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ABSTRACT

Thermally stimulated techniques—thermally stimulated current (TSC) spectroscopy and thermally stimulated depolarization current (TSDC) spectroscopy—were used to comparatively study the electrical properties and deep level defects in β-Ga_2O_3 pulsed laser deposited thin films and Czochralski-grown bulk crystals. It was found that the samples are highly resistive and each sample may have different dark current activation energy. Deep level defects revealed by the thermally stimulated techniques vary from sample to sample. In addition to the common traps E_1 (~0.56 eV), E_2 (~0.84 eV), and E_3 (~0.99 eV), reported in the literature and revealed by DLTS studies of Ga_2O_3 bulk crystals, that were also found in our samples by the thermally stimulated techniques, a trap at ~110 meV and several other traps are revealed specifically by TSDC between 105 and 225 K.

I. INTRODUCTION

Transparent semiconducting oxides such as the beta phase of gallium sesquioxide (β-Ga_2O_3) have attracted a lot of attention recently because of their extended transparency to the deep ultraviolet.[1] β-Ga_2O_3 has a bandgap around 4.7 eV; therefore, the absorption edge can reach below 260 nm. Optoelectronic and power electronic devices such as MOSFETs based on β-Ga_2O_3 have been demonstrated.[2,3] Bulk β-Ga_2O_3 grown by several different techniques has been reported and its electrical properties have been investigated;[4–6] among them, the deep level defects (traps) of bulk crystals have been studied by deep level transient spectroscopy (DLTS) and by optically and thermally stimulated defect spectroscopy.[6–9] Electron and hole trap densities in β-Ga_2O_3 films grown by hydride vapor phase epitaxy (HVPE) and deep level defects in Ge-doped β-Ga_2O_3 layers grown by plasma-assisted molecular beam epitaxy were also reported.[10,11] Recently, the growth of β-Ga_2O_3 thin films by pulsed laser deposition (PLD)[12,13] has also attracted a lot of attention since this method is more flexible than other film growth methods, and the PLD films have been fabricated into several kinds of devices;[14] therefore, it is necessary to understand basic electronic properties such as carrier transport and electrically active defects in these materials. However, deep level defects in these films, especially those in highly-resistive Ga_2O_3 materials, have not been fully explored because of experimental difficulties; e.g., they are not amenable to capacitance-based defect analysis techniques, such as deep level transient spectroscopy (DLTS). Although deep level defects of bulk Ga_2O_3 have been studied by several groups, there is still some confusion about revelations and interpretations of trap energy levels in the literature, and moreover, there are few comparisons of defects in bulk materials with those in thin films, especially those grown by PLD.

In this paper, we use two different thermally stimulated techniques[15]—thermally stimulated current (TSC) spectroscopy and thermally stimulated depolarization current (TSDC) spectroscopy—to comparatively study deep-level defects in highly resistive thin films grown by PLD with those in bulk single crystals grown by the Czochralski (CZ) method.

TSC spectroscopy involves filling electron and hole traps in the material by illumination at low temperature and then warming the sample in the dark while recording the current due to the thermal emission of carriers from the traps.[16] In other words, traps at different energy levels are first filled by either optical or electrical

injection, usually at a relatively low temperature. Subsequently, electrons or holes are emitted by raising the temperature. TSC measurements can, therefore, detect the trap—a peak in the current observed at a given temperature; but unlike the case for DLTS, TSC cannot tell whether a peak is due to an electron or a hole trap.

The emission is thermally activated, so the emission rate e_n (for electrons) is given by the usual formula determined from detailed-balance considerations:

$$e_n = \sigma_n N_c v_{th} \exp(-E_T/kT), \tag{1}$$

where σ_n is the capture cross section for the trap, N_C is the effective conduction-band density of states, v_{th} is the thermal velocity, and E_T is the trap energy with respect to the conduction band. A similar formula can be written for hole emission. A given trap will begin to emit at a characteristic temperature with the emission rate increasing rapidly according to Eq. (1). However, the emission probability will drop as the trap is depleted of electrons (or holes), so that the current I_{TSC} will go through a peak

$$I_{TSC} = CV_b e\mu_n \tau_n N_T e_n \exp\left(-\int e_n/\beta dT'\right), \tag{2}$$

where e is the electronic charge, μ is the electron mobility, τ is the free-electron lifetime, N_T is the trap density, V_b is the bias voltage, and C is a constant related to sample geometry. Thus, a fit of the integral Eq. (2) to a TSC spectrum of a given trap will yield σ_n and E_T.

In the variable heating rate method, the TSC peaks shift when the heating rate is changed, and the relationship between the temperature of the TSC peak T_m and the heating rate β is given by

$$E_T = kT_m \ln\frac{T_m^4}{\beta} + kT_m \ln(N_c v_{th} k\sigma_n/E_T), \tag{3}$$

where k is Boltzmann's constant, $N_c = 2(2\pi m^* kT_m/h^2)^{3/2}$. Since the second term on the right side of the equation is usually much smaller than the first term, so that the second term is neglected, an approximate activation energy of a trap at T_m can then be determined from

$$E_T = kT_m \ln\frac{T_m^4}{\beta}. \tag{4}$$

The TSDC technique is a very sensitive method for the study of dipolar relaxations in polymers and dielectrics through a polarization-depolarization process.[17] The technique has been widely employed to investigate and characterize relaxation processes, charge-storage, and charge-decay processes in a number of materials. TSDC, the electric field-induced thermally stimulated current, may be generated by various mechanisms: (1) orientation of permanent dipoles (in polar materials), (2) trapping of charge by structural defects and impurity centers, and (3) build-up of charges near heterogeneities such as amorphous-crystalline interfaces in semi-crystalline polymers, grain boundaries in polycrystalline materials, and electronic defects in single crystals.

The relaxation frequency for the dipole disorientation α(T) is often envisaged to follow an Arrhenius shift, therefore

$$\alpha(T) = \alpha_0 \exp\left(-\frac{E}{kT}\right), \tag{5}$$

where α_0 is the characteristic relaxation frequency ($t\to\infty$) and E is the activation energy for dipole disorientation at temperature T. The TSD current $I_{TSDC}(T)$ generated by the decay in polarization follows:

$$I_{TSDC}(T) = \alpha_0 \exp\left(-\frac{E}{kT}\right) P_0 \exp\left[-\frac{1}{r}\int_{t_d}^{t} \alpha(T)d(t)\right]. \tag{6}$$

Here, P_0 is the initial equilibrium polarization, $r = dT/dt$, and t_d is the time of commencement of TSD. Since the temperature is raised linearly with time, $r = \beta$, where β is a constant heating rate.

The peak temperature, T_m, for the current peak can be obtained by differentiating Eq. (6):

$$T_m = \left[\frac{\beta E}{\alpha_0 k}\exp\left(\frac{E}{kT_m}\right)\right]^{1/2}. \tag{7}$$

Therefore, the activation energy E of the trap at the peak T_m is approximately

$$E = kT_m \ln(T_m^2/\beta). \tag{8}$$

From Eq. (8), it can be seen that T_m will shift towards a higher temperature if a higher heating rate β is employed. T_m is independent of the forming conditions, such as polarization field E_p and temperature T_p, provided that the equilibrium polarization has been attained.

The activation energy of a trap can thus be obtained from the slope of $\ln(T_m^2/\beta)$ vs $1000/T_m$. Alternatively, the activation energy can also be calculated by the shift of the TSD current maximum with the heating rate. If the heating rate is changed from β_1 to β_2, the activation energy for the relaxation can be estimated from the corresponding shift of the peak temperature T_{m1} to T_{m2}:

$$E = \frac{k(T_{m1}T_{m2})}{T_{m1} - T_{m2}} \ln\left(\frac{\beta_1 T_{m2}^2}{\beta_2 T_{m1}^2}\right). \tag{9}$$

In this paper, TSC and TSDC spectroscopies are used to study both highly resistive β-Ga_2O_3 thin films and bulk crystals. Because it is difficult to employ the DLTS technique to study deep level defects of highly resistive materials, both TSC and TSDC spectroscopies have been used in the past to study defects in many semiconductors such as GaAs,[18] GaN,[19] and SiC,[20] and dielectrics such as oxides and halides.[21–24] For semi-insulating materials, they have a distinct advantage over DLTS.

II. EXPERIMENTAL

In this study, highly resistive β-Ga_2O_3 thin films with thicknesses from 152 nm to 519 nm were grown on α-Al_2O_3 (0001) in a Neocera Pioneer 180 PLD system with a KrF excimer laser (Coherent COMPexPro 110, λ = 248 nm, 10 ns pulse duration). The chamber base pressure was 2.66×10^{-6} Pa with O_2 or Ar gas introduced during deposition to a working pressure of 5–50 mTorr. Substrates were heated by a backside heater to between 550 and 650 °C. The laser operated at a pulse rate of 10 Hz with an energy density of 3 J cm^2 measured at the target. The target was a 50 mm diameter by 6 mm thick 99.99% pure sintered oxide ceramic disk of Ga_2O_3 with 0.1 wt. % SnO_2. For a different growth experiment (film-2), a 950 nm thick film was grown from a pure Ga_2O_3 target (99.995%) in a mixture of 50% O_2/50% Ar at a pressure of 100 mTorr and a substrate temperature of 650 °C. After growth, 5×5 mm^2 samples were soldered with indium dots forming ohmic contacts at diagonal corners. The bulk single crystals were grown by the CZ method at Northrop Grumman SYNOPTICS. An $8 \times 8 \times 2$ mm^3 sample with (010) orientation of unintentionally-doped resistive single crystal was used for TSC and TSDC studies.

The dark current (DC), TSC, and TSDC experiments were carried out in a modified BioRad 4600 DLTS spectrometer using an electrometer (Keithley 617) for measuring currents and a cryostat equipped with a liquid nitrogen pump for controlling temperature from 83 to 450 K.

During the TSC study, samples were first cooled from 450 to 83 K in the dark. The traps were filled at 83 K by illumination with a 400-nm light (LED) or combination with a white light (note: despite the fact that Ga_2O_3 has a ultra-wide bandgap, a longer-wavelength light source such as a 400 nm LED can often be used to fill traps of energy less than 3.1 eV from a band edge). The photocurrent (PC) response was recorded at 83 K during a 5–60 min illumination period and the decay of persistent photocurrent (PPC) (if any) was then recorded for 30–600 s after switching the light off. After that, the TSC spectrum was measured during warming at a rate β = 0.1–0.4 K/s under a bias of 75–100 V. When no illumination was applied, the dark current (DC) was measured as a function of temperature through both the cooling and warm-up processes for comparison.

For TSDC measurements, the contacts were on two opposite (010) faces of the bulk crystal. The crystal was set on an indium buffered aluminum foil which was grounded and used as one contact; an indium dot was soldered on the central area of the top face for the other contact with bias. Thus, the configuration for crystal TSDC spectral measurements is a sandwich structure; whereas for thin films, two contacts were on the same top face, similar to the TSC configuration. The contacts were connected to an electrometer (Keithley 617).

We performed TSDC measurements between 83 and 450 K at a heating rate β = 0.1–0.4 K/s after polarization. Before the measurements, a dc electric field $E_p = -100$ V was applied to the sample at a polarization temperature T_p, variable from room temperature (RT) to 450 K for a polarization time t_p, and then the sample was cooled down to 83 K while still under the field. When the temperature reached 83 K, the bias was turned off immediately. The system was then kept at the temperature for 1 min to stabilize before warming up and measuring the TSDC.

III. RESULTS AND DISCUSSION

A. Deep levels in PLD-grown β-Ga_2O_3 thin films

TSC spectra of a PLD-grown β-Ga_2O_3 thin film (film-1) using three different heating rates are shown in Fig. 1(a). Several peaks can be found from these spectra. The dominant peak E_1 shifts with the heating rates. However, other small peaks do not seem to appear in every measurement because the sample possesses some persistent photocurrent (PPC) and generates more dark current which overlaps the peaks. For the 0.3 K/s heating rate, which was measured first and had the smallest DC, the peaks are more obvious. But continuing with more measurements, some PPC gradually accumulates and the DC increases, so peaks E_1 and E_2 at heating rates 0.25 K/s and 0.2 K/s gradually become invisible.[24] The dominant peak actually consists of two overlapping peaks E_{1a} and E_{1b}, as shown in Fig. 1(b). Overall, at least six traps between 200 and 450 K could be postulated in this sample.

Comparison of a TSC spectrum with the DC is shown in Fig. 1(c). The dominant peak containing E_{1a} and E_{1b} is clearly shown in TSC and the dark current activation energy is ∼0.62 eV. The net TSC (total TSC minus DC) is shown in Fig. 1(d). The peak near 425 K can be fitted with a modified Gaussian, yielding one peak at ∼414 K with E_a at 0.90 eV (E_2) and another at ∼441 K with E_a = ∼0.99 eV (E_3), with the calculations based on Eq. (4).

TSC and DC spectra of the second thin film (film-2) are shown in Fig. 2. The DCs were about 1 pA at RT and less than 65 pA at 450 K, indicating the sample is highly resistive at room temperature (RT). The dark current activation energy (E_{DC}) is ∼0.84 eV. TSC measurements show that no peaks were observed in this sample. But the TSC and DC are different from 300 to 450 K, and the net TSC shows a broad peak near 420 K which can be subjected to a Gaussian fitting, yielding one peak at ∼388 K with E_a = ∼0.84 eV (E_2) and another at ∼435 K with E_a = ∼0.97 eV (E_3).

A 152 nm thick PLD-grown β-Ga_2O_3 thin film-3 was studied by TSDC and is shown in Fig. 3. The sample was kept under a bias of −100 V at 425 K initially for 5 min before cooling down to 83 K, and then the bias was turned off and the TSDC was measured while raising the temperature. It can be seen that the dominant peak at ∼112 K shifts with the heating rate, with an activation energy of ∼0.105 eV obtained through Eq. (8). A bump between 350 and 400 K can be also seen, indicating that one or two other peaks (i.e., E_2 and/or E_3 peaks) may also be present.

B. Deep levels in CZ-grown β-Ga_2O_3 bulk crystals

Similarly, the deep level traps in CZ-grown β-Ga_2O_3 bulk crystals were also studied using both TSC and TSDC techniques. Figure 4(a) shows the DC under 100 V bias as a function of inverse temperature. Note that the resistance at about 385 K (1000/T = 2.6) is approximately 100 V/1000 pA = 10^{11} Ω, indicating that the crystal is semi-insulating despite the fact that it was unintentionally doped. On the other hand, the DC activation energy is 0.3 eV, which in a simple conduction model would be near the energy of the dominant donor and would seemingly generate a much lower resistivity at 385 K. This inconsistency can possibly be explained by the high light sensitivity of this material, which produces not only photocurrent but also persistent photocurrent (PPC), i.e., the failure of the traps to

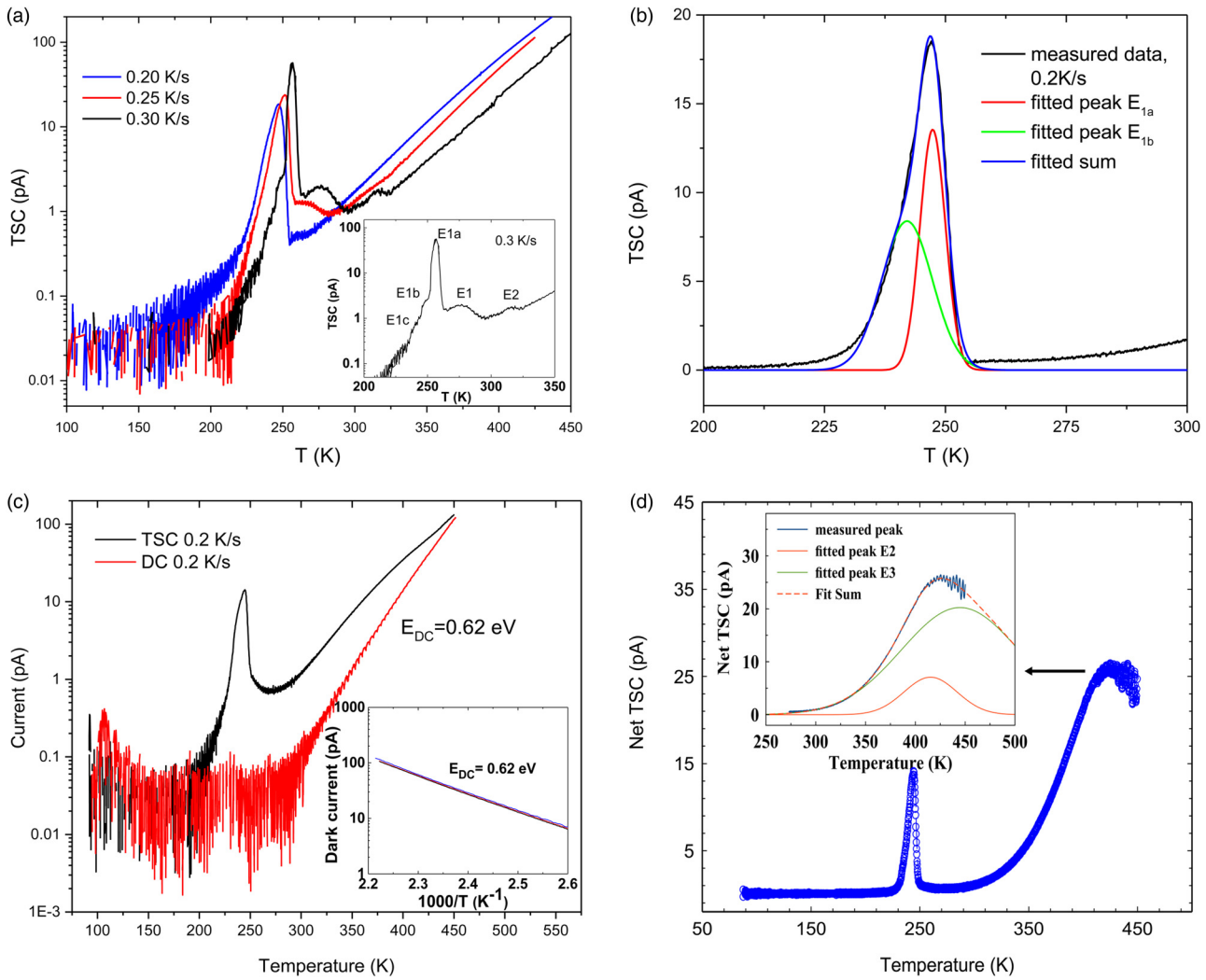

FIG. 1. TSC spectra of Ga_2O_3 thin film-1. (a) TSC after illumination of 400 nm LED mixed with white light at 83 K, at a bias of 100 V for 30 min with different sweeping rates, at least five traps were found between 200 and 350 K through these measurements. (b) Two peaks E_{1a} and E_{1b} contained in the dominant peak can be fitted by a Gaussian curve fit. (c) Comparison of TSC and DC, the E_{DC} is 0.62 eV. (d) The peak at 425 K appears in the net TSC, which can be fitted by Gaussian fit producing peaks E_2 at ~414 K and E_3 at ~441 K.

empty quickly after the light is removed. Moreover, because the crystal is very sensitive to light, a stronger light and/or longer illumination produced more PC and thus more PPC, as shown in Fig. 4(b).

Because of the strong PPC, TSC spectra were not easily measurable in the bulk crystal and thus the defects were primarily studied by TSDC. Figure 5 shows TSDC spectra under two different polarization conditions. At least 9 peaks, including those obtained in the thin films, were found in these spectra. Despite the differences in TSC and TSDC, their respective spectra are comparable. As seen in Fig. 5, peaks E_1, E_2, and E_3 that appeared in Figs. 1 and 2 were also found in the TSDC spectra; in addition, a peak around 225 K (E_{1a}) appears in both spectra. However, the peaks at ~150 K and a spike between E_{1a} and E_1 at ~230 K in the TSDC spectra are not seen in the TSC spectra.

C. Discussion

The dark currents generated in each sample were different, so that the activation energies were different. Earlier we estimated from Fig. 4(a) that the resistance of the bulk sample was about 10^{11} Ω at 385 K. From Figs. 1(c) and 2(b), it is clear that the PLD thin films have similarly high resistances. Since such high resistances are not compatible with low DC activation energies, we

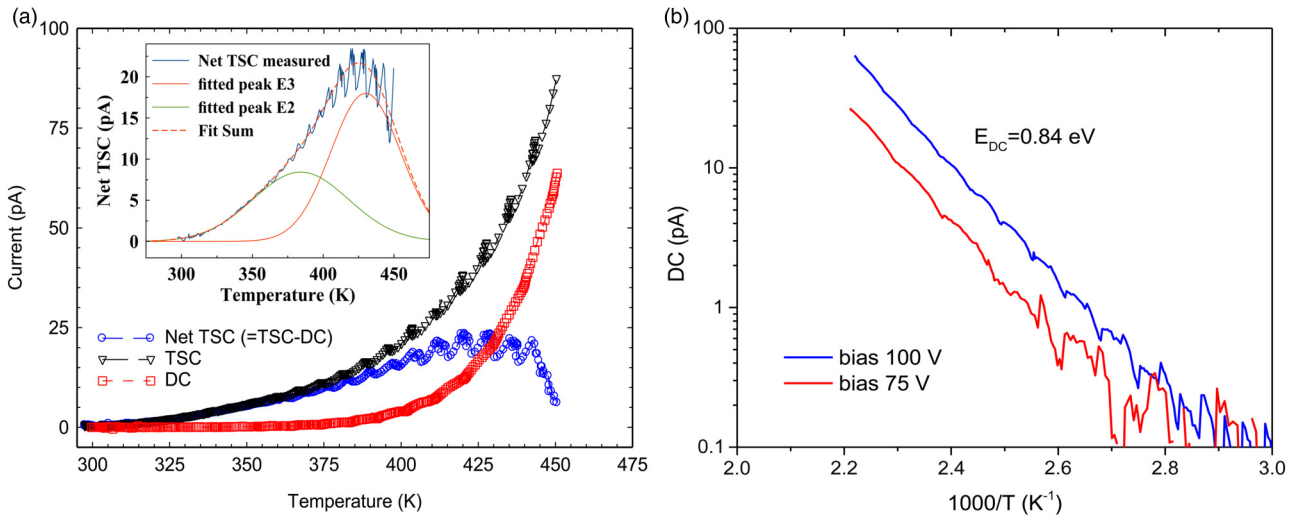

FIG. 2. (a) TSC spectra of β-Ga_2O_3 thin film-2. No clear peaks appear after a number of light illuminations, but the net TSC generates a broad peak at ~425 K producing peaks E_2 at ~388 K and E_3 at ~435 K (inset), through a Gaussian fit. (b) The DC activation energy for this sample is ~0.84 eV.

believe the latter can sometimes be influenced by the traps themselves, perhaps by stray light or PPC following intentional light irradiation. Even weak stray light could continuously fill a trap while thermal excitations were emptying it. The net result would be an equilibrium electron concentration and current at a given temperature, with the measured E_{DC} related to the trap energy.

The E_{DC} of thin film-1 is 0.62 eV, E_{DC} of thin film-2 is 0.84 eV, while the bulk has an E_{DC} ~0.30 eV. An E_{DC} for thin film-3 was not obtainable. From the E_{DC} we obtained, it is suggested that the electrical conductions in thin film-2 and the bulk crystal are trap-assisted tunneling conduction as 0.84 eV and 0.30 eV, respectively, are one of their traps as revealed by TSC or TSDC. The observed variation of different dark current domination may be related to different preparation conditions. The background *n*-type conductivity of β-Ga_2O_3 may result from an oxygen deficiency and deviation from the stoichiometry, which can lead to oxygen vacancies or Ga interstitials.[25,26] But a widely reported unintentional background donor for melt-grown bulk Ga_2O_3 is silicon,[6,7] while the films' conduction may be controlled by Fe and other impurities since 0.84 eV is attributed to iron.[27]

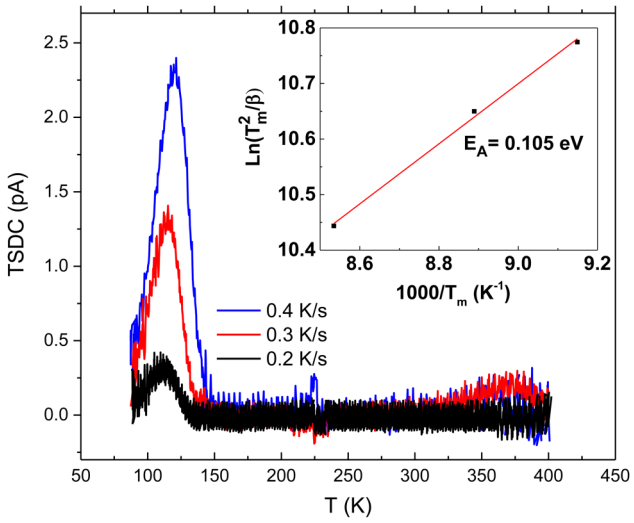

FIG. 3. TSDC spectra of a 152 nm β-Ga_2O_3 thin film-3, initially under a bias of −100 V at 425 K for 5 min before cooling down to 83 K. The inset is the Arrhenius plot which leads to an activation energy of ~0.105 eV.

Depending on the growth conditions and orientations, each Ga_2O_3 sample may have a slightly different bandgap E_g as well. It is reported that E_g varies from 4.5 to 4.9 eV depending on sample stoichiometry and crystal quality.[1] For our samples, optical measurements also give an E_g around 4.5–4.9 eV. The traps around 0.1 to 1 eV revealed by our thermally stimulated techniques in both thin films and the bulk crystal are listed in Table I. Each sample clearly has different *dominant* traps; also, in some cases, a particular trap may show slightly different energy levels.

The dominant peak in thin film-1 contains two traps 0.52 eV and 0.49 eV. These two traps can be assigned as E_{1a} and E_{1b}. The dominant traps in thin film-2 are 0.84 eV (E_2) and 0.99 (E_3), while 0.1 eV is the only dominant peak in thin film-3. The bulk crystal has a dominant trap at 0.3 eV plus E_1, E_2, and E_3.

Traps E_1, E_2, and E_3 in Table I have been reported in DLTS experiments previously,[8,9] but some differences in energy for a specific trap have been noted earlier. The energy level E_1 varies from 0.54 to 0.62 eV, E_2 is between 0.76 and 0.85 eV, and E_3 varies from 0.99 to 1.06 eV below the conduction band. Another reported trap, E_4 at ~1.48 eV, is not observable in our experimental system since a temperature higher than 500 °C is required to reveal it.

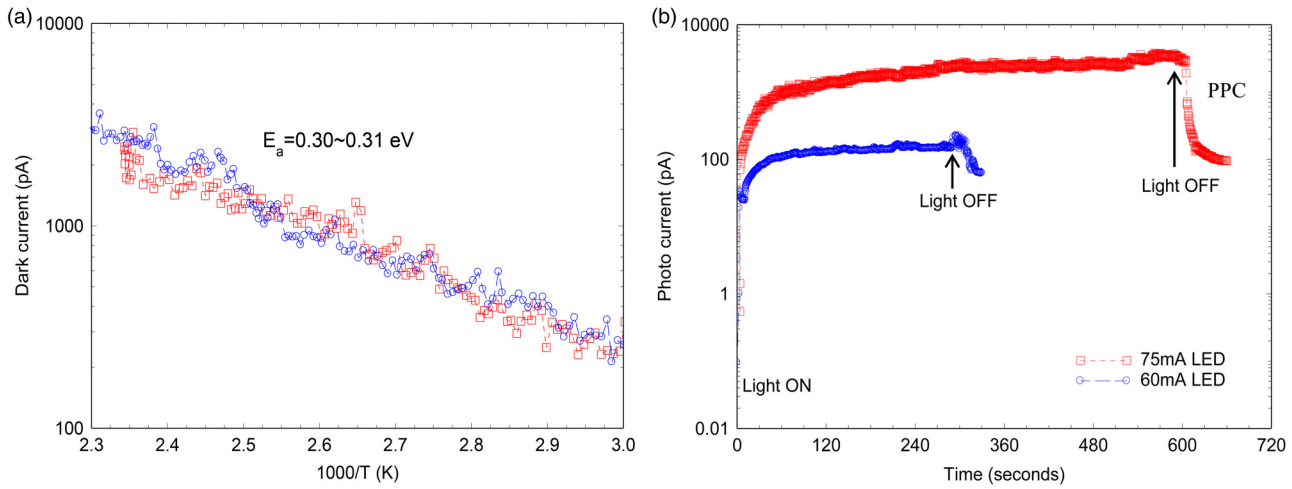

FIG. 4. DC and PC of bulk Ga_2O_3. (a) The dark currents were measured with 0.2 K/s and 0.3 K/s heating rates, both showing a DC activation energy of ~0.30 eV. (b) The photo currents were obtained under different LED intensities. A stronger light and longer illumination produce more PC and generate more persistent photocurrent (PPC).

The targets of film-1 and film-3 were all doped with Sn. Tin is assumed to be a shallow donor, but the grown films were not conductive. Therefore, tin might not be activated or did not go in as a donor in our cases. A similar case was found in Sn-doped β-Ga_2O_3 layers on sapphire by MOVPE.[28] Difficulties in achieving Sn-doped β-Ga_2O_3 electrically conductive have been attributed to the compensation Sn donor by deep acceptor species ascribed to gallium vacancies or carbon-related states.[29] Nevertheless, most of the traps we found match with what have been reported in the literature. For film-2, which was grown at a high T (~650 °C) in O_2 + Ar, the DC activation energy was ~0.84 eV, and the only broad TSC peak at ~425 K produced peaks E_2 at ~388 K and E_3 at ~435 K. For this sample, E_2 is lower than what we found in film-1, but closer to what has been reported for E_2 in bulk crystals.

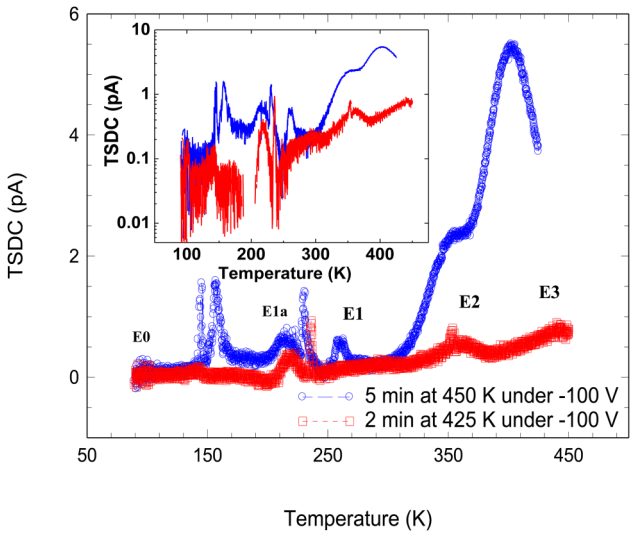

FIG. 5. TSDC spectra of bulk β-Ga_2O_3. The inset contains a log plot for greater clarity. Before TSDC measurements, the sample was initially polarized under a dc electric field $E_p = -100$ V, at temperatures $T_p = 425$ and 450 K for polarization times $t_p = 2$ min and 5 min, respectively. (Since some heating fluctuations occurred when the temperature was at ~400 K or above in cryostat or because of different polarization conditions, slight differences in peak positions such as E_3 can be seen.)

Comparing the bulk crystal spectra with those of the thin films, some peaks appear in the spectra of both thin films and bulk crystals, but more peaks were found in the TSDC spectra of the bulk crystal because the electronic defects or crystal lattice deformation such as impurity-induced defects or structural changes with temperature in a crystal could be more easily reflected by TSDC processes. Note that thermally stimulated processes induced by polarization are not only related to the individual defects but also to the crystal field, and thus may lead to some different spectra in the single crystals than in the films and in the TSDC than TSC.[23]

TSDC spectra depend on the polarization process. Applying a bias on the sample at high temperature facilitates quicker polarization of the crystal structure and produces more TSD current, and the corresponding peaks are more observable in the TSDC measurements. At the same high T, a longer polarization time t_p at the same field E_p could produce stronger TSDC too, as seen in Fig. 5. Therefore, in the actual measurement, we first raised the sample temperature to 450 K without bias, and then applied the bias at this temperature for 5 min or more before cooling down to 83 K at a constant rate to reach the equilibrium polarization. In addition, different polarization conditions may lead to slightly different spectra so that a specific peak may have a different intensity or the position may be slightly different. For example, E_1 and E_3 show some difference in each TSDC spectra. The slightly different spectra might also result from some thermal non-uniformity in the crystal since β-Ga_2O_3 has a small thermal conductivity.[1]

TABLE I. Comparison of traps and their activation energies found in β-Ga_2O_3 thin films and bulk crystals by thermally stimulated techniques.

		Traps found by thermally stimulated techniques							
Ga_2O_3 samples	Growth conditions	E_{DC}	E_0	E_{1c}	E_{1b}	E_{1a}	E_1	E_2	E_3
Thin film-1	PLD	0.62		0.43	0.49	0.52	0.56	0.91	0.99
~519 nm	50 mTorr O_2, 550 °C								
Thin film-2	PLD	0.84						0.84	0.97
~950 nm	100 mTorr, 50%O_2 + 50%Ar, 650 °C								
Thin film-3	PLD		0.105					~0.80	
~152 nm	5 mTorr Ar, 550 °C								
Bulk	CZ	0.30	~0.1	0.30	0.43	0.54	0.62	0.82	~1.00
E309-176#9	(010) plate								
$8 \times 8 \times 2$ mm^3	Unintentionally-doped								

Despite different dwelling conditions (T_p and t_p) producing slightly different TSDC spectra in Fig. 5, the TSDC spectra of the crystal are similar to the TSC spectra we found in the thin films and the DLTS of other crystals reported in the literature. Therefore, the dominant peaks such as E_1, E_2, and E_3 have been readily detected by both TSC and TSDC. On the other hand, because TSDC can reveal crystal lattice relaxation, some of the traps at ~150 K that might be related to the Ga_2O_3 crystal lattice relaxation upon crystal field variation only appear in the TSDC spectra of the bulk crystal.

It is understandable that different growth conditions or methods produce samples that may contain different deep level defects; even a same trap in the similar samples may appear at a slightly different energy level. The different trace impurities or defect centers in each sample may be responsible for the spectral differences between samples. Besides, the different measurement conditions may also lead to some differences in the spectra. Nevertheless, the most characteristic traps we found in the resistive PLD films as well as in the bulk crystals either by TSC or by TSDC are generally similar to those reported in the literature by other techniques such as DLTS.

Several featured trap identities in β-Ga_2O_3 have been proposed. Irmscher *et al.*[6] believe that Fe and Co, common contaminants, may be involved in the levels at around 0.54 (E_1) and 1.0 eV (E_3) below the conduction band minimum (CBM). Fe_{Ga} is a likely candidate for the 0.84 eV (E_2) level.[27] Zhang *et al.*[7] report a level appearing in the vicinity of 0.80 eV (E_2) below the CBM. This center, conventionally labeled E_2, has been identified in numerous samples grown from independent techniques and may result from the most dominant source–background compensation of iron in most of β-Ga_2O_3 samples.

A donor at ~110 meV was studied by Neal *et al.* via temperature dependent Hall-effect measurements up to 1000 K and by temperature dependent admittance spectroscopy.[30] They believe that a native defect such as an anti-site or interstitial is possibly responsible for this center, since oxygen and gallium vacancies have been determined to be deeper donors and acceptors. Another possibility is that silicon on the octahedrally coordinated Ga(II) could be responsible for the 110 meV donor. Interestingly, we find this peak only in TSDC spectra, and only in CZ-grown bulk and thin film-3. With respect to the other thin films, film-3 is thinner and was grown in a low pressure Ar atmosphere; these reasons might lead to this particular trap being dominant in this sample, but the exact reasons are unknown.

Deep level defects at 0.62 eV, 0.82 eV, 1.00 eV, 2.16 eV, and 4.40 eV have been detected in (010) β-Ga_2O_3 by optically and thermally stimulated defect spectroscopy.[7,11] By employing a steady-state photo-capacitance (SSPC) spectroscopy technique, Nakano[9] revealed defects located at ~0.80, ~2.04, ~2.71, ~3.71, ~3.87, and ~4.30 eV, respectively.

Self-trapped holes and gallium vacancies in the deep level region have also been found in β-Ga_2O_3 crystals using electron paramagnetic resonance (EPR)[31,32] and identification of one oxygen vacancy-related and two gallium vacancy-related energy levels in various β-Ga_2O_3 samples by depth-resolved cathodoluminescence spectroscopy and surface photovoltage spectroscopy.[33] Since the TSC and TSDC techniques cannot distinguish whether the trapped carriers are holes or electrons, it is not ruled out that some of the traps we found could be attributed from these vacancy-related deep level defects.

IV. SUMMARY

By comparatively studying the thermally stimulated current spectroscopy and thermally stimulated depolarization current spectroscopy of β-Ga_2O_3 films grown by PLD and bulk crystals by CZ, we not only have found conventional traps such as E_1, E_2, and E_3 reported in the literature using DLTS but also other traps. This work demonstrates that current-based trap emission, such as that associated with TSC and TSDC, can effectively reveal deep level defects in highly-resistive semiconductor materials, especially those not amenable to capacitance-based analytical techniques, such as DLTS.

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REFERENCES

[1]S. J. Pearton, J. Yang, P. H. Cary, F. Ren, J. Kim, M. J. Tadjer, and M. A. Mastro, "A review of Ga_2O_3 materials, processing, and devices," Appl. Phys. Rev. **5**, 011301 (2018).

[2]M. Higashiwaki, K. Sasaki, H. Murakami, Y. Kumagai, A. Koukitu, A. Kuramata, T. Masui, and S. Yamakoshi, "Recent progress in Ga_2O_3 power devices," Semicond. Sci. Technol. **31**, 034001 (2016).

[3]K. D. Chabak, N. Moser, A. J. Green, D. E. Walker, Jr., S. E. Tetlak, E. Heller, A. Crespo, R. Fitch, J. P. McCandless, K. Leedy, M. Baldini, G. Wagner, Z. Galazka, X. Li, and G. Jessen, "Enhancement-mode Ga_2O_3 wrap-gate fin field-effect transistors on native (100) β-Ga_2O_3 substrate with high breakdown voltage," Appl. Phys. Lett. **109**, 213501 (2016).

[4]F. Zhang, K. Saito, T. Tanaka, M. Nishio, and Q. Guo, "Electrical properties of Si doped Ga_2O_3 films grown by pulsed laser deposition," J. Mater. Sci. Mater Electron. **26**(12), 9624–9629 (2015).

[5]E. G. Víllora, K. Shimamura, Y. Yoshikawa, T. Ujiie, and K. Aoki, "Electrical conductivity and carrier concentration control in β-Ga_2O_3 by Si doping," Appl. Phys. Lett. **92**, 202120 (2008).

[6]K. Irmscher, Z. Galazka, M. Pietsch, R. Uecker, and R. Fornari, "Electrical properties of β-Ga_2O_3 single crystals grown by the Czochralski method," J. Appl. Phys. **110**, 063720 (2011).

[7]Z. Zhang, E. Farzana, A. R. Arehart, and S. A. Ringel, "Deep level defects throughout the bandgap of (010) β-Ga_2O_3 detected by optically and thermally stimulated defect spectroscopy," Appl. Phys. Lett. **108**, 052105 (2016).

[8]M. E. Ingebrigtsen, L. Vines, G. Alfieri, A. Mihaila, U. Badstübner, B. G. Svensson, and A. Kuznetsov, "Bulk β-Ga_2O_3 with (010) and (-201) surface orientation: Schottky contacts and point defects," Mater. Sci. Forum **897**, 755–758 (2017).

[9]Y. Nakano, "Electrical characterization of β-Ga_2O_3 single crystal substrates," ECS J. Solid State Sci. Technol **6**(9), 615–617 (2017).

[10]A. Y. Polyakov, N. B. Smirnov, I. V. Shchemerov, E. B. Yakimov, S. J. Pearton, C. Fares, J. Yang, F. Ren, J. Kim, P. B. Lagov, V. S. Stolbunov, and A. Kochkova, "Defects responsible for charge carrier removal and correlation with deep level introduction in irradiated β-Ga_2O_3," Appl. Phys. Lett. **113**, 092102 (2018).

[11]E. Farzana, E. Ahmadi, J. S. Speck, A. R. Arehart, and S. A. Ringel, "Deep level defects in Ge-doped (010) β-Ga_2O_3 layers grown by plasma-assisted molecular beam epitaxy," J. Appl. Phys. **123**, 161410 (2018).

[12]M. Orita, H. Ohta, M. Hirano, and H. Hosono, "Deep ultraviolet transparent conductive in β-Ga_2O_3 thin films," Appl. Phys. Lett. **77**, 4166 (2000).

[13]K. D. Leedy, K. D. Chabak, V. Vasilyev, D. C. Look, J. Boeckl, J. L. Brown, S. E. Tetlak, A. J. Green, N. A. Moser, A. Crespo, D. B. Thomson, R. C. Fitch, J. P. McCandless, and G. H. Jessen, "Highly conductive homoepitaxial Si-doped Ga_2O_3 films on (010) β-Ga_2O_3 by pulsed laser deposition," Appl. Phys. Lett. **111**, 012103 (2017).

[14]X. Chen, S. Han, Y. Lu, P. Cao, W. Liu, Y. Zeng, F. Jia, W. Xu, X. K. Liu, and D. Zhu, "High signal/noise ratio and high-speed deep UV detector on β-Ga_2O_3 thin film composed of both (400) and (-201) orientation β-Ga_2O_3 deposited by the PLD method," J. Alloys Compd. **747**, 869–878 (2018).

[15]R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes* (Pergamon Press, New York, 1981).

[16]D. C. Look, "The electrical and photoelectronic properties of semi-insulating GaAs," Semiconduct. Semimet. **10**, 75–170 (1983).

[17]J. Vanderschueren and J. Gasiot, "Field-induced thermally stimulated currents," in Thermally Stimulated Relaxation in Solids, Topics in Applied Physics, edited by P. Braunlich (Springer, Berlin, 1979), Vol. 37, p. 135, ISBN 978-3-540-34797-2.

[18]D. C. Look, Z.-Q. Fang, J. W. Hemsky, and P. Kengkan, "Identification of electron-irradiation defects in semi-insulating GaAs by normalized thermally stimulated current measurements," Phys. Rev. **55**, 2214 (1997).

[19]Z.-Q. Fang, D. C. Look, B. Claflin, S. Haffouz, H. Tang, and J. Webb, "Thermally stimulated current spectroscopy and photoluminescence of carbon-doped semi-insulating GaN grown by ammonia-based molecular beam epitaxy," Phys. Status Solidi C **2**(7), 2757–2760 (2005).

[20]P. G. Muzykov, R. M. Krishna, and K. C. Mandal, "Characterization of deep levels in n-type and semi-insulating 4H-SiC epitaxial layers by thermally stimulated current spectroscopy," J. Appl. Phys. **111**, 014910 (2012).

[21]F. E. Kamel, P. Gonon, F. Jomni, and B. Yangui, "Thermally stimulated currents in amorphous barium titanate thin films deposited by RF magnetron sputtering," J. Appl. Phys. **100**, 054107 (2006).

[22]M. Ouwerkerk, F. J. Veldkamp, and J. Schoonman, "Thermally stimulated depolarization current measurements on $Ba_{1-x}La_xF_{2+x}$ and $Ba_{1-x}U_xF_{2+2x}$ solid solutions," Solid State Ion. **22**, 173 (1987).

[23]B. Wang, P. Saadatkia, F. A. Selim, and D. Look, "Study of trapping phenomena in $SrTiO_3$ by thermally stimulated techniques," J. Electron. Mater. **47**, 604–611 (2018).

[24]B. Wang, J. Anders, K. Leedy, M. Schuette, and D. Look, "Persistent photocurrent and deep level traps in PLD-grown In-Ga-Zn-O thin films studied by thermally stimulated current spectroscopy," Proc. SPIE **10533**, 1053314 (2018).

[25]J. B. Varley, J. R. Weber, A. Janotti, and C. G. Van de Walle, "Oxygen vacancies and donor impurities in β-Ga_2O_3," App. Phys. Lett. **97**, 142106 (2010).

[26]E. Korhonen, F. Tuomisto, D. Gogova, G. Wagner, M. Baldini, Z. Galazka, R. Schewski, and M. Albrecht, "Electrical compensation by Ga vacancies in Ga_2O_3 thin films," Appl. Phys. Lett. **106**, 242103 (2015).

[27]M. E. Ingebrigtsen, J. B. Varley, A. Yu. Kuznetsov, B. G. Svensson, G. Alfieri, A. Mihaila, U. Badstübner, and L. Vines, "Iron and intrinsic deep level states in Ga_2O_3," Appl. Phys. Lett. **112**, 042104 (2018).

[28]D. Gogova, M. Schmidbauer, and A. Kwasniewski, "Homo- and heteroepitaxial growth of Sn-doped β-Ga_2O_3 layers by MOVPE," Cryst. Eng. Comm. **17**, 6744 (2015).

[29]A. Y. Polyakov, N. B. Smirnov, I. V. Shchemerov, D. Gogova, S. A. Tarelkin, and S. J. Pearton, "Compensation and persistent photocapacitance in homoepitaxial Sn-doped β-Ga_2O_3," J. Appl. Phys. **123**, 115702 (2018).

[30]A. T. Neal, S. Mou, R. Lopez, J. V. Li, D. B. Thomson, K. D. Chabak, and G. H. Jessen, "Incomplete ionization of a 110 meV unintentional donor in β-Ga_2O_3 and its effect on power devices," Sci. Rep. **7**, 13218 (2017).

[31]B. E. Kananen, N. C. Giles, L. E. Halliburton, G. K. Foundos, K. B. Chang, and K. T. Stevens, "Self-trapped holes in β-Ga_2O_3 crystals," J. Appl. Phys. **122**, 215703 (2017).

[32]B. E. Kananen, L. E. Halliburton, K. T. Stevens, G. K. Foundos, and N. C. Giles, "Gallium vacancies in β-Ga_2O_3 crystals," Appl. Phys. Lett. **110**, 202104 (2017).

[33]H. Gao, S. Muralidharan, N. Pronin, M. Karim, S. M. White, T. Asel, G. Foster, S. Krishnamoorthy, S. Rajan, L. Cao, M. Higashiwaki, H. von Wenckstern, M. Grundmann, H. Zhao, D. C. Look, and L. J. Brillson, "Optical signatures of deep level defects in Ga_2O_3," Appl. Phys. Lett. **112**, 242102 (2018).