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METASTABLE STATES IN SEMI–INSULATING GaAs REVEALED BY THERMALLY STIMULATED CURRENT SPECTROSCOPY

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ABSTRACT

Thermally stimulated current spectroscopy (TSC) with near band–edge and infrared (IR) light excitation, in conjunction with photocurrent responses at low temperatures, has proved to be a very useful technique for investigating the quenching and recovery of EL2. During the IR quenching process, changes in trap species and carrier lifetime are correlated with the normal and metastable state of EL2. The traps observed in TSC spectra before and after IR quenching are believed to be due to point defects and their complexes, especially complexes involving As_{Ga}, and show a very clear stoichiometry dependence.

Introduction

The midgap donor level EL2 is responsible for the semi–insulating (SI) nature of undoped GaAs. The presence of an optically induced metastable configuration is the most prominent characteristic of this defect. Several phenomena, such as infrared (IR) quenching (of photoconductivity [1], photocapacitance [2], photoluminescence [3], infrared absorption [4] and electron paramagnetic resonance (EPR) [5]), neutralization of shallow acceptors [6], persistent photoconductivity [7] ; the appearance of deep acceptors [8], have been correlated with the transformation of EL2 from its normal state (EL2) to the metastable state (EL2*). The normal state has been well studied experimentally and theoretically, but the metastable state has not, due to the difficulty in detecting it by direct electrical and optical means. Therefore a general consensus concerning the atomic structure of EL2 has not been reached, although it is well accepted that EL2 at least contains the arsenic antisite (As_{Ga}).

In this paper the processes of quenching and thermal/optical recovery of EL2 were studied by thermally stimulated current (TSC) spectroscopy with near band–edge light ($h\nu = 1.46$ eV) and IR light ($h\nu \leq 1.12$ eV) in conjunction with photocurrent response and Hall effect measurements on SI–GaAs samples with different crystal stoichiometries. In contrast to using 1.46 eV light, the application of IR light at low temperatures ($T \leq 100$K) leads to a well–known photocurrent quenching and a corresponding basic change in the features of the TSC spectrum, both of which are highly dependent on crystal stoichiometry. Hall effect measurements during the TSC scan confirm that some deep traps developed after IR quenching are hole traps. For all samples, the quenched–state TSC spectrum can be reversibly changed back to that obtained before IR quenching by raising the temperature to around 120K or higher, which is exactly the same as the temperature of thermal recovery for the EL2* → EL2 transformation. The optical recovery of the TSC spectrum was also checked by using 1.46 eV and 0.9 eV light at $\leq$ 90K, which produce identical results with those of IR absorption studies on the optical recovery of EL2*. All data are consistent with the traps observed in the TSC spectra having a direct association with EL2 and EL2*; note that the other possibility would be an indirect association which could result from a change in the dominant free carrier (being trapped) as EL2 transforms to EL2*. The EL2 quenching/recovery process is thus considered to be controlled by one basic defect (probably As_{Ga}) while the various TSC peaks represent complexes formed from this basic defect and other defects or impurities.

Experimental and Results

The three undoped SI–GaAs samples (113, 059 and 189) used in this study were cut from the centers of their respective wafers, which in turn were taken from ingot–annealed crystals grown by a high–pressure liquid encapsulated Czochrolski (LEC) technique using different melt stoichiometries. For samples 113, 059 and 189, the EL2 concentrations measured by 1.1 μm absorption were 1.1×10^{16} cm^{-3}, 7.4×10^{15} cm^{-3} and 4.0×10^{14} cm^{-3}, corresponding to crystal stoichiometries ranging from As–rich to Ga–rich, and the carbon concentrations determined by 582 cm^{-1} local vibrational mode absorption at room temperature were $< 3 \times 10^{14}$ cm^{-3}, 1×10^{15} cm^{-3}, and 7.4×10^{14} cm^{-3} respectively. Rectangular Hall bar samples ($10 \times 2.5 \times 0.7$ mm^3) with six In contacts, alloyed at 450°C for a few minutes in N_2 flow, were used for the photocurrent (I_{ph}) and TSC measurements. The near band–edge light (1.46 eV) and the IR light ($\leq$ 1.12 eV) were respectively provided by an 100 mW GaAs laser diode and a tungsten lamp (25W) filtered through a Si wafer. The intensity of the IR light source could be varied by a factor of about three. Both the photocurrent response (I_{ph} vs. t) at low temperature ($\leq$ 90K) and the TSC spectrum in a thermal scan were measured under a bias of 20 V by an electrometer (Keithley 616). To keep the same initial conditions for both I_{ph} vs. t and the TSC measurements, the tested sample was always quickly cooled down from 310K to

90K in the dark. The IR photoquenching of I_{ph} at 90K was recorded over periods of up to a few minutes under different IR light intensities. To observe a transformation in the basic TSC spectral features as a function of I_{ph} quenching, the sample was exposed to IR light for various times from 1 sec to a few minutes or longer at $T \leq 90K$ in different runs, then heated from $\leq$ 90K to 270K at a rate of 0.2K/s. To study the thermal recovery of the transformed spectrum, the sample was first excited by IR light for 5 min at 90K to ensure a complete quenching of EL2 and the quenchable TSC traps, then it was warmed up to a certain recovery temperature (T_r) ranging from 90K to 150K, next the sample was quickly cooled back to 90K, and finally the sample was exposed to the same IR light for 1 sec to fill the traps before the TSC thermal scan. To check the optical recovery of the TSC spectrum, both 1.46 eV light from the laser diode, and 0.9 eV light from a monochromator with a tungsten lamp light source (maximum power of 250 W) and a Si filter, were in turn applied to sample 059 which had been completely quenched by IR light (or 1.13 eV light), for a period of from a few seconds to twenty minutes or longer at 90K; this treatment was followed by a standard thermal scan to observe the recovered TSC spectrum. To determine the type (n or p) of the sample after the photoquenching of EL2, and the type of carrier released during the TSC scan (i.e., trap type), Hall effect measurements were carried out by placing the sample on a small rare–earth permanent magnet with a magnetic field strength of 2.4 kG.

The dark currents of the three SI–GaAs samples in the temperature range from 250K to 360K were shown to be controlled by the EL2 donor as deduced from an activation energy of 0.78 eV. TSC spectra after 1.46 eV light excitation for 1 min at 90K are shown in Fig. 1(a) with the I_{ph} vs. t curves at 90K in the inset. The amplitudes of I_{ph} for these three samples show a clear relationship with the crystal stoichiometry or the EL2 concentration, i.e., the more As–rich the crystal (or the more the EL2), the larger the I_{ph}. During the period of excitation (5 min) the I_{ph}'s show no significant photoquenching (at 1.46 eV), except for sample 189 (more Ga–rich) which has a slight reduction of I_{ph}. Correspondingly, TSC spectra, including the spectral structure and the peak height, do not show any change, and the spectra given in Fig. 1(a) are typical ones for the samples with different times of excitation. As seen in the spectra, at least seven traps, with energy levels of 0.49 eV (T_2), 0.42 eV (T_3), 0.29 eV (T_4), 0.27 eV (T_5), 0.23 ($T_5\star$), 0.21 eV (T_6), and 0.17 eV ($T_6\star$) can be deduced. Based on the trap depths and the the stoichiometry dependence of their peak heights, the observed traps are believed to be due to point defects or their complexes with each other and with impurities, as described in our previous paper [9]. From these considerations, T_2 and T_5 may well be related to V_{Ga}, As_{Ga} or As_i and T_3, T_6 and $T_6\star$ to V_{As} or Ga_{As}.

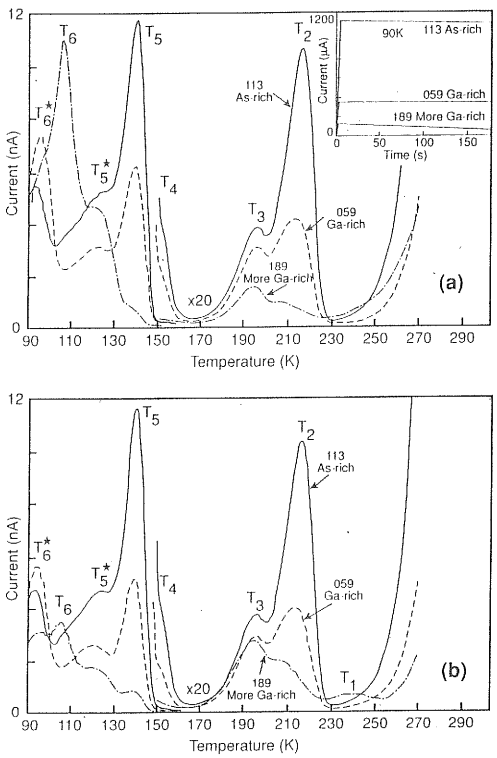

Fig. 1

TSC spectra with (a) 1 min 1.46 eV light and (b) 1 sec IR ($\leq$ 1.12 eV) excitation for three samples.

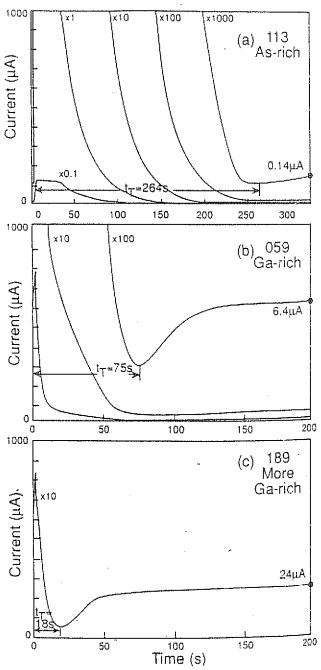

Fig. 2 IR quenching in I_{ph} for three samples.

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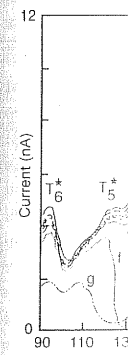

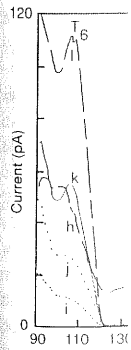

Fig. 3 TSC

In contrast to using 1.46 eV light, the exposure to IR light leads to a significant quenching in I_{ph} for the three samples, as shown in Fig. 2. The quenching behaviors, which involve an initial fast decay in I_{ph} (for sample 113, a nearly steady I_{ph} can be observed before quenching) followed by a slow enhancement in I_{ph} after a transition time (t_T), were found to be quite stoichiometry–dependent; i.e., 1) the initial I_{ph}'s are proportional to the EL2 concentration, 2) the quenching times characterized by the t_T and the magnitudes of I_{ph} quenching are increased with crystal stoichiometry changing from Ga–rich to As–rich, and 3) the final I_{ph}'s after complete quenching are also dependent on EL2 concentrations, but in a reverse order, as labeled in Fig. 2. An interesting observation is that the product of t_T and the corresponding I_{ph} at 300K was found to be constant when the sample was exposed to IR light with different intensities. Since the I_{ph} at 300K was shown to be proportional to the light intensity, the constancy of the product implies that the minimum in the I_{ph} curve is mainly sensitive to the total dose of absorbed photons (Ref. [10]). This observation holds for all three samples. TSC spectra obtained by using only 1 sec IR excitation and shown in Fig. 1(b) are basically the same as those obtained by using 1 min. 1.46 eV light (Fig. 1(a)), although peaks T_3 and T_6 changed somewhat for sample 189 (more Ga–rich). We designate this basic spectrum as TSC feature I, which reveals at least seven traps and is believed to be associated with the normal state of EL2. However, the TSC spectra taken as a function of IR photoquenching of EL2, as depicted in Fig. 3(a), (b) and (c) for the three samples, show several drastic changes: i.e., (1) for all three samples the TSC peaks T_4, T_5 and $T_5\star$ are largely quenched at the initial stage; (2) after a short while, TSC peaks T_2 and T_3 began to be fully or partially transformed into a new peak $T_2\star$, depending on the crystal stoichiometry (for the Ga–rich sample a full transformation can be observed after 20 sec. of IR excitation, while for the As–rich sample and the more Ga–rich sample a partial transformation, with T_2 and T_3 surviving, were found after 3 min and 10 sec IR excitation respectively); (3) accompanying the transformation of T_2/T_3 into $T_2\star$, new TSC peaks T_1 and T_0 are gradually developed (for the As–rich sample, the development takes quite a long time, longer than 10 min); (4) after longer term excitation, TSC signals at around 90K with T_6 and $T_6\star$ as shoulder features are stimulated, and are also stoichiometry related (the more Ga–rich the crystal, the stronger the TSC signals); and (5) for the As–rich sample some of the TSC spectra taken during the IR quenching process show a thermal quenching behavior of T_5 (the thermal quenching was defined as a sudden drop of TSC at the peak position of T_5 so that without this quenching behavior the whole TSC peak of T_5 would be observed) and the temperatures of the thermal quenching are dependent on the excita-

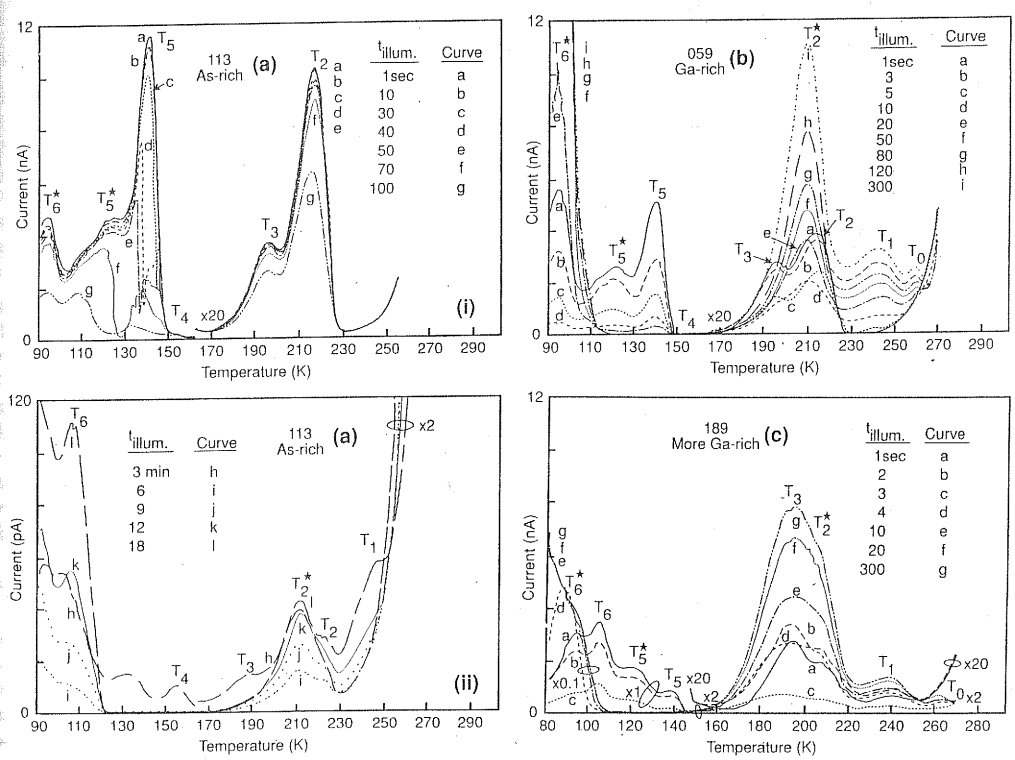

Fig. 3 TSC spectra taken as a function of IR quenching of EL2 for samples (a) 113, (b) 059 and (c) 189.

tion time. The final TSC spectra obtained after the complete photoquenching of EL2 are referred to as TSC feature II, which reveals T_0, T_1, $T_2\star$ and TSC signals around 90K. Without taking account of the correction contributed by capture cross section, the trap depths for T_0, T_1 and $T_2\star$ were determined to be 0.54 eV, 0.49 eV, and 0.42 eV respectively. Because of the dosage dependence in the IR quenching of I_{ph}, the use of IR light with lower intensity has no effect on the observation of the two TSC features and their transformation, but retards the process of quenching and makes it easier to follow. Photo–Hall measurements, performed at 90K for excitation times $t >> t_T$, indicate that the samples had converted from n to p type with hole concentrations ranging from 10^{10} to 10^{11} cm^{-3}, corresponding to sample stoichiometry changing from As–rich to more Ga–rich. Hall effect measurements carried out during a TSC scan after complete IR quenching of EL2 present evidence that T_0, T_1 and $T_2\star$ in TSC feature II are hole traps and $T_6\star$ is probably an electron trap.

For all samples the TSC spectra can be reversibly changed from feature II back to feature I by raising the temperature up to around 120K, which is exactly the same temperature as that needed for the thermal recovery of EL2* → EL2 [4]. The TSC spectra as a function of the recovery temperatures (T_r's) for the Ga–rich SI–GaAs sample (059) have been published earlier [10]. Here we present the results for the As–rich sample (113) and more Ga–rich sample (189), shown in Fig. 4(a) and (b). Similar to the Ga–rich sample (059), when T_r = 150K the TSC spectra are fully recovered for both samples (compare curves g in Fig. 4(a) and (b) with curves a in Fig. 3(a) and (c)). For the As–rich sample, a thermal quenching of T_5 was observed when T_r = 123K, which clearly indicates that the behavior of T_5 is closely connected with the processes of IR quenching and the thermal recovery of EL2.

Optical recovery of TSC spectra from feature II to feature I were also checked by using 1.46 eV and 0.9 eV light at $\leq$ 90K on the Ga–rich sample (059). The TSC spectra, as a function of the excitation time by for each wavelength after a complete IR quenching of EL2, are shown in Fig. 5(a) and (b) with the photocurrent responses in the insets, respectively. For the case of the 0.9 eV light recovery, 1.13 eV light from a monochromator was used to cause IR quenching. Due to the dosage dependence of the IR quenching of

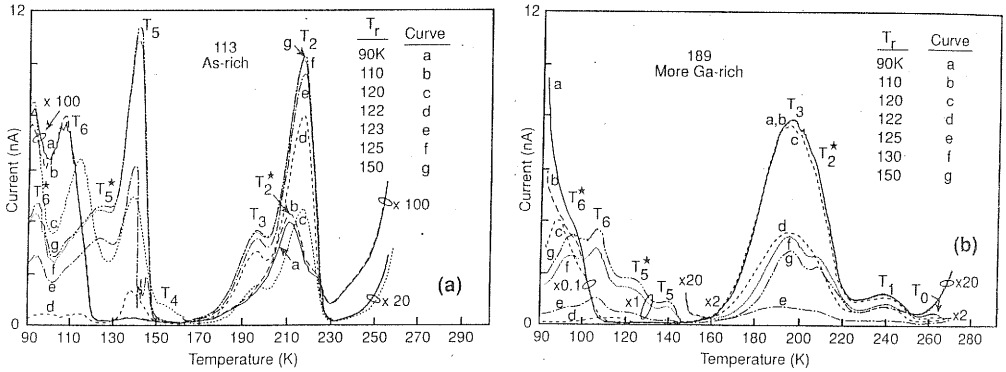

Fig. 4 Thermal recovery of TSC spectra for (a) sample 113 and (b) sample 189.

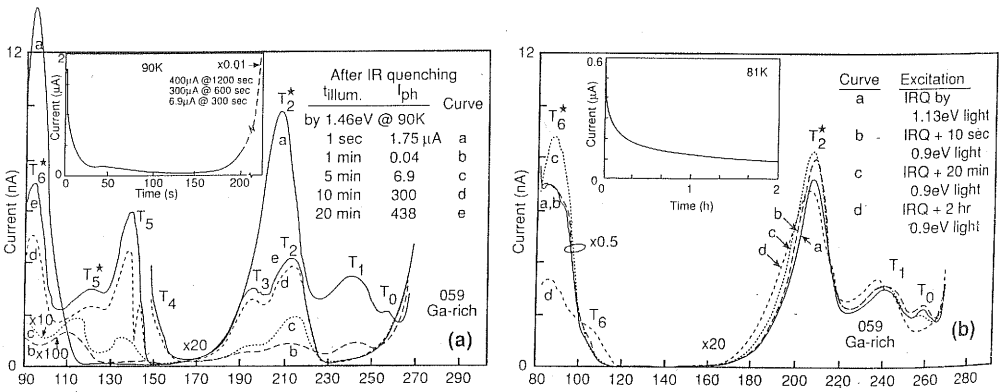

Fig. 5 Optical recovery of TSC spectra by (a) 1.46 eV and (b) 0.9 eV light at $\leq$ 90K.

EL2, the curve a (the excitation time t = 30 min) in Fig. 5(b) corresponds to the curve h (t = 2 min) in Fig. 3(b). The application of both 1.46 eV and 0.9 eV light results in a spike–like photocurrent at the initial stage of the excitation, which is very similar to that reported by Nojima in his two beam photoconductivity studies (so–called slow relaxation phenomena or spike photoconductivity) [1]. However, the long–term excitation shows a difference for the two lights. In the case of 1.46 eV light, the I_{ph} gradually increased and finally recovered to an I_{ph}, which was nearly equal to that observed by only using 1.46 eV light without IR quenching of EL2 (see the insert of Fig. 1(a)). Accompanying the enhancement of I_{ph}, a full recovery of the TSC spectrum from feature II back to feature I was realized. Also, in a certain stage of recovery (t = 10 min) the thermal quenching behavior of T_5 can be observed. In contrast to the case of 1.46 eV light, the use of 0.9 eV light, which is close to the optimum photon energy for the optical recovery of the EL2 IR absorption in spite of poor recovery efficiency [12], cannot stimulate an enhancement of I_{ph} and only results in a partial recovery of TSC feature II, showing a reduction in the peak heights of T_0 and $T_6\star$ and a peak shift of $T_2\star$ towards T_3, after 2 hours excitation at 81K.

Discussion and Conclusions

On the basis of the literature [11–16], the main characteristics of EL2 in undoped SI–GaAs can be summarized as follows: 1) EL2 is a thermally stable native defect or defect complex with the arsenic antisite (As_{Ga}) as a core, and the concentration of EL2 is controlled by the crystal stoichiometry; 2) EL2 possesses both normal and metastable states and the transformation of EL2 $\rightarrow$ EL2* can be achieved by strong white light or 1.1 eV light excitation at low temperatures ($T \leq 100K$) which results in a number of quenching effects; 3) EL2* can be preserved for a long time at low temperatures in the dark unless the temperature of a IR–quenched sample is raised to $T \geq 120K$ (the temperature for full recovery of EL2* $\rightarrow$ EL2 is $\sim$ 140K); 4) the transformation of EL2* $\rightarrow$ EL2 can also be optically induced by light of appropriate energies, and an optical recovery, which is measured by the EL2–related near IR absorption, has been shown to occur in the 1.41 – 1.51 eV region and to be more efficient than that in the 0.9 eV region; 5) the EL2 defect is a double donor with two energy levels in the band gap, i.e., the singly ionized one at $E_C - 0.75$ eV and the double ionized one at $E_V + 0.52$ eV; 6) there is no net change in charge state in the transformation of EL2 $\rightleftarrows$ EL2*, but accompanying the quenching and recovery of As^{+}_{Ga}, a charge transfer to some neutralized deep acceptors, such as $ST1^0$, $FR1^0$, $FR2^0$ and Fe^0_{Ga}, has been observed by EPR studies; 7) EL2 is anti–correlated with other important electron traps, such as EL3, EL5 and EL6, depending on the crystal stoichiometry and one of the latter deep centers may determine the free–carrier lifetime in as–grown and ingot annealed substrates.

In contrast to the difficulty in detecting EL2* by the usual electrical and optical techniques, often due to quenching of the tested parameter (such as from photocapacitance, photoconductivity, photoluminescence, IR absorption and EPR), TSC spectroscopy is able to reveal the traps in both the normal and metastable states of EL2. Through a comparison of all the TSC data described above and the main characteristics listed for EL2, it turns out that they are consistent with each other in every aspect and the traps observed in TSC features I and II appear to have a direct association with EL2 and EL2* respectively, rather than an indirect association which could result from a change in the dominant free carrier (being trapped) as EL2 transforms to EL2*. The evidence from IR quenching and optical recovery (using 1.46 eV light) of the TSC spectra indicates that traps T_2, T_3, T_4, T_5 and $T_5\star$ themselves undergo a transformation, accompanying the EL2 $\rightarrow$ EL2* transition, and finally disappear from the TSC spectrum. Furthermore, a comparative study of TSC and photocurrent provides additional information concerning the carrier lifetimes and recombination centers in the IR quenched samples. In principle, the TSC peak height for a given trap depends not only on the trap density, but also on the carrier lifetime, if the excitation conditions at low temperatures and the heating rate of the thermal scan are kept unchanged. Therefore, in the transformation of EL2 $\rightarrow$ EL2*, we must consider changes both in the trap species and in the carrier lifetime. The weak TSC signals observed in the IR quenched As–rich sample (see Fig. 3(a)) do not necessarily imply a low trap density, since after IR quenching of EL2 the I_{ph} in the sample (113) is two orders of magnitude lower than that in more Ga–rich sample (189) (see Fig. 2), and thus implies a shorter lifetime. Here we have to point out that the absorption coefficient of 1.46 eV photons is about 5 cm^{-1} at 90K according to measurements of the intrinsic absorption edge in SI–GaAs at five temperatures from 10K to 294K [17]. Therefore the 1.46 eV light acts as a near band edge light at 294K and as a near penetrating light at 90K, which can explain why there is nearly no difference between the TSC spectra with 1–min/1.46 eV and 1–sec/IR ($\leq$ 1.12 eV) excitation for As–rich and Ga–rich SI–GaAs samples at 90K (see Fig. 1(a) and (b)). Although many authors speculate that the $EL2^0 \rightarrow$ EL2* transformation occurs through an internal transition [18], it is possible that some deep donors shallower than EL2, such as EL5 and EL6 (perhaps T_3 and T_4 in the TSC spectra), take part in the IR quenching of EL2 since the photon energies of the optimum quenching light are so close to the energy difference between either of these donors (especially EL5 at $E_C - 0.42$ eV) and the valence band. To help identify some of the TSC traps, we can compare with electron–irradiation induced

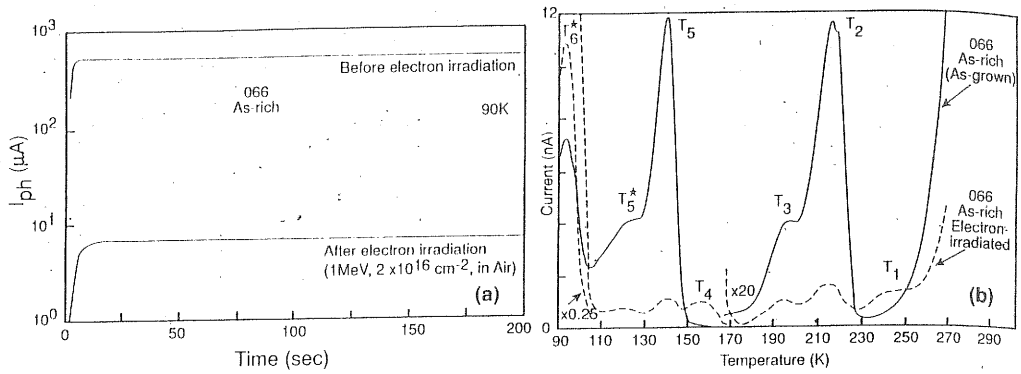

Fig. 6 A comparison of (a) I_{ph} and (b) spectra before and after election irradiation.

defect spectra. A comparison of photocurrent responses and TSC spectra with 1.46 eV light for an undoped SI–GaAs sample (066, As–rich), before and after electron–irradiation (1 MeV, 2 × 10^{16} cm^{-2} in air) is shown in Fig. 6(a) and (b). After the irradiation, the carrier lifetime (as estimated from I_{ph}) is much reduced and a major change in the TSC peak structure is observed, specially a large increase in $T_6\star$. Assuming a unity value for the current collection factor G in the equation $N_t = Q/eVG$ [19], the trap density of $T_6\star$ can be estimated to be at least 3 × 10^{15} cm^{-3} after irradiation. Based on the trap depth (0.17 eV)and trap density, $T_6\star$ can be reasonably assigned to E2 (0.14 eV) which is the dominant defect induced by electron irradiation and which is ascribed to the creation of V_{As} [20]. This appears to be the first positive identification of a TSC peak for irradiation-induced defects in GaAs.

In summary, TSC spectroscopy in conjunction with 1.46 eV and IR photocurrent responses at low temperatures has proved to be a very useful technique for investigating the quenching and recovery of EL2, even though EL2 is not directly observed as a TSC trap because of the high dark current at its emission temperature. The outstanding result of this study is the observation of the close relationships between the EL2 ⇉ EL2* transition, as revealed by photocurrent, and the TSC spectral changes during EL2 quenching and recovery. The most likely model is that most of the TSC peaks are defect and possibly impurity complexes involving As_{Ga} and thus appear to be "EL2–like" or "EL2*–like" in many of their properties.

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