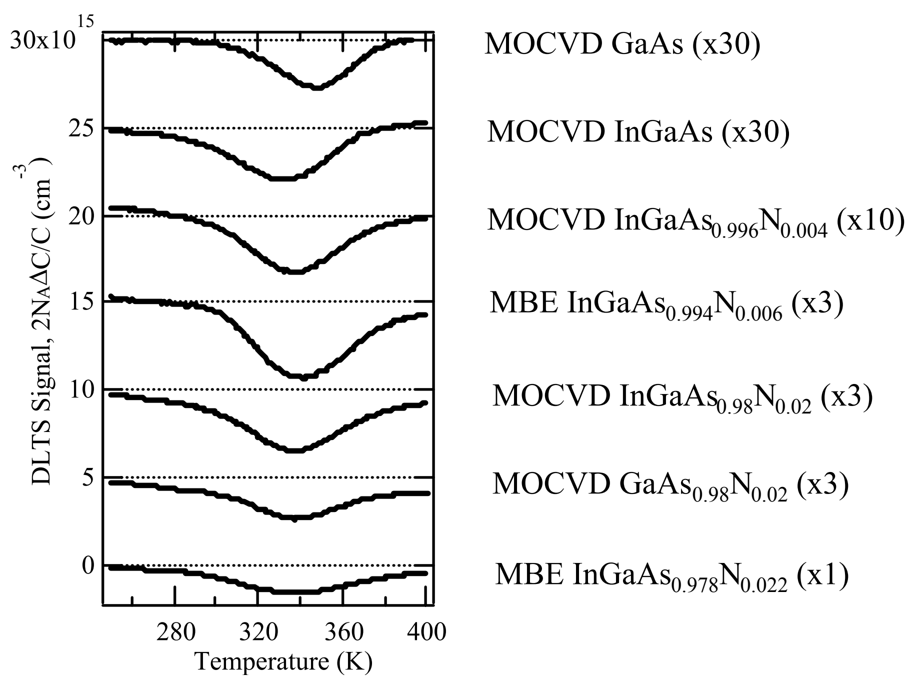

Figure 1. Trap concentration from DLTS measurement using 0.2-ms rate window. For clarity, each trace is offset by $5x10^{15}$ and multiplied by the factor shown on the right in parentheses.

A representative DLTS scan of a GaAs sample is shown in the inset of figure 2 and displays data from all 12 rate windows during the heating cycle. The negative peaks correspond to majority-carrier hole traps with a density of about 10^{14} cm^{-3}. The maximum temperature points are then plotted on an Arrhenius plot with the corresponding rate-window time constants, τ, as shown in figure 2. The data points are fit by linear equations, giving slope and intercept values. The activation energies, E_a, are determined from the Arrhenius plots' slope [17] and are also shown in figure 2. The standard deviation of each linear fit corresponds to ± 0.005 eV. Errors in temperature of ± 1K would give uncertainties for E_a of up to ± 0.01 eV. The ΔC data of figure 1 show that each sample contains a hole trap with the peak occurring near 350 K. The corresponding activation energies range from 0.5 to 0.8 eV. The amount of added N ranges from 0% to 2%, and In is either not included or added in a small percentage proportional to N to increase lattice matching. Although peaks due to hole traps are consistently seen near 350 K, their calculated activation energies are not a constant value and vary beyond the corresponding fits' standard deviations. The activation energies also do not show a relation to N content.

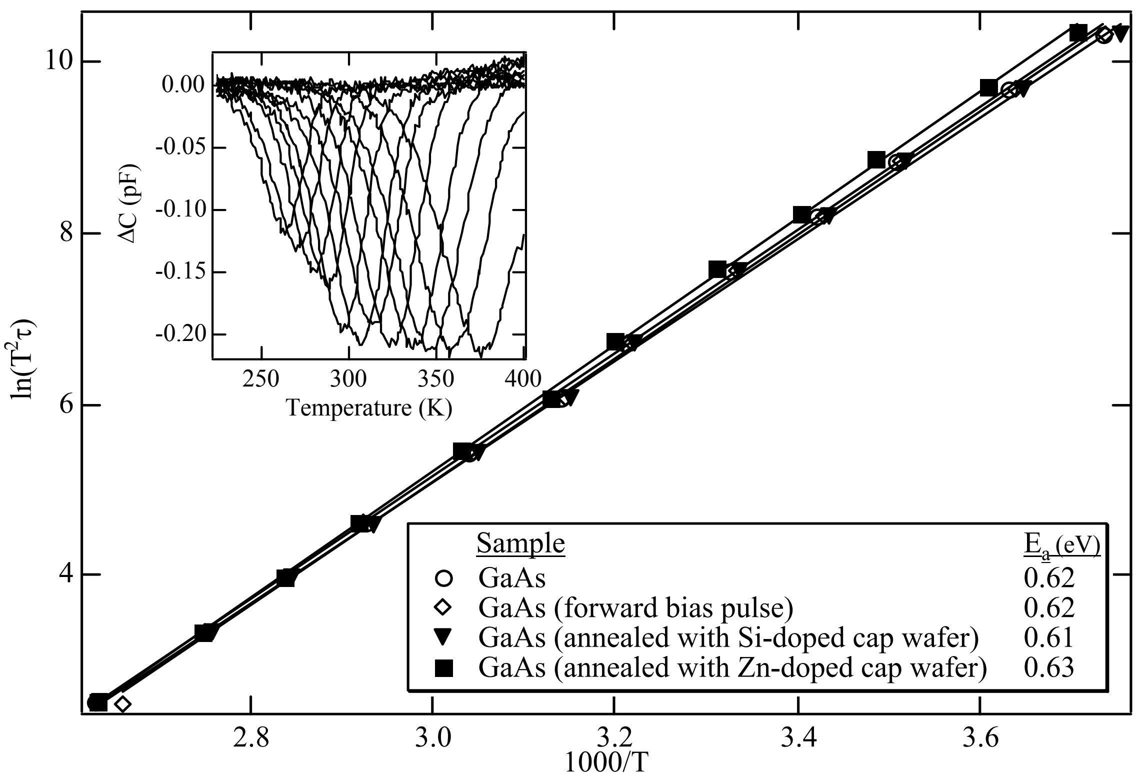

Figure 2. Arrhenius plot for the hole trap in MOCVD-grown GaAs samples. The data points correspond to peak temperature values for the 12 DLTS rate windows. The inset graph shows the hole-trap DLTS signal for the 12 available rate windows.

Meyer-Neldel rule

All alloys studied (GaAs, GaAsN, InGaAs, and InGaAsN) show a deep hole-trap with E_a varying from 0.5 to 0.8 eV. E_a is found from the expression for carrier emission from a trap, which is given by the following [17]:

$$\frac{1}{\tau} = \nu_0 e^{-\frac{E_a}{k_B T}} = N_B v_T \sigma e^{-\frac{E_a}{k_B T}} = \gamma T^2 \sigma e^{-\frac{E_a}{k_B T}} \quad (1)$$

where ν_0 is a constant, k_B is the Boltzmann constant, N_B is the band density-of-states, v_T is the thermal velocity, σ is the capture-cross section, and $\gamma = N_B v_T T^{-2}$. In addition, the Meyer-Neldel [20] rule (MNR) states that:

$$\ln(\nu_0) = \ln(\nu_{00}) + \frac{E_a}{k_B T_{iso}}. \quad (2)$$

Here, ν_{00} is a constant and T_{iso} is the isokinetic temperature. Substituting Eq. (2) into (1):

$$\frac{1}{\tau} = \nu_{00} e^{\frac{E_{act}}{k_B T_{iso}}} e^{-\frac{E_{act}}{k_B T}}, \quad (3)$$

which shows that the increase in the term $E_{act}/k_B T_{iso}$ compensates somewhat for the Boltzmann factor. For this reason the MNR is frequently called the "compensation law" [21]. Each measured sample's linear fit on an Arrhenius plot has a slope (E_a/k_B) and a y-intercept value ($\ln(\gamma\sigma)$). These points are plotted in figure 3, and this type of plot is often called a Meyer-Neldel plot. The different growth methods and alloy types are shown by different symbols. The figure clearly shows that $\ln(\gamma\sigma)$ varies linearly with E_a by as much as five orders of magnitude. Because γ is roughly constant over this alloy range, we might conclude that σ varies by orders of magnitude for what could be the same defect in the different alloys.

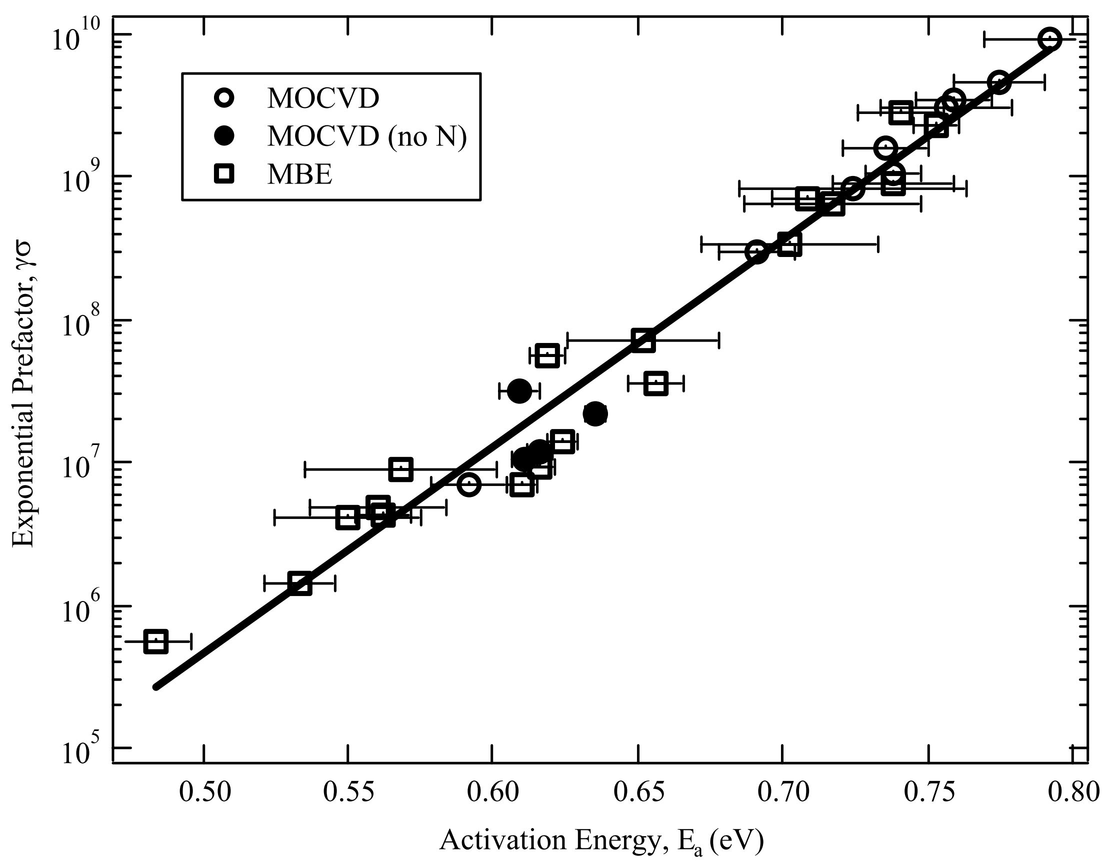

Figure 3. MNR plot of DLTS determination of the exponential prefactor, γσ, vs. E_a for the principal deep hole-trap. Note that the vertical axis is logarithmic.

A consequence of the MNR is that at $T=T_{iso}$ the detrapping rate is independent of E_a. According to the MNR, the slope of a line through the data in figure 3 is $(k_B T_{iso})^{-1}$. A least-square-error fit of the data gives $T_{iso}=350\pm15$ K. Then, when the material is at this temperature, both shallow and deep levels may have the same detrimental impact on device performance because their emission rates are similar.

The MNR has been addressed by many articles [22-24], including one by Crandall in this conference proceedings [25]. The physical explanation of this rule is based on the realization that there is considerable entropy, ΔS_{ph}, associated with the assembly of a large number of system excitations at a particular site to produce a thermally activated jump over an energy barrier [22-25]. The following expression [26] shows the emission rate with the entropy contribution:

$$\frac{1}{\tau} = N_C v_T \sigma e^{-\frac{\Delta G}{k_B T}} = N_C v_T \sigma e^{-\frac{\Delta H - T\Delta S}{k_B T}}. \tag{4}$$

Here, ΔG is the change in Gibbs free energy, $\Delta H = E_a$, and ΔS is the entropy change. If we assume that the only entropy contribution to the free energy is the phonon entropy from MNR, that is, $\Delta S=E_a/T_{iso}$, we see that Eq. (4) is equivalent to Eq. (3), the MNR. Knowledge of σ permits determination of this entropy, and by correctly accounting for this entropy term, we see that σ is the same for all traps that fall along the MNR line. This is reasonable because we expect that the trap will correspond to the same defect for the range of alloys presented here. Using the known physical constants [27], we find that $\sigma=2\text{x}10^{-23}$ cm^2. This value is exceedingly small, but in line with that found by others who observed the MNR in similar alloys [28,29]. Some preliminary results from measuring capture rate by varying the filling pulse time [17] suggest that σ is temperature dependent following a model of a Coulomb-repulsive center having a potential barrier [30]. We plan to measure σ as a function of temperature, and use those results to calculate more accurate values of entropy, defect energy level, and trap potential barrier.

SUMMARY

We have used DLTS to measure hole traps in a series of p-type InGaAsN alloys grown by MOCVD and MBE methods. Hole traps were seen in each sample and may be attributed to a native defect or defect complex. All data presented above show that carrier emission obeys the Meyer-Neldel Rule with an isokinetic temperature of 350 K.

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