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Thermoelectric effect spectroscopy measurements on semi-insulating GaN

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Abstract

A simplified setup for thermoelectric effect spectroscopy (TEES) was introduced. This was applied for measurements on semi-insulating GaN, grown on a sapphire substrate in order to investigate deep level traps. TEES currents were found to be negative at lower temperatures and positive at higher temperatures, indicating that shallower levels belong to electron traps, and deeper levels to hole traps. Traps were fully characterized by using the thermally stimulated current measurements and the simultaneous multiple peak analysis method. The shallowest observed electron and hole traps have activation energies $E_C - 0.09\,\text{eV}$ and $E_V + 0.167\,\text{eV}$, respectively. The possible microscopic origin of analyzed defects was discussed.

Keywords: Thermoelectric effect spectroscopy; Thermally stimulated currents; Semi-insulating GaN; Deep levels

1. Introduction

For good performance of electrical and optical devices, such as light-emitting diodes, laser diodes, detectors, or transistors, which are built on highly resistive or semi-insulating (SI) substrates, defects with deep levels (traps) can be very important, and thus must be understood and well characterized. Among different methods for trap characterization, thermoelectric effect spectroscopy (TEES) is one of the few which is efficiently applicable on highly resistive or semi-insulating (SI) materials, enabling the sign of deep traps to be determined. This information is very important for more reliable assignation of deep trap microscopic origin and for better understanding of compensation mechanisms. TEES methodology was first developed [1] and successfully applied in SI GaAs [1–3].

In this work, a new, simplified setup for the TEES, particularly suitable for thin film-on-substrate sample type, was introduced and applied for measurements on SI gallium nitride (GaN) which is nowadays one of the most promising III–V nitride semiconductors (because of its unique electronic and optical properties). Based on GaN, short-wavelength light-emitting diodes as well as laser diodes, field effect transistors and ultraviolet detectors are presently being developed and commercialized [4–7]. There are several reports [8,9] on deep levels in conductive GaN,

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obtained by deep level transient spectroscopy (DLTS) measurements. Although there are a number of studies of SI GaN [10–13], very little is known about deep levels in this material, because DLTS is not applicable to SI or highly resistive materials. Thermally stimulated current (TSC) spectroscopy is very useful method for characterization of SI or high-resistance samples and it has been applied extensively to SI GaAs [14–16]. There are few reports [13,17] in which TSC spectroscopy was used in SI GaN characterization. In these papers, a variety of deep levels were reported. Huang et al. [17] found at least five main deep levels in 0.11–0.62 eV range, while Look et al. [13] have found one shallow and one deeper trap, with activation energies $E_A = 0.09$ and 0.17 eV, respectively, as well as one more trap at 130 K. In these reports, it was not possible to determine whether observed levels belong to electron or hole traps. This is not the case with TEES measurements which can distinguish electron and hole traps.

In our experiments, TEES currents were found negative at lower temperatures and positive at higher temperatures, indicating that shallower levels belong to electron traps, and deeper levels to hole traps. Deep traps were further characterized by combining the TSC measurements and the simultaneous multiple peak analysis (SIMPA) method. The shallowest observed electron and hole traps had activation energies $E_C - 0.09$ eV and $E_V + 0.167$ eV, for which is argued that they are probably related to N-vacancy and Ga-vacancy, respectively. Both hole and electron traps were found in relatively high concentrations causing electrical compensation and high resistivity.

2. Experimental

SI GaN, grown by molecular beam epitaxy (MBE) [13], was studied by TEES, TSC and low-temperature photoconductivity (I_{PC}) measurements. Measurements were performed on 6 μm thick SI GaN layer grown at 800°C on a *c*-plane sapphire (Al_2O_3). In TEES deep traps are filled by illumination at low temperature. The subsequent increase of temperature in dark conditions at a constant rate causes the release of trapped carriers, shallower traps being released at lower and deeper traps at higher temperatures. In addition to the temperature ramp, a temperature gradient is established along the sample, which induces the drift of liberated charge carriers to the electric contacts producing the thermoelectric effect and therefore the current in the outer circuit [1]. The sign of the current depends on the type of the dominant charge carriers at a particular temperature, which enables electron and hole traps to be distinguished. Fig. 1 presents a simplified experimental configuration for TEES measurement, particularly applicable to film-on-substrate type of samples with planar contacts. To obtain sufficient temperature gradient, the sample was

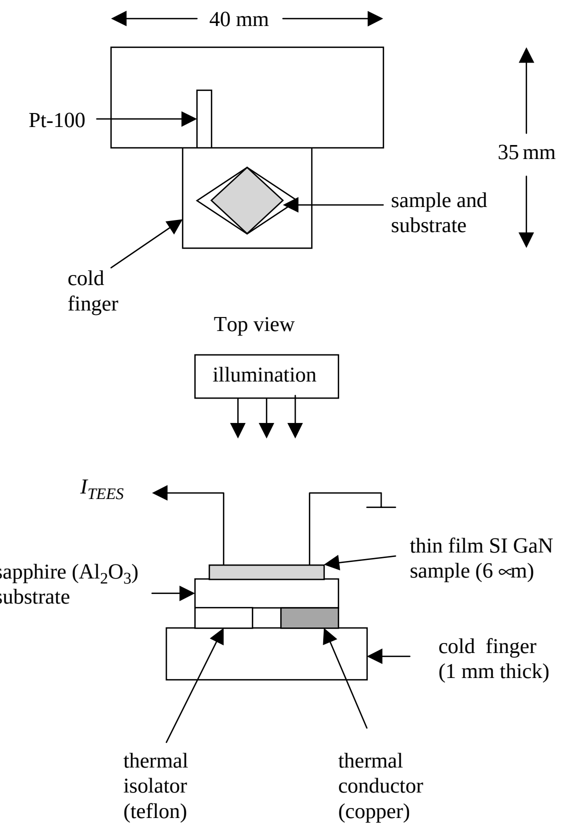

Fig. 1. Simple setup for TEES, particularly suitable for measurements on thin-film-on-substrate samples.

placed on two equally thick materials having very different thermal conductivity (c). Under one-half of the sample, a thermal isolator (teflon, $c = 0.19\,\mathrm{W\,cm^{-1}\,K^{-1}}$) was placed, while on the other side, a thermal conductor (copper, $c = 4\,\mathrm{Wcm^{-1}\,K^{-1}}$) was situated. Electrical contacts were placed to correspond to "cold" and "warm" parts of the sample. This simple configuration excludes the additional heater, used in the original setup [1], eliminating its detrimental impact on measurement quality. The obtained temperature gradient was sufficient to produce TEES currents (I_{TEES}) of a few pico-amperes, which are values comparable to those obtained in standard TEES measurements [1–3]. According to these values, the temperature difference between "cold" and "warm" contact is estimated to be around 1 K. This sample was illuminated with white light at 86 K, which assures sufficient production of free charge carriers. TEES currents were measured with a Keithley 617 electrometer. Sample temperature was determined by a platinum element Pt-100 whose position is shown in Fig. 1 (top view). The TSC as well as I_{PC} measurements were performed with the standard procedure, often used for SI GaAs characterization, and are described in detail elsewhere [16,18]. Both TEES and TSC measurements were obtained for different heating rates, β, in the range 0.4–0.8 K/s.

3. Results and discussion

Fig. 2 presents (a) TEES and (b) TSC spectra, both obtained with different heating rates ($\beta = 0.4$, 0.6 and 0.8 K/s). Both the TEES and TSC intensities increase with an increase of β, accompanied by a shift of the peak maxima towards higher temperatures. The whole TSC signal is of the same sign, because both trap types contribute to the TSC current. However, the analogous TEES signal which reflects the difference between positive and negative charges reveals that carriers giving rise to TSC peak A, are partly electrons and partly holes, while the majority of carriers related to the TEES signal at higher temperatures have a positive sign. There are two arguments supporting the assignment of peak A to a composite peak,

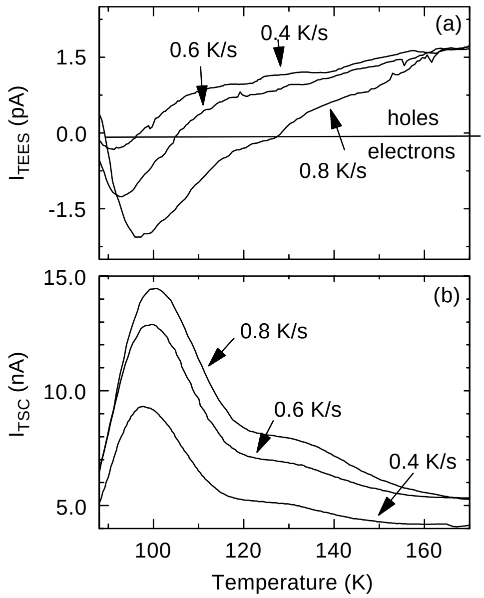

Fig. 2. (a, b) TEES and TSC measured curves, respectively, measured at heating rates $\beta = 0.4$, 0.6 and 0.8 K/s.

resulting from both positive and negative carriers: (a) the maximum of peak A (at any β) does not occur at the same T in TSC and TEES, as would have been expected if both of the sub-peaks had had the same sign [1]; and (b) for lower β, the integral of the TEES negative peak covers a narrower T range, and the peak maximum is shifted towards lower T in comparison to the maximum of A in the TSC spectra. This is in agreement with the opinion that for lower β the thermoelectric effect separate electrons and holes less effectively.

On the basis of TSC peak A shape only, Look et al. [13] concluded that A has to be a composite peak and extracted activation energies $E_{A_1} = 0.09\,\mathrm{eV}$ and $E_{A_2} = 0.17\,\mathrm{eV}$ for two of its components. In this paper, we have applied simultaneous multiple peak analysis (SIMPA) [16,18] to the whole TSC spectrum in order to determine all components of peak A.

SIMPA method is based on the description of TSC spectrum as a sum of TSC peaks belonging to specific deep levels, and dark current, I_{dark}. A temperature-dependent fitting function, $I_{SIMPA}(T)$, comprising the sum of all features of TSC spectrum was formed as

$$I_{SIMPA}(T) = \sum_{i=1}^{m} I^i_{TSC}(T) + I_{dark}(T), \quad (1)$$

where $I^i_{TSC}(T)$ represents a single ith TSC peak and m is the total number of deep traps taken in calculations.

In the "first-order kinetics" approximation, a single TSC peak, resulting from an electron trap can be described as [18]

$$I^i_{TSC}(T) = K_G \mu N_i \tau D_t T^2 \exp\left[-\frac{E_{a,i}}{kT} - \frac{kD_{t,i}}{\beta E_{a,i}} T^4 e^{-E_{a,i}/kT} \times \left(1 - 4\frac{kT}{E_{a,i}} + 20\frac{k^2T^2}{E^2_{a,i}} \right)\right]. \quad (2)$$

K_G denotes the geometrical factor expressed as $K_G = eAE$, where e is an electron charge, A is the area of electrode and E is the applied electric field. N_i is the carrier density of the filled ith deep traps at the beginning of the temperature ramp. μ and τ denote the carrier mobility and free lifetime, respectively. $E_{a,i}$ is the ith trap activation energy and β denotes heating rate. $D_{t,i}$ is the trap-dependent coefficient which includes electron (or hole) capture cross-section (σ_i) and it is defined as [18] $D_{t,i} = C(m^*/m_0)\sigma_i$, with a constant C which is different for electrons and holes, as well as m_0 and m^* representing electron (or hole) rest and effective mass, respectively. In these calculations, it was assumed that σ_i is practically T independent for deep traps in SI GaN. A function defined with Eq. (1) was used as the fitting function, with $E_{a,i}$, σ_i, as well as the product $(\mu N \tau)$ taken as unknowns. K_G and β are known constants. Analysis shows, however, that the influence of these parameters on peak characteristics can be resolved. N, $E_{a,i}$ and σ_i, primarily determine the peak height, position and width, respectively. Due to interconnection of these parameters, the change of σ_i up to 20% from the best-fit value can be compensated by the change of E_a (for $\approx$1%) and N (for $\approx$5%) still giving fair enough fits. Hence, the uniqueness of the fit is ensured within confidence limits of $\pm$20%, $\pm$1% and $\pm$5%, for σ_i, E_a and N, respectively. None of the deep levels used in simulations was constructed artificially or taken without experimental support, i.e. without being clearly observed as a well resolved or even dominant peak in at least one of the analyzed TSC spectra.

Fig. 3 shows that we have successfully simulated peak A with three deep traps A_1, A_2 and A_3. The sign of the TEES spectra indicates that A_1, the lowest-energy trap contributing to the A peak, is an electron trap, and the highest-energy trap, A_3, is a hole trap. As the TEES signal changes its sign just in the T range corresponding to the A_2 trap, it is not possible to determine its sign with certainty. Namely, the activation energies of all the three A_1, A_2 and A_3 traps are relatively close, and the TEES signal from the A_2 trap might be overpowered either by electron trap A_1 or by hole trap A_3. The SIMPA analysis gave the following trap parameters: $E_{A_1} = E_C - (0.090 \pm 0.004)$ eV, $\sigma_{A_1} = (4.5 \pm 1.5) \times 10^{-22}$ cm^2, and $E_{A_3} = E_V + (0.167 \pm 0.008)$ eV, $\sigma_{A_3} = (5.0 \pm 1.5) \times 10^{-19}$ cm^2. The values of E_{A_2} and σ_{A_2} come out as either $E_{A_2} = E_C - (0.165 \pm 0.006)$ eV and $\sigma_{A_1} = 9.4 \times 10^{-19}$ cm^2 or $E_{A_2} = E_V \pm (0.165 \pm$

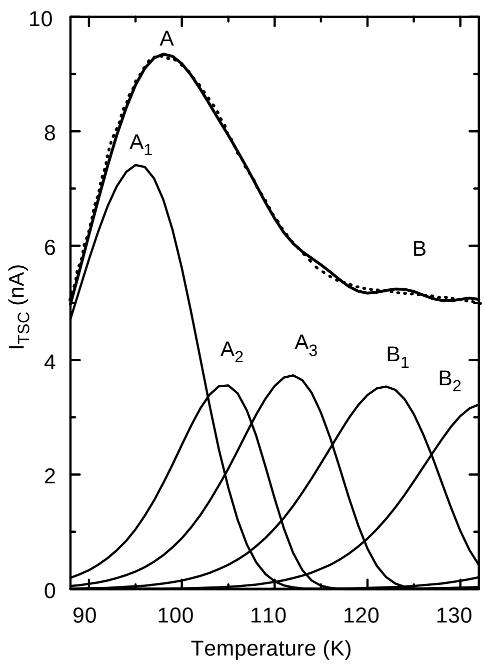

Fig. 3. SIMPA fit (thick solid curve) of the measured TSC spectrum (thick dotted curve). A_1, A_2, A_3, B_1, and B_2 are particular SIMPA peaks representing components of peaks A and B, respectively.

0.008) eV and $\sigma_{A_2} = 6.7 \times 10^{-19}\,cm^2$, depending on whether A_2 is an electron or a hole trap, respectively. The product $N\tau\mu$, is 7.8×10^{13}, 2.5×10^{13}, $3.1 \times 10^{13}\,cm^{-1}\,V^{-1}$, for traps A_1, A_2 and A_3, respectively. This suggests high concentrations of all the three traps, in the $10^{17}\,cm^{-3}$ range.

Peak B, which in the TSC spectrum, and occurs as a shoulder at around 130 K, was fitted with two components B_1 and B_2, as shown in Fig. 3. According to TEES results presented in Fig. 2, they should be hole traps, with the best-fit parameters: $E_{B_1} = E_V + (0.176 \pm 0.008\,eV)$; $\sigma_{B_1} = 8.7 \pm 10^{-20}\,cm^2$ and $E_{B_2} = EV + (0.214 \pm 0.009)\,eV$; $\sigma_{B_2} = 5.4 \times 10^{-19}\,cm^2$, respectively. This product $N\tau\mu$, for B_1 trap is $3.3 \times 10^{13}\,cm^{-1}\,V^{-1}$, and for B_2 is $2.9 \times 10^{13}\,cm^{-1}\,V^{-1}$.

The measured temporal evolution of $I_{PC}(t)$ during constant-intensity white-light illumination of SI GaN sample at 86 K (not presented here) shows clear photocurrent quenching (PCQ) effect in the early stage of the transient. An analogous quenching of I_{PC} was observed previously in SI GaAs during low-T illumination [1,19,20] in samples which contained both electron and hole deep traps [1]. This finding additionally supports the above TEES results.

The question arises as to which microscopic defects comprise the donor level at $E_C - 0.09\,eV$ and acceptor level at $E_V + 0.167\,eV$, as well as the other levels observed in this analysis. Based on the comparison of trap parameters, the most plausible candidate for the electron trap A_1 is a defect related to the N-vacancy. From the temperature-dependent Hall data, the thermal activation energy (E_T) for the N-vacancy donor, induced by electron-irradiation (EI) has been determined [21] to be 0.07 eV. In addition, a broad, low-temperature DLTS peak (E), induced by 1 MeV EI, has an apparent activation energy of 0.18 eV [22]. However, detailed DLTS fitting shows that: (i) E consists of ED1 and ED2; (ii) both centers have the same E_T, 0.06 eV, which is very close to the 0.07 eV found for the EI-induced N-vacancy donor; and (iii) both centers have different and small capture cross sections ($1–3 \times 10^{-20}\,cm^2$ for ED1 and $5–8 \times 10^{-19}\,cm^2$ for ED2), with that of ED2 being temperature dependent and having an activation energy of 0.06 eV [23]. We speculate that the hole trap (A_3) is due to the Ga-vacancy, which is often the dominant acceptor in undoped GaN, especially that grown by hydride vapor phase epitaxy, as confirmed by a positron annihilation study [24]. According to theoretical calculations [25], (i) the N-vacancy (a donor) has the lowest formation energy in p-type GaN, and the Ga-vacancy (an acceptor) in n-type GaN; and (ii) the isolated Ga-vacancy in the negative charge state is triply occupied, with levels close to the valence band. There are many reports about deep levels related to impurity acceptors (such as Mg [Refs. 26,27]); however, so far there are no reports about any DLTS centers related to the Ga-vacancy. It is possible that the TEES/TSC trap A_3 at $E_V + 0.167\,eV$ is related to a Ga-vacancy. Since this activation energy is close to the reported activation energies for Mg (such as 136 meV by admittance measurements [26], 135–155 meV by Hall effect measurements, and 80–115 meV by admittance measurements [27], respectively), we should not rule out the possibility that A_3 is due to Mg, owing to possible contamination and memory effect during MBE growth. To confirm the above-stated "Ga-vacancy" hypothesis, further TEES studies on high-resistive or SI GaN materials grown by other techniques are needed.

The interpretation of B peak (B_1 and B_2 components) origin is a more complex goal. This is so partly because of lack of studies on deep levels in high-resistive GaN materials. Huang and co-workers [17] in their semi-insulating GaN samples observed level T2 with activation energy of 0.24 eV, which is close to the B_2 level. They did not speculate about its origin there. Fang et al. [28] in their undoped n-GaN samples, grown by hydride vapor phase epitaxy, in the 125–140 K T-range, observed DLTS level D with activation energy $0.17\,eV < E_D < 0.23\,eV$ (depending on sample thickness) and attributed it to the complex defect comprising Ga vacancy, such as an N vacancy–Ga vacancy pair. This level has activation energy in range similar to our B_1 and B_2 levels.

4. Conclusions

An experimental configuration, suitable for thin film samples, was devised and successfully applied in TEES measurements on SI GaN thin films deposited on sapphire. TEES currents were found negative at lower and positive at higher temperatures. Hence shallower levels belong to electron, and deeper levels belong to hole traps. Characterization of deep traps with the SIMPA analytical method showed that the shallowest electron trap has an activation energy $E_C - 0.09\,\text{eV}$, and the shallowest hole trap $E_V + 0.167\,\text{eV}$. On the basis of SIMPA and TEES results, as well as from the results of other authors, it was concluded that N-vacancy and Ga-vacancy are possible candidates for the observed electron and hole traps, respectively. The presence of both positive and negative deep traps in relatively high concentrations probably causes electrical compensation and high resistivity of the studied material. To clarify these issues, as well as to identify the origin of other observed levels, further TEES studies on high-resistive or SI GaN samples grown by other techniques are necessary.

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