Anomalous photoquenching in semi-insulating GaAs attributed to the presence of the deep donor ELO

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An anomalous reduction in the photoquenching efficiency at 80 K has been observed in some semi-insulating GaAs samples during illumination with 1.1-eV light. The effect has been observed in photocurrent and infrared-absorption quenching experiments. Photoluminescence experiments on normal and anomalous samples indicate that the effects are produced by the presence of oxygen as indicated by the photoluminescence emission from the oxygen-related deep donor ELO. Oxygen was found to produce a photoassisted thermal-recovery effect with 1.1-eV light that competes with the EL2 photoquenching effect. No infrared absorption was found that could be attributed directly to ELO. In contrast, the photocurrent was found to be dominated by photoionization of ELO rather than EL2, and the anomalous effect is attributed to the reduced photoquenching temperature of ELO.

INTRODUCTION

Metastability effects in GaAs have been the focus of considerable attention for some time now. It is well known that the intrinsic deep donor EL2 exhibits a photoinduced metastability at temperatures below 120 K. When illuminated with light in a band centered near 1.1 eV, this defect undergoes a reconfiguration, transforming from its normal state into a metastable state that has eluded direct detection.[1] In general, sample temperatures near 80 K are sufficiently low to ensure complete photoquenching or bleaching of the defect. Annealing at temperatures above 120 K restores the original, normal state. Other defects in GaAs similar to EL2 with activation energies near midgap have been reported.[2–4] Of these, the most widely studied, and the most similar to EL2, is the oxygen-related defect denoted ELO.[3] This defect is found in samples intentionally doped with oxygen and most likely is a complex including oxygen,[5] although this has not been verified. During a study of photoquenching of the extrinsic photocurrent (PC) and the infrared (ir) absorption in bulk semi-insulating (si) GaAs, we have observed an anomolous reduction in the photoquenching efficiency at 80 K in several si GaAs samples. This reduction has been correlated with the presence of ELO as determined by deep-level photoluminescence (PL). The data suggest that the 1.1-eV PC in these samples is primarily due to photoionization of ELO rather than EL2. We were not able to identify any ir absorption that could be attributed directly to ELO; rather, the apparent reduced quenching efficiency of the ir absorption is attributed to an ELO- or oxygen-induced photoassisted thermal-recovery process such as that reported by Parker and Bray.[6]

EXPERIMENT

Several si GaAs samples from a variety of sources were studied. Both liquid-encapsulated-Czochralski- (LEC-) and horizontal-Bridgman- (HB-) grown material were included. Some of the LEC samples were intentionally doped with Ga_2O_3 by the crystal grower to introduce oxygen. The HB samples were all undoped. Table I gives source and growth technique for the principal samples of this study. Supplier B stated that many of their LEC crystals are doped with Ga_2O_3, but we did not have specific data on the samples in this study. Temperature-dependent dark Hall-effect measurements near room temperature indicated that the activation energy for all samples was 0.76 ± 0.02 eV. Infrared-absorption measurements at 1.2 eV were used to determine EL2 concentrations which were found to vary between 0.5 and 2.0×10^{16} cm^{-3}. Samples from the same boules were examined by photocurrent, ir absorption, and photoluminescence. Efforts were made to ensure that the various samples for each experiment were taken from as close as possible to each other, usually from the same quarter of a wafer.

Photocurrent and photo-Hall experiments were performed at various temperatures by illuminating the sample with 1.13-eV light from a quartz-halogen lamp and a narrow-bandpass filter (full width at half maximum 0.01 eV). The van der Pauw sample current and voltage were recorded as a function of time as the illumination produced the quenching effect. Infrared absorption spectroscopy experiments were performed on a Cary model 2300 spectrophotometer. A variable-temperature closed-cycle refrigerator system was used to cool the samples to a minimum of 9 K. Quenching illumination for these experiments was provided by a similar quartz-halogen

TABLE I. Summary of principal samples used in this study, including growth technique (LEC—liquid-encapsulated Czochralski, HB—horizontal Bridgman) and deep-level photoluminescence. The 80-K quenching results for photocurrent (PC) and infrared-absorption (Abs) experiments are given as the percentage of the initial signal that remains after quenching. NM denotes not measured.

Sample	Supplier	Growth technique	PL (eV)	PC(80 K) (%)	Abs(80 K) (%)
1	A	HB	0.68	0.0	0.0
2	B	LEC[a]	0.68	0.0	0.0
3	C	LEC	0.63	75.5	68.0
4	C	LEC	0.63	65.5	75.5
5	C	LEC	NM	75.0	87.5
6	D	LEC	NM	74.0	85.0
7	E	HB	NM	0.0	NM
8	B	LEC	0.68	0.0	NM
9	E	LEC[b]	0.63	48.9	NM

[a]Indium alloyed.
[b]Ga_2O_3 doped.

lamp. Both white and monochromated light were used to quench EL2 absorption.

PHOTOCURRENT RESULTS

The anomalous quenching effect is seen in Fig. 1, where the 1.13-eV PC versus time for an LEC sample (no. 5) is plotted for various samples temperatures. The PC at 80 K remains at a high value for extended period; in some samples the illumination was kept on for times exceeding 2 h and no change was observed after the saturation seen in the figure was achieved. For temperatures at or below 60 K, the PC quenched completely, dropping several orders of magnitude. The time to quench was nearly constant below 60 K. The transition from anomalous to "normal" behavior occurred over a very narrow temperature range. The magnitude of the reduction in the 80-K PC varied somewhat among the anomalous samples, but in none of these did the PC drop by as much as an order of magnitude. We thus define 90% reduction as the definition of "anomalous." The temperature dependence of the PC in what will be referred to as "normal" samples is shown in Fig. 2, which shows the results for an undoped HB sample (no. 1). The residual PC in both samples is due to the temperature dependence of the

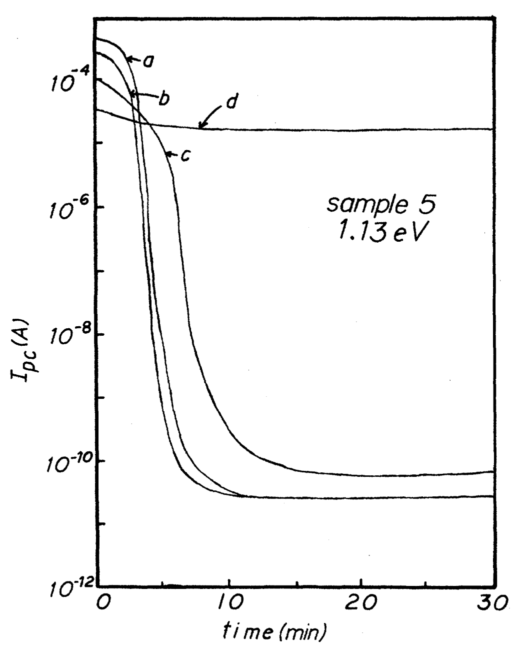

FIG. 1. Photocurrent vs time for LEC sample 5 showing the anomalous photocurrent quenching. *a*, 10 K; *b*, 60 K; *c*, 70 K; *d*, 80 K.

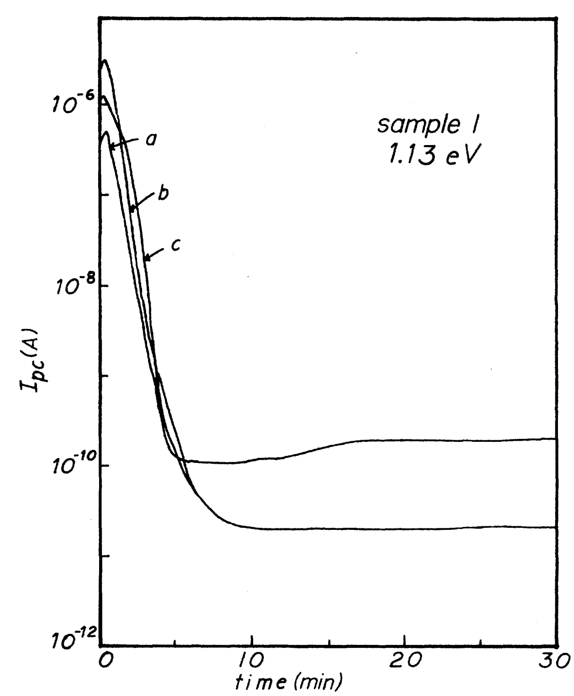

FIG. 2. Photocurrent vs time for HB sample 1 showing normal photocurrent quenching. *a*, 10 K; *b*, 40 K; *c*, 80 K.

p-type PC that exists at low levels after quenching and is not believed to be due to EL2-like defects. A complete discussion of this effect is beyond the scope of this study. The normal samples showed PC quenching of more than 2 orders of magnitude for all temperatures below 110 K, where thermal recovery of EL2 starts to dominate the quenching.

While the temperature at which the quenching of the PC becomes significant is reduced in the anomalous samples, the thermal recover of the PC after quenching is not affected, as shown in Figs. 3 and 4. Here the 1.13-eV PC after quenching at 8 and 80 K is plotted as a function of temperature for sample 5, an anomalous sample, and sample 7, a normal sample, respectively. For both sample types the PC recovers in the range 110–120 K, as expected for EL2.[1] The anomalous samples tended to recover at a slightly lower temperature than the normal samples, as seen in the figures, but this could be attributed to variations in the heating rate, which was not controlled. Again, the residual PC prior to recovery is not believed to be due to EL2-like defects. Another trend seen in Figs. 1–4 is that the initial PC in the anomalous samples tended to be higher than that in the normal samples, but this was not a universal effect and might be due to variations in contacting. Since both *n*- and *p*-type contacts were used, this is quite possible.

Photo-Hall-effect–versus–time studies at 80 K were performed on selected van der Pauw samples to better understand this effect. Separate quenches followed by recovery at 135 K were performed for each van der Pauw–resistivity and Hall-effect configuration, and for both plus and minus current and magnetic field for a total of eight separate quenches. Field and current directions were averaged and the van der Pauw procedure was used to average the resistivity positions. This gave resistivity, carrier concentration and type, and mobility at each time. The carrier-concentration and mobility results for an anomalous sample (no. 3) are presented in Fig. 5. The carrier concentration remained *n* type throughout the quench. In the normal sample studied for comparison, the carrier concentration dropped several orders of magnitude in the first few minutes and converted from *n* to *p*-type conduction during the decay. The type conversion has been previously reported by others.[7,8] The mobility in this sample increased sharply initially, but then the data became erratic, most likely due to contact effects after the type conversion. The results observed in Fig. 5 were essentially repeated in the other anomalous sample studied in this manner. These results show that the quenching of the PC in the normal sample is principally due to the reduction in the carrier concentration, while that in the anomalous samples is due instead to a mobility reduction.

Many but not all of the anomalous samples were intentionally oxygen doped. One undoped sample which showed a PC reduction of 50% was the only LEC sample studied that was grown from a quartz crucible. A persistent photocurrent has been reported[9] in undoped LEC samples in experiments similar to ours. This effect is characterized by a strong *p*-type current that persists at 80 K after the illumination has been removed. We have observed this effect in some LEC samples. However, despite the large photocurrent, none of the anomalous samples exhibited any measurable persistent current at any temperature.

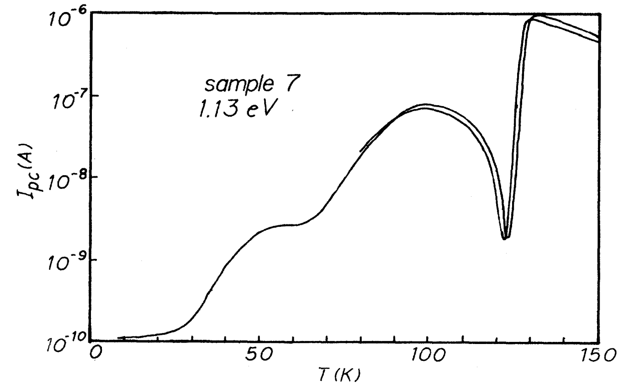

FIG. 4. Photocurrent vs temperature for normal HB sample 7 after quenching at 8 K with 1.13-eV light.

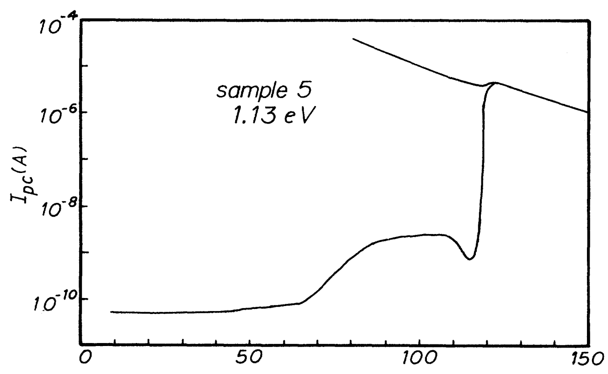

FIG. 3. Photocurrent vs temperature for anomalous sample 5 after quenching at 8 K with 1.13-eV light.

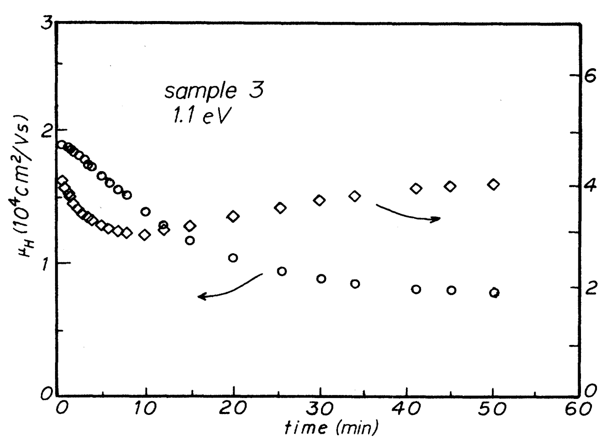

FIG. 5. Carrier concentration and Hall mobility vs time at 78 K during illumination with 1.1-eV light, sample 3.

INFRARED-ABSORPTION RESULTS

Infrared-absorption quenching results show effects similar in appearance to those of the PC quenching experiments. Results of quenching experiments at 80 and 9 K are presented in Figs. 6 and 7, respectively, for several samples. Here the percentage of the broad absorption band at 1.2 eV remaining compared to the initial, unquenched concentration is plotted versus quenching time. Both the quenching with 1.12-eV light and the absorption spectroscopy with low-intensity light were performed at the indicated temperature. The samples that show only partial quenching of the absorption at 80 K in Fig. 6 also showed anomalous PC quenching, while normal, complete quenching was observed in both experiments for the same samples. For the purposes of this paper, we will define anomolous absorption quenching as any measurable 1.2-eV absorption in the 9-K spectrum after quenching at 80 K that is above the absorption at that wavelength after quenching at 9 K. As can be seen in Fig. 7, all samples showed complete absorption quenching at 9 K, in agreement with the PC results. The PC and absorption results for 80-K quenching are compared in Table I, where the percentages of the initial signal remaining after quenching are given.

Since there is some question as to whether or not the broad band absorption at 1.2 eV is due solely to EL2 or includes effects due to both EL2 and ELO, studies of the quenching of the EL2-related zero-phonon line (ZPL) at 1.039 eV were performed on the anomalous sample (no. 4) from an oxygen-doped LEC boule. The ZPL spectra were taken at 9 K since it is not resolvable at 80 K. After an initial ZPL absorption coefficient was determined, the sample was heated to 80 K, where it was quenched in the usual manner and then returned to 9 K, where the ZPL was remeasured. The percentage of reduction of the ZPL absorption was found to be identical to that of the broad 1.2-eV absorption. The ZPL quenched completely when the quenching was performed at 9 K. In addition, examinations of the ZPL in particular and the whole near-band-edge absorption spectra were made on normal, undoped samples, and on anomalous oxygen-doped samples in an attempt to find a variation in the spectra that could be attributed to oxygen or ELO. We were not able to find any feature in the 0.7–1.5-eV range that could be attributed to oxygen.

Thermal-recovery experiments were also performed for the absorption quenching. When the anomalous sample (no. 4) was quenched at 9 K and then heated in the dark to 80 K, there was negligible recovery of the 1.2-eV absorption. However, if the sample was then illuminated with 1.12-eV light at 80 K, the absorption started to recover and eventually achieved a value almost identical to

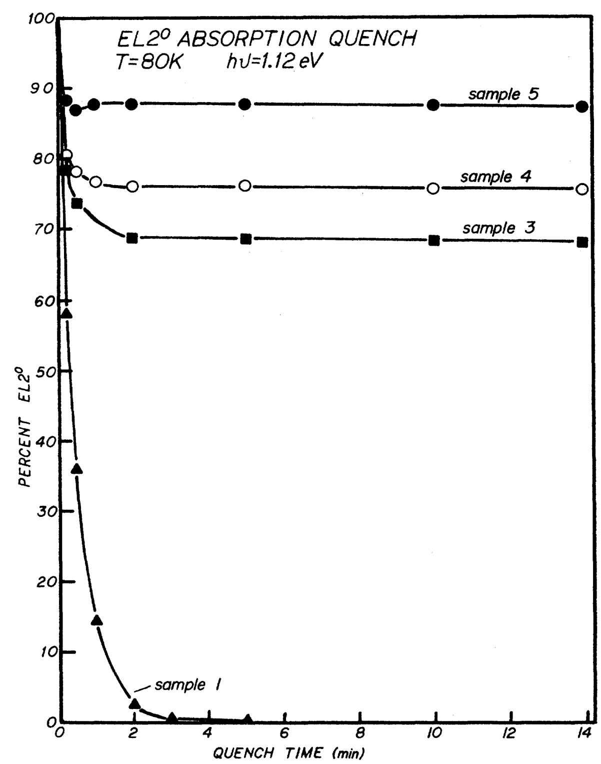

FIG. 6. Amount of $EL2^0$ ir absorption at 1.18 eV, which is quenched at 80 K as a function of time. Monochromatic light at 1.12 eV and 1.1 mW/cm^2 is used for the quench. Samples normalized at 100% before quench.

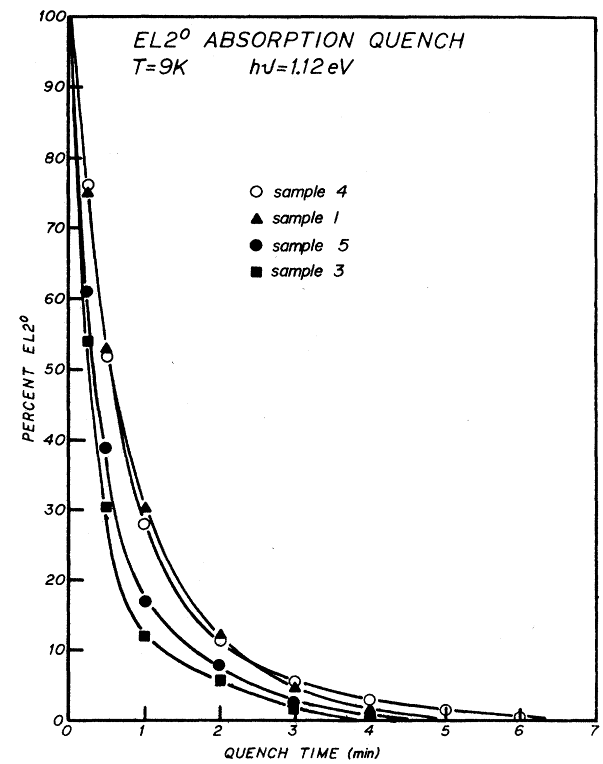

FIG. 7. Amount of $EL2^0$ ir absorption at 1.18 eV, which is quenched at 9 K as a function of time. Monochromatic light at 1.12 eV and 1.1 mW/cm^2 is used for the quench. Samples are normalized at 100% before quench.

that after quenching at 80 K. This photoassisted thermal recovery (PATR) is very similar to that reported by Parker and Bray[6] for two LEC samples, one oxygen doped and the other undoped. If, as we suspect, we are observing the same PATR as Parker and Bray, then the apparent reduction in the absorption quenching efficiency seen in Fig. 6 is not a reduction in quenching but rather an increase in the recovery that is thermally activated and induced by the same light that produces the quenching, with the two effects competing. We did not study the detailed temperature dependence of the PATR, but the results of Parker and Bray show that this effect commences at 60 K, which is very similar to the temperature dependence of the anomalous PC quenching as seen in Fig. 1.

PHOTOLUMINESCENCE RESULTS

Two deep-level PL emission spectra reported in the literature are often associated with EL2. One, at 0.68 eV,[10–12] is certainly due to EL2. There has been considerable discussion, however, over the second level at 0.63 eV. Yu and Walters[13] have correlated this band to the presence of oxygen and assigned it to ELO. This conclusion has been corroborated by the work of Kazuna, Sawada, and Yokoyama.[14] However, others have suggested that both bands are due to EL2.[15–17] Tajima and co-workers[16,17] have shown that the peak energy of the 0.68-eV EL2 band can vary with excitation energy and can be shifted to 0.63 eV under proper excitation conditions. For this study, three PL sources were used to ensure that ELO and EL2 were not confused by this effect. The lasers used were (1) the 2.41-eV line of an Ar laser, (2) the 1.92-eV line of a Kr laser, and (3) the 1.77-eV line of a dye laser. For the samples studied for this report, the peak energies remained at 0.68 and 0.63 eV regardless of the excitation energy; however, one EL2 sample did show an enhancement of emission intensity near 0.63 eV with the 1.77-eV source, but this intensity was still well below that seen in ELO samples. We are therefore confident that our PL experiments are able to discriminate between EL2 and ELO. Results are given in the table.

Quenching studies of the 0.63-eV emission band were conducted at low temperatures and have been reported elsewhere.[18] These experiments showed that this band quenches at temperatures near 10 K with a quenching band very similar to that of EL2, but with a considerably reduced efficiency. The quenching efficiency dropped off rapidly with increasing temperature and was negligible by 80 K.

The deep-level PL spectra were examined for samples that exhibited normal and anomalous PC and absorption quenching. All samples that exhibited the normal behavior were found to show only the 0.68-eV EL2 emission, while the anomalous samples that had the least quenching all had strong 0.63-eV ELO emission. The ELO-related emission is characterized by 1–2 orders of magnitude stronger emission intensity than the EL2-related emission, so a purely 0.63-eV emission does not imply that the EL2 concentration is negligible, although a purely 0.68-eV emission does indicate that ELO is not present in the material. Three of the samples with strong pure ELO emission studied by PC did not show the anomalous quenching reduction. Two of these were reported as "heavily" oxygen doped by the supplier. The other was indium doped. Some samples showed mixed PL with both emission lines present. In general, these were not anomalous, but a thorough study of these mixed samples has not been made at this time.

DISCUSSION

These results suggest that oxygen, either as ELO or in some other form, produces the anomalous reduction in quenching seen in the PC and absorption quenching experiments. Absorption experiments, both these and those of Parker and Bray,[6] indicate that oxygen doping, intentional or otherwise, induces a photoassisted thermal recovery with an onset near 60 K. This PATR effect is not observed in the PC experiments, as can be seen clearly in Fig. 3. The slight increase in the PC in this figure at 70 K was observed in all samples that exhibited complete PC quenching at 8 K whether they quenched at 80 K or not. Similar structures in this temperature range were also observed in dark temperature scans of the current after quenching at 8 K for both types of samples. In these experiments the structures appeared as TSC-like (thermally stimulated current) peaks and have been observed in true TSC experiments,[19–21] and are most likely not directly related to EL2 or ELO. The absorption PATR cannot be an Auger-type recovery induced by optical excitation of electrons because, as can be seen in Fig. 5, the electron concentration is much too low to produce this effect.[22]

We propose that two oxygen-related effects are necessary to explain our results. First, oxygen in some form induces a PATR effect in quenched EL2 that is not Auger related. This recovery effect competes with the quenching effect producing the apparent reduction in absorption quenching efficiency. Secondly, we propose that the PC in the anomalous samples is dominated by photoionization of the ELO defect rather than EL2, and that this defect quenches at lower temperatures than EL2, but recovers at nearly the same temperature.

The basis for our conclusion that the PATR effect affects EL2 and not ELO is that the ZPL behaves in exactly the same manner under the influence of the PATR as the broad 1.2-eV absorption. The ZPL is too fine a structure (the half-width is about 0.005 eV) to be due to two different defects, and we have observed no variation in either the half-width or peak position in EL2 or ELO samples. Our failure to observe an ELO-related absorption coupled with the fact that the ZPL tracks the 1.2-eV absorption supports the hypothesis that the 1.2-eV absorption is due solely to EL2.[23]

The 80-K PC is believed to be dominated by ELO for two reasons. First, the photoelectron concentration after the quench is nearly identical to that at the start, indicating no net change in the concentration of ionizable centers, yet the EL2 absorption quenches by 30% in a sample from the same wafer as the sample in Fig. 5 (sample 3) under similar quenching conditions. Secondly, while the EL2 absorption partially recovers after quenching at 9 K when reilluminated, the PC shows no significant recovery when heated under illumination, as seen in Fig. 3. These effects indicate that the PC is produced by ionization of some defect other than EL2, and the PL experiments suggest that this other defect is ELO. The PL results indicate that ELO does not quench at 80 K but does at lower temperatures. This explains why the PC does not quench at 80 K but does at 8 K.

Two effects remain unexplained. These are the dip in the carrier concentration and the reduction in mobility at 80 K in the anomalous samples. Two anomalous samples (no. 3 and no. 5) were studied by time-dependent photo-Hall experiments, and these effects were observed in both. It seems reasonable to attribute these to the transformation of EL2 into its metastable state during the quench, but why such a transformation should produce these effects is unclear. One might argue that the metastable state is a more effective scattering center and so explain the mobility decrease, but without a better understanding of both the transformation process and the EL2 metastable-state configuration this is pure speculation. At present, we cannot offer satisfactory explanations for these effects.

CONCLUSIONS

We have shown that the presence of ELO in si GaAs can significantly affect the temperature dependence of the photoquenching and recovery effects. Photocurrent quenching is significantly reduced at 80 K compared to 8 K in ELO-dominated samples, and the reduction is due more to a reduction in *n*-type mobility than to a carrier-concentration reduction. The photocurrent in these samples is believed to be dominated by photoionization of ELO. The presence of oxygen also produces an photoassisted thermal-recovery effect on quenched EL2 that results in an apparent reduction in quenching efficiency at 80 K. This PATR is believed to be the same as that reported by Parker and Bray.[6] How oxygen affects EL2 in these samples is not understood at this time. The near-band-edge absorption at 1.2 eV was found to be due entirely to EL2 and so cannot be used to measure the total deep-donor concentration.

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