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Investigation of deep levels in semi-insulating GaAs by means of the temperature change piezoelectric photo-thermal measurements

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The temperature variation of the piezoelectric photo-thermal (PPT) signal intensity of semi-insulating (SI) GaAs from 20 to 150 K was measured. Four peaks at 50, 70, 110, and 125 K were observed in the PPT signal. From the theoretical analysis based on the rate equations of electrons in the conduction band and deep levels, we concluded that the observed four peaks were due to the nonradiative electron transitions through $EL6$, $EL7$, $EL15$, and an unspecified deep level, respectively. Deep levels with extremely low concentration (10^{12}–$10^{15}\,\mathrm{cm}^{-3}$) were clearly identified in SI GaAs by using the PPT method.
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I. INTRODUCTION

Semi-insulating (SI) GaAs grown by the liquid encapsulated Czochralski (LEC) method is a very important material for the GaAs based microwave devices and high-speed integrated circuits. It is commonly understood that this SI property is due to a compensation of the shallow acceptor such as carbon by the $EL2$ midgap donor level ($E_c - 0.75\,\mathrm{eV}$).[1] However, in the melt grown GaAs materials including LEC grown SI GaAs, a large amount of other deep levels in addition to $EL2$ exist and act as a trap center in the GaAs based devices. Therefore, detection and control of such deep levels in SI GaAs are necessary. Although the deep level transient spectroscopy (DLTS) is known to be a powerful tool to detect deep levels in semiconductors, this technique cannot be applied to the high resistive materials such as SI GaAs crystal. The near-infrared optical absorption (NIR) and photoluminescence (PL) techniques have been extensively used to investigate $EL2$ in SI GaAs crystals. However, the sensitivity of these techniques is not sufficient to detect deep levels other than $EL2$ in SI GaAs.

The great advantage of the piezoelectric photo-thermal (PPT) technique is that it is a direct monitor of the nonradiative recombination processes in semiconductors. Heat generated by the nonradiative recombination of photoexcited electrons is detected by the piezoelectric transducer (PZT) directly attached to the rear surface of the sample. Therefore, the PPT technique may complement the NIR and PL techniques, which can directly detect the photoexcitation and radiative recombination processes, respectively. Another advantage is that the PPT technique is sensitive to a very small optical absorption coefficient region. We have already reported[2,3] that the electron transitions involving $EL2$ and $EL6$ in SI GaAs could be clearly resolved by this technique.

In this article, we propose an aspect for investigating deep levels in SI GaAs by measuring the temperature variation of the PPT signal intensity. Four peaks at 50, 70, 110, and 125 K were observed in the PPT signal. From the theoretical analysis based on the rate equations of electrons in the conduction band and deep levels, we identified the observed four peaks as the nonradiative electron transitions through $EL6$, $EL7$, $EL15$, and an unspecified deep level, respectively. Deep levels with extremely low concentration (10^{12}–$10^{15}\,\mathrm{cm}^{-3}$) were clearly detected in SI GaAs by using the PPT method.

II. EXPERIMENTS AND RESULTS

The sample is a GaAs wafer cut to $1\times1\times0.05\,\mathrm{cm}^3$ from an undoped, LEC-grown SI crystal, which has undergone a three-stage ingot annealing[4] to improve the uniformity within a wafer and to remove the irrelevant intrinsic defects. The resistivity of the sample is about $24\times10^7\,\Omega\,\mathrm{cm}$. The concentrations of $EL2$ deep donor and carbon acceptor are 1.3 and $1.1\times10^{16}\,\mathrm{cm}^{-3}$, respectively. After a disk shaped PZT was attached to the rear surface of the sample using a silver conducting paste, the sample was placed on the cryostat. The probing light to measure the PPT signal was mechanically

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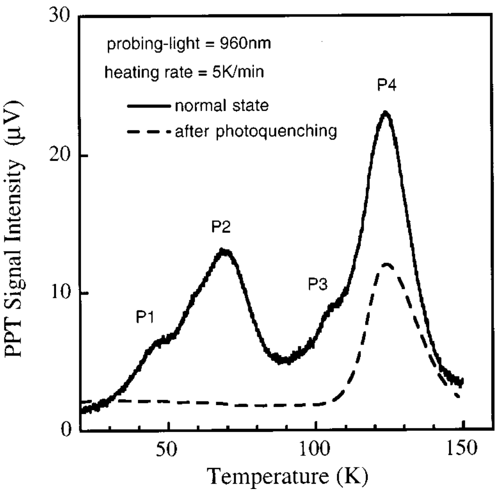

FIG. 1. Temperature variations of the PPT signal intensity from 20 to 150 K. An effect of the photoquenching of EL2 is also shown by the broken curve.

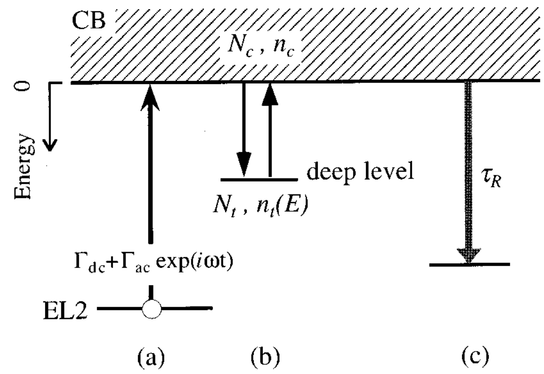

FIG. 2. Proposed electron generation and recombination dynamics to explain the observed temperature variation of the PPT signal. Process (a) is the photoexcitation of electron process from EL2 deep donor, (b) is the trapping and detrapping processes of electron by the deep level and (c) is the other trapping effects such as surface recombination.

chopped at a frequency of 200 Hz and was always focused on the surface of the sample. Heat generated by the nonradiative recombination was detected by PZT. The detected signal was amplified as the PPT signal in a lock-in amplifier. A detailed description on the measurement is given in our earlier paper.[5]

The temperature variation of the PPT signal intensity from 20 to 150 K was measured as follows. The sample was first cooled down to 20 K in the dark. Next, the temperature of the sample was increased to 150 K with a constant heating rate of 5 K/min. The PPT signal intensity at the probing light wavelength of 960 nm was simultaneously recorded as a function of temperature. It was ascertained that the intensity of the probing light was sufficiently weak (0.17 mW/cm^2) not to introduce any additional effects such as photoquenching of $EL2$ (Ref. 2) during the heating runs. The result is shown in Fig. 1 by the solid curve. We observed four distinctive peaks at 50, 70, 110, and 125 K. These peaks were reproducible both for heating and cooling runs. No effect of the heating rate changing from 2 to 10 K/min on the shapes of the curves was observed. We, hereafter, refer to these peaks as $P1$, $P2$, $P3$, and $P4$ peaks, respectively.

To clarify the contribution of $EL2$ to the observed four PPT peaks, we consider a photoquenching effect of $EL2$. This is a phenomenon in which all the optical and electrical activities of $EL2$ are extinguished when a GaAs sample is illuminated by a light at a wavelength about 1 μm below 130 K.[2,3,6] The photoquenched state is said to be metastable because the optical and electrical activities can recover upon annealing the sample at around 150 K for a few minutes. The photoquenching measurements in the present study was carried out as follows. The sample was cooled down to 20 K in the dark and the quenching light of 1.1 μm (4.5 mW/cm^2) was illuminated on the sample for 30 min. After the quenching light was cut off, the PPT signal intensity at 960 nm was also recorded with increasing the temperature with a heating rate of 5 K/min. The result was shown in Fig. 1 by the broken curve. Three peaks of $P1$, $P2$, and $P3$ completely disappeared and the intensity of the $P4$ peak decreased by the photoquenching of $EL2$. All peaks appeared again after the sample was annealed at 150 K for 5 min and was subsequently cooled down to 20 K. This means that the thermal recovery of $EL2$ does occur. We then consider that $EL2$ plays an important role in generating the PPT signal peaks observed in the present temperature region.

III. DISCUSSION

Considering the effect of the photoquenching of $EL2$ on the temperature variation of the PPT signal, it is found that $EL2$ contributes to the signal generation mechanism of these peaks. First of all, we attempt to explain the experimental results by the model that all the four peaks are due to the nonradiative recombination through only $EL2$. Since $EL2$ is a double donor which has two energy levels in the band gap at $E_c - 0.75(EL2^{0/+})$ and $E_v + 0.54\,\mathrm{eV}(EL2^{+/++})$,[7,8] the nonradiative recombination of electrons through these two energy levels of $EL2$ may cause the four PPT signal peaks. However, the second energy level $EL2^{+/++}$ is supposed to be negligible or inactive in the SI sample. The reason is that the concentration of $EL2$ is larger than that of the carbon acceptor and only the first energy level of $EL2$ exists. We may, therefore, reasonably concluded that the experimental results could not be explained by this model.

We then consider that observed four peaks are due to capturing the photoexcited electrons from $EL2$ by certain deep levels other than $EL2$. In this model, $EL2$ only acts as a source of the photoexcited electrons. We propose the electron generation and recombination dynamics to explain the temperature variation of the PPT signal based on the modulated photocurrent technique proposed by Oheda.[9] Transition processes of electrons are schematically illustrated in Fig. 2. The process (a) in Fig. 2 indicates a photoexcitation of electron from $EL2$. Since the probing light of 960 nm has a photon energy of 1.29 eV lower than the band gap energy of GaAs (1.51 eV at 77 K), we only consider electrons excited from $EL2$ deep donor. This is a valid assumption because the concentrations of donor levels other than $EL2$ are considered to be smaller than that of $EL2$.[1] The intensity of the probing light varies with time t, involving a constant term as well as an oscillatory term like $\exp(i\omega t)$, where ω is an angular frequency. Therefore, the rate of photoexcitation of electrons can be expressed by $\Gamma=\Gamma_{\mathrm{dc}}+\Gamma_{\mathrm{ac}}\exp(i\omega t)$. The process (b) represents the trapping and detrapping process of electron by the deep level. Trapping effects due to other mechanisms such as surface recombination are included in terms of carrier lifetime τ_R (process (c)). The rate equations for electrons in the conduction band (CB) and a deep level can be described as

$$\frac{dn_c}{dt}=\Gamma_{\mathrm{dc}}+\Gamma_{\mathrm{ac}}\exp(i\omega t)-\frac{dn_t(E)}{dt}-\frac{n_c-n_{c0}}{\tau_R} \tag{1}$$

and

$$\frac{dn_t(E)}{dt}=n_c\{N_t(E)-n_t(E)\}\sigma_t v_{th}$$
$$-N_c\sigma_t v_{th} n_t(E)\exp(-E/kT), \tag{2}$$

where n_c and $n_t(E)$ are the electron concentrations in the CB and the deep level with an activation energy E and a concentration $N_t(E),\sigma_t$ a capture cross section for electrons of the deep level, v_{th} thermal velocity, and N_c an effective density of states of the CB, respectively. Since the photoexcitation is modulated at an angular frequency of ω, as discussed, the solutions of Eqs. (1) and (2) are expected to have the following forms:

$$n_c=n_{cd}+n_{ca}\exp(i\omega t) \tag{3}$$

and

$$n_t(E)=n_{td}(E)+n_{ta}(E)\exp(i\omega t). \tag{4}$$

Using Eqs. (1)–(4), n_{ca}, $n_{td}(E)$, and $n_{ta}(E)$ are solved exactly as

$$n_{ca}=\Gamma_{\mathrm{ac}}\Bigg(1/\tau_R+i\omega$$
$$+\frac{i\omega N_t(E)\sigma_t v_{th}}{i\omega+N_c\sigma_t v_{th}\{\exp(-E_F/kT)+\exp(-E/kT)\}}$$
$$\times\frac{1}{1+\exp\{-(E_F-E)/kT\}}\Bigg)^{-1}, \tag{5}$$

$$n_{td}(E)=\frac{N_t(E)}{1+\exp\{(E_F-E)/kT\}}, \tag{6}$$

and

$$n_{ta}(E)=\frac{n_{ca}\{N_t(E)-n_{td}(E)\}\sigma_t v_{th}}{i\omega+\{n_{cd}+N_c\exp(-E/kT)\}\sigma_t v_{th}}, \tag{7}$$

respectively. In Eqs. (5)–(7), the quasi-Fermi level for an electron E_F is defined as

$$n_{cd}=N_c\exp(-E_F/kT). \tag{8}$$

Next, we consider how the PPT signal does occur by using the present theoretical analysis given. We can suppose two signal generation mechanisms in the electron generation and recombination dynamics as shown in Fig. 2. One is the phonon emission accompanied by a nonradiative recombination of electron to the deep level indicated in the process (b) by a downward arrow. Another is a phonon absorption caused by the thermal emission of electron from deep level to the CB shown in the process (b) by the upward arrow. As a result, the PPT signal is expected to be the sum of these two mechanisms. One note that the sum of two signal generation mechanisms is the same as the right-hand side of Eq. (2). Therefore, the PPT signal is expected to be proportional to the modulation part of $dn_t(E)/dt$. Since we observed four peaks in the experimental results, this model should be expanded to the multilevel case. The PPT signal is then given by

$$V_{\mathrm{ac}}=A\times\sum_j\left(\frac{dn_t(E^j)}{dt}\right)_{\mathrm{ac}}$$
$$=A\times\sum_j\,[n_{ca}^j\{N_t(E^j)-n_{td}(E^j)\}\sigma_t^j v_{th}-n_{cd}n_{ta}(E^j)\sigma_t^j v_{th}$$
$$-N_c n_{ta}(E^j)\sigma_t^j v_{th}\exp(-E^j/kT)], \tag{9}$$

where A is a constant. In this model, we considered that there is no interaction between the deep levels. We also took into account the temperature variations of the thermal conductivity and the specific heat of GaAs. Since these parameters contribute to the PPT signal generation,[10] these effects were involved in the constant A in Eq. (9) in our model.

The temperature variations of the experimental and calculated PPT amplitude signals given by Eq. (9) are shown in Fig. 3. Since four peaks are independently contributed to the signal, as we have mentioned before, each component contribution is separately illustrated by the four dotted curves. The calculated curve shown by the open circles is the sum of these four curves. Very good agreement between the experimental and calculated PPT signals is accomplished. The best fitted parameters for E, N_t, and σ_t are listed in Table I. We used here $E_{EL2}=0.75\,\mathrm{eV}$, $N_{EL2}=1\times10^{16}\,\mathrm{cm}^{-3}$, and $\sigma_{EL2}=5\times10^{-13}\,\mathrm{cm}^2$ for $EL2$ that act as a source of photoexcited electrons. From the similarity of the parameters with those

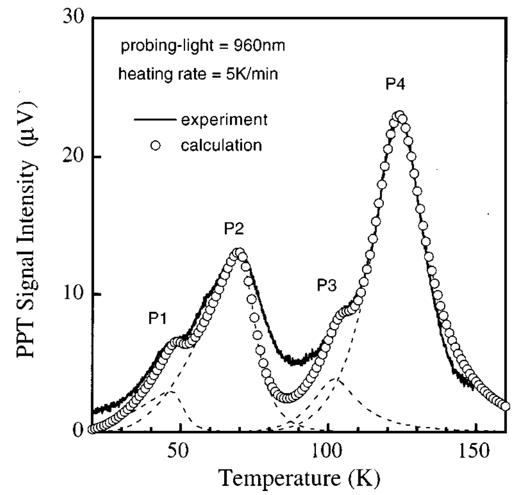

FIG. 3. Temperature variations of the experimental and calculated PPT signal intensities. Good agreement is observed. Since four peaks are independently contributed to the signal, each component contribution is separately illustrated by the four dotted curves. The calculated curve shown by the open circles is the sum of these four curves.

TABLE I. The best fitted parameters of E, N_t, and σ_t for deep levels. We used here $E_{EL2}=0.75$ eV, $N_{EL2}=1\times10^{16}$ cm^{-3}, and $\sigma_{EL2}=5\times10^{-13}$ cm^2 for $EL2$ that act as a source of photoexcited electrons. E and σ_t for $EL15$, $EL7$, and $EL6$ reported in the conductive GaAs samples by using the DLTS method[1] are also listed in the last two columns.

Peak	E (eV)	N_t (cm^{-3})	σ_t (cm^2)	Identification	E in Ref. 1	σ_t in Ref. 1
$P1$	0.085	1×10^{12}	5×10^{-14}	...	...	...
$P2$	0.135	1.2×10^{12}	5×10^{-14}	$EL15$	0.15	5.7×10^{-13}
$P3$	0.290	2×10^{14}	5×10^{-13}	$EL7$	0.30	7.2×10^{-15}
$P4$	0.340	1×10^{15}	2.5×10^{-13}	$EL6$	0.35	1.5×10^{-13}

reported in the conductive GaAs samples by using the DLTS method,[1] we identified the deep levels concerning $P2$, $P3$, and $P4$ as $EL15$, $EL7$, and $EL6$, respectively. No deep level with an activation energy of 0.085 eV has been reported so far. It should be concluded that four peaks, $P1$, $P2$, $P3$, and $P4$ are due to the nonradiative transitions of electrons photoexcited from $EL2$ through an unspecified deep level, $EL15$, $EL7$, and $EL6$, respectively.

It is noted here that $P4$ peak due to $EL6$ remains after the photoquenching of $EL2$ as shown in Fig. 1. This is because that the thermal recovery of $EL2$ may partially occur during the heating run. The thermal recovery from the photoquenched $EL2$ to normal $EL2$ occurs by heating the sample above 130 K.[2,11] Therefore, the shape of the $P4$ peak after the photoquenching of $EL2$ is considered to be distorted by two effects, thermal recovery and generation of the peak due to Eq. (9), which simultaneously occur in this temperature region.

IV. CONCLUSION

We proposed an aspect for investigating deep defect levels in SI GaAs by the PPT technique. Four distinctive peaks were observed in the temperature variation of the PPT signal intensity from 20 to 150 K. To explain the experimental results, the theoretical analysis based on the rate equations of electrons in the CB and corresponding deep levels was carried out. In this analysis, we considered that the PPT signal is proportional to the modulation part of $dn_t(E)/dt$. From the similarity of the parameters obtained by the theoretical analysis with those reported in the conductive GaAs samples by the DLTS method, we concluded that the observed four peaks were due to the nonradiative transitions of electrons photoexcited from $EL2$ through an unspecified deep level, $EL15$, $EL7$, and $EL6$, respectively. In the present study, deep levels which have a very low concentration (10^{12}–10^{15} cm^{-3}) were clearly detected in SI GaAs. Since the PPT method does not necessitate the fabrication of electrodes, the usefulness of this method for studying deep levels in SI materials is pointed out.

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