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Thermal recovery of photoquenched $EL2$ infrared absorption in GaAs

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The thermal recovery of the GaAs $EL2$ infrared absorption from the metastable ($EL2^*$) back to the normal ($EL2^0$) state after it has been completely photoquenched ($EL2^0 \rightarrow EL2^*$) has been studied for the temperature range $70\ \mathrm{K} \le T \le 150\ \mathrm{K}$ and compared to previous photocapacitance recovery measurements. Complete recovery profiles (absorption coefficient versus time) were measured at 2-K intervals for $106\ \mathrm{K} \le T \le 150\ \mathrm{K}$ and partial profiles were measured for $T < 106$ K. For $100\ \mathrm{K} \le T \le 120\ \mathrm{K}$, the absorption recovery was in good agreement with published photocapacitance recovery data. One sample exhibited an activation energy of 0.30 ± 0.01 eV, but a second sample showed an energy of 0.25 ± 0.01 eV. These energies are believed to represent the thermal barrier between $EL2^*$ and the conduction band. The different values probably reflect the fact that $EL2$ is a "family" of defects with different configurations exhibiting different thermal recovery barriers. For $T > 120$ K, the absorption recovers much more slowly than the photocapacitance, with an apparent activation energy of about 0.07 eV.

I. INTRODUCTION

As has been stated in numerous previous publications the rationale behind most of the studies of the $EL2$ defect involves the fact that undoped semi-insulating (si) GaAs has become the material of choice for many high-speed integrated-circuit applications. This material contains a midgap donor level, $EL2$, which is believed to cause the si behavior by compensating the shallow impurities. A major objective of most of the work reported to date has been to discover the identity of this defect. Despite the rather large number of papers which have been devoted to this subject, no general consensus has yet been reached on the exact structure of $EL2$. It is known to be an intrinsic double donor and for a while various data seemed to indicate that it might be the isolated arsenic antisite, $\mathrm{As_{Ga}}$. Lately, however, there seems to be growing evidence that $EL2$ is probably a complex involving $\mathrm{As_{Ga}}$ and one or more other intrinsic defects[1,2] and also that there is a "family" of $EL2$ defects rather than only one.[3] For a more complete background and review of the various aspects of $EL2$ the reader is directed to some of the recent literature[1,2,4–7] and references cited therein.

Perhaps the most discussed and intriguing property of $EL2$ is its photoquenching behavior, which has been observed in photocapacitance,[8] photoluminescence,[9] photoconductivity,[10] and infrared absorption.[11] It is well known, for instance, that si GaAs exhibits an absorption band in the 1.0–1.3-eV range which has been attributed to the $EL2$ defect.[11–16] This absorption is believed to be due to an intracenter transition between the $EL2$ ground state ($EL2^0$) at midgap and an excited state resonant with the conduction band.[12–15] It can be completely quenched by irradiating the material with photons of about 1.1–1.2-eV energy. This photoquenching effect ($EL2^0 \rightarrow EL2^*$) occurs when the defect is transformed from its normal state ($EL2^0$) to a metastable state ($EL2^*$).[8]

Very little is known about the structure of $EL2^*$. It is commonly assumed to arise from a large lattice relaxation and to lie in the band gap[2,8,17] but no conclusive evidence can be cited to pinpoint the exact location of this level. For some time it has been known that after $EL2$ has been transformed to the metastable state ($EL2^0 \rightarrow EL2^*$), recovery to the normal state ($EL2^* \rightarrow EL2^0$) can occur by heating the sample to the appropriate temperature,[8] ($T > 120$ K). This thermally induced recovery was reported to have an activation energy of about 0.3 eV,[8,18–20] which was used as the basis for positioning the $EL2^*$ level. Such level placement is not unambiguous, however, because there are alternative ways to account for the 0.3-eV thermal barrier.

In an effort to learn more about $EL2^*$, this author studied the photon-induced recovery ($EL2^* \rightarrow EL2^0$) of the intracenter absorption.[21] It was found that after the $EL2$ absorption had been completely quenched ($EL2^0 \rightarrow EL2^*$), it could be partially recovered by photon excitation in the energy range 0.7–1.0 eV and that the relative amount of recovery was dependent on the photon energy. These results were used to suggest a placement of the $EL2^*$ level which was different from that of previous workers (near the conduction band instead of near $EL2^0$) but still consistent with the various experimental data. The results shown in that paper[21] were obtained at 77 K but it was also mentioned that the photon-induced recovery effects seemed to be temperature dependent. Subsequent work has confirmed this fact but attempts to determine a reliable temperature-dependent relationship have proved to be difficult at temperatures where the thermal recovery itself was starting to occur. The thermal recovery process for $EL2$ has already been thoroughly investigated by means of the photocapacitance technique[8,18] but problems were en-

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countered in trying to apply those results to the infrared absorption, as will become evident in Sec. III. It was, therefore, deemed desirable to perform a thermal recovery study for the $EL2$ absorption in order to try to separate the thermal-only effects from the photon-induced effects at the temperatures for which both were occurring. These experimental results are presented and discussed in Sec. III.

II. EXPERIMENTAL PROCEDURES

Infrared absorption spectra were obtained with a Cary model 2300 spectrophotometer on samples of si GaAs grown by the liquid-encapsulated Czochralski (LEC) technique by two different vendors. Typical sample sizes were 13 mm square and 2–5 mm thick. $EL2$ concentrations were between 1×10^{16} and 2×10^{16} cm^{-3}, as determined by absorption measurements.[11] Samples were mounted on the cold finger of a closed-cycle refrigeration system and the temperature was variable between 8 and 300 K with an accuracy of ±0.5 K. Temperature was measured by means of a calibrated silicon diode mounted on the edge of the sample.

The experimental sequence used to obtain the absorption data is as follows. The sample was first cooled to about 8 K in the dark and the absorption spectrum measured (solid curve, Fig. 1). The absorption was then totally quenched using a white light source at about 100 W (dashed curve, Fig. 1). The $EL2$ peak absorption coefficient was determined by measuring the transmittance at the peak of the $EL2$ intracenter absorption and at an appropriate background position (arrows in Fig. 1). For temperatures below 100 K the sample was heated immediately to the target temperature in less than 1 min. As soon as the sample reached the desired temperature, the transmittance values at peak and background were monitored with time. For temperatures above 100 K, the sample was first heated to about 90 K and held there for about 10 min. It was then heated to the desired temperature and measurements were initiated. In most cases the sample reached temperature in less than a minute.

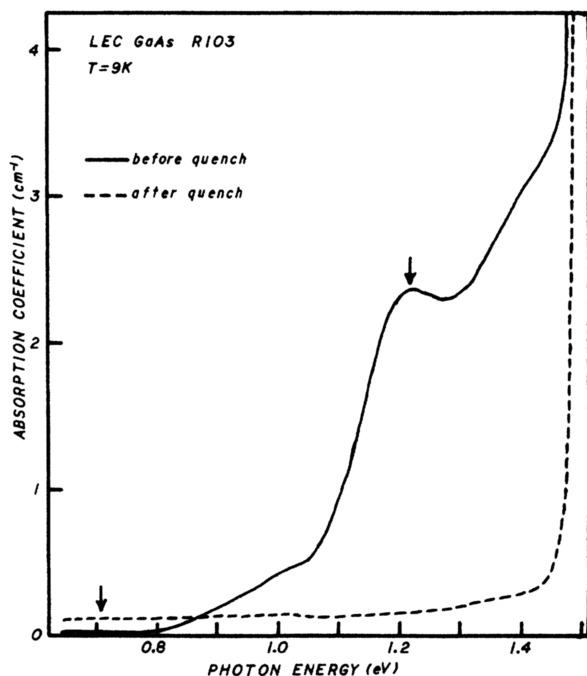

FIG. 1. $EL2$ absorption spectra from LEC si GaAs sample R103 recorded at 9 K. Solid line obtained after cooling in dark (before quench). Dashed line obtained after total quench ($EL2^0 \rightarrow EL2^*$) with white light source. Arrows indicate points where absorption was monitored with time during thermal recovery ($EL2^* \rightarrow EL2^0$).

III. RESULTS AND DISCUSSION

The $EL2$ absorption spectrum obtained at 9 K for sample R103 before and after quench is illustrated in Fig. 1. These spectra are virtually identical to those which have been published previously.[11,22] Other samples investigated also yielded these same spectra. As mentioned in the Introduction, the absorption component which peaks at about 1.2 eV is believed to be due to an intracenter transition between the $EL2$ ground state at midgap ($EL2^0$) and an excited state resonant with the conduction band. After photoquenching ($EL2^0 \rightarrow EL2^*$), the $EL2$ absorption disappears because the defect has been transformed to its metastable state, $EL2^*$. Converting $EL2^0$ entirely to $EL2^*$ is a necessary starting point for the results about to be presented.

It is now certainly well known that after $EL2^0$ has been transformed to $EL2^*$, the $EL2^0$ state can be recovered by heating the sample to about 120 K or higher for a short period of time. As this $EL2^* \rightarrow EL2^0$ recovery occurs, the absorption at 1.2 eV should return with an intensity which is directly proportional to the percentage of recovery. The amount of recovery at any given time and temperature should therefore be directly measurable by monitoring the transmittance at 1.2 eV and at an appropriate background position. The two monitoring points chosen for this study are indicated by the arrows in Fig. 1.

At the beginning of this study it was assumed that the $EL2^* \rightarrow EL2^0$ thermal recovery would follow the Boltzmann distribution law with an activation energy of about 0.3 eV for the entire temperature range of interest.[8,18–20] It soon became apparent, however, that some of the data points did not confirm to this preconceived notion. This led to a much more detailed study involving more samples and more temperatures than originally envisioned. Thermal recovery profiles were determined at every 2 K for 106 K $\leq T \leq$ 150 K for samples R103 and C1317. Each profile represents at least two separate sets of measurements to ensure reproducibility.

The complete $EL2$ absorption thermal recovery profiles at a number of temperatures for sample R103 are shown in Fig. 2. Complete recovery is defined as the point at which the $EL2$ absorption coefficient returns to

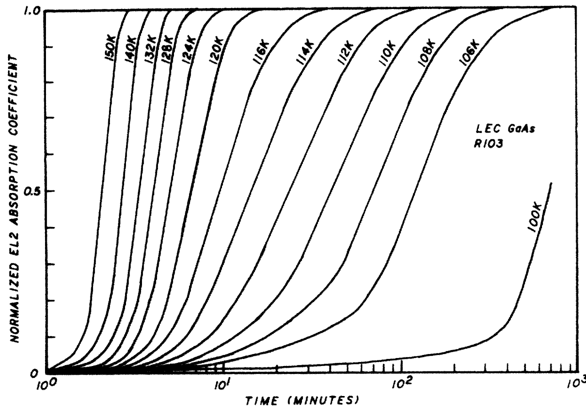

FIG. 2. $EL2^* \rightarrow EL2^0$ thermal recovery profiles for $EL2$ intracenter absorption at selected temperatures for GaAs sample R103.

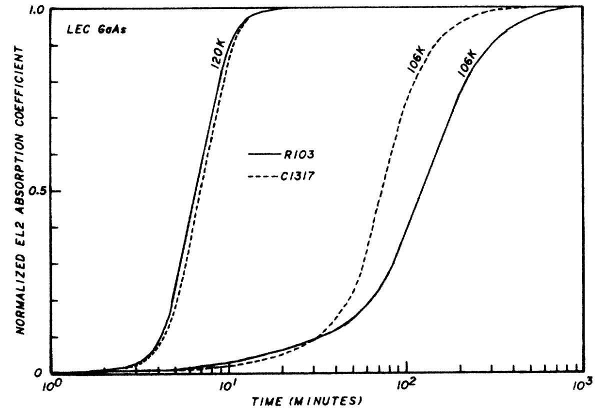

FIG. 3. Comparison of $EL2^* \rightarrow EL2^0$ intracenter absorption thermal recovery for samples R103 (solid lines) and C1317 (dashed lines) at $T = 106$ and 120 K.

the value it had at that same temperature before it was quenched. The actual value of the peak absorption coefficient varies as a function of temperature and so it is normalized to 1.0 in Fig. 2 for comparison purposes. The lowest temperature for which a complete profile was measured was 106 K because of the time involved (in excess of 12 h). At the other extreme, 150 K is the highest temperature for which the data are considered reasonably reliable because the time required to heat the sample to higher temperatures becomes a significant fraction of the total recovery time (less than 2 min). Another sample, however, exhibited some differences in recovery profiles compared to Fig. 2. This is demonstrated in Figs. 3 and 4.

Illustrated in Fig. 3 are the $EL2^* \rightarrow EL2^0$ thermal recovery profiles for samples R103 and C1317 for two different temperatures, 106 and 120 K. As can be seen, the two samples exhibit significant differences in their thermal recovery at 106 K. Sample R103 fully recovers in 840 min, whereas sample C1317 recovers in only 470 min. As the temperature is increased, the difference between the recovery rates becomes progressively less, until at 120 K the two are almost the same. At temperatures above 120 K, the recovery profiles are identical for both samples. The observed differences are consistently reproducible and are therefore believed to be real. There is no distinguishable difference between the $EL2$ absorption spectra (see Fig. 1) for these two samples. Furthermore, their quenching rates are virtually identical. It is only their recovery rates that exhibit differences.

Once thermal recovery times (or rates) for a range of temperatures have been determined, one can deduce thermal activation energies by means of an Arrhenius plot such as is shown in Fig. 4. Error bars show the range of values measured for two to four separate determinations of each data point. Part of the data illustrated in Fig. 4 follows the expected pattern, but another part of it was quite unexpected. First, let us look at the data for sample R103 for 106 K $\leq T \leq$ 120 K. The data points lie along a straight line corresponding to an activation energy of 0.30±0.01 eV. This is in excellent

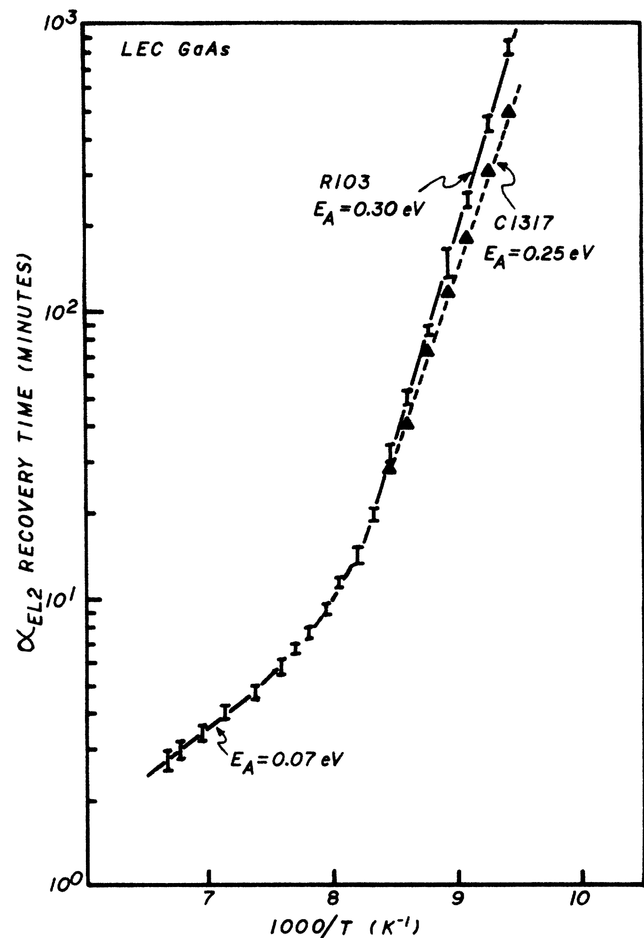

FIG. 4. Plot of logarithm of $EL2$ absorption recovery time (i.e., time to achieve 100% recovery) vs $1000/T$ for samples R103 and C1317 over temperature range 106 K $\leq T \leq$ 150 K. Activation energies determined by slope of lines drawn through data points.

agreement with the 0.30-eV energy determined by Vincent *et al.*[8] using the photocapacitance technique. Others have also measured the $EL2^* \rightarrow EL2^0$ thermal activation energy[18–20] using capacitance techniques, obtaining values in the 0.30–0.36-eV range. The data points for sample C1317 in Fig. 4, on the other hand, lie on a line corresponding to an activation energy of 0.25 eV for the range 106 K $\leq T \leq$ 120 K. This reflects the recovery differences already discussed in relation to Fig. 3. It is believed that these activation energies all correspond to the same thermal barrier which, according to a model suggested previously,[21] is the energy required to thermally excite an electron from $EL2^*$ to the conduction band from which it could then return to $EL2^0$. The different activation energies observed for different samples appear to add further support to the growing consensus that $EL2$ is a "family" of defects, rather than a single defect.[1,2,3,16] The different family configurations could then exhibit different thermal barrier energies. One member of the family may dominate in a given sample, another member in another sample, resulting in the sort of sample-to-sample differences illustrated in Figs. 3 and 4.

Perhaps the most surprising aspect of Fig. 4 is the behavior of the data points at $T > 120$ K. As the temperature increases above this point, the data deviate further and further from the lower-temperature slope in the direction of *lower* activation energy. This is significantly different from the results reported for photocapacitance recovery[8,18] where the activation energy remained the same throughout the 100 K $< T <$ 150 K range. This means that the $EL2$ infrared absorption is thermally recovering much more slowly than the photocapacitance (hundreds of seconds instead of tens of seconds) for $T > 130$ K. At first it was suspected that there was something wrong with the absorption data, particularly the temperature measurement. It was felt that the slower than expected recovery times might be the result of a time lag involved in the sample reaching the same temperature as the cold finger of the refrigerator. This prompted a redesign of the temperature measurement technique in such a way that the silicon diode sensor was firmly attached to the sample itself. The result was only a minor difference in the data. Recovery times for the $EL2$ absorption at higher temperatures were still much slower than anticipated. It is obvious that absorption and photocapacitance measurements probe different features of the $EL2$ structure but it is not clear why the thermal recovery from $EL2^*$ to $EL2^0$ should be so much slower for the absorption at $T > 130$ K. The data points for absorption recovery at 130 K $< T <$ 150 K (Fig. 4) fall on a line corresponding to an activation energy of about 0.07 eV. This may or may not be a meaningful activation energy, but it is noted that 0.07 eV is approximately twice the longitudinal-optic (LO) -phonon energy in GaAs.[23]

A different than expected thermal recovery behavior was also observed at temperatures below 100 K. At these lower temperatures, thermal recovery is very slow and complete recovery would take too long to measure in a practical sense. So a different approach was taken.

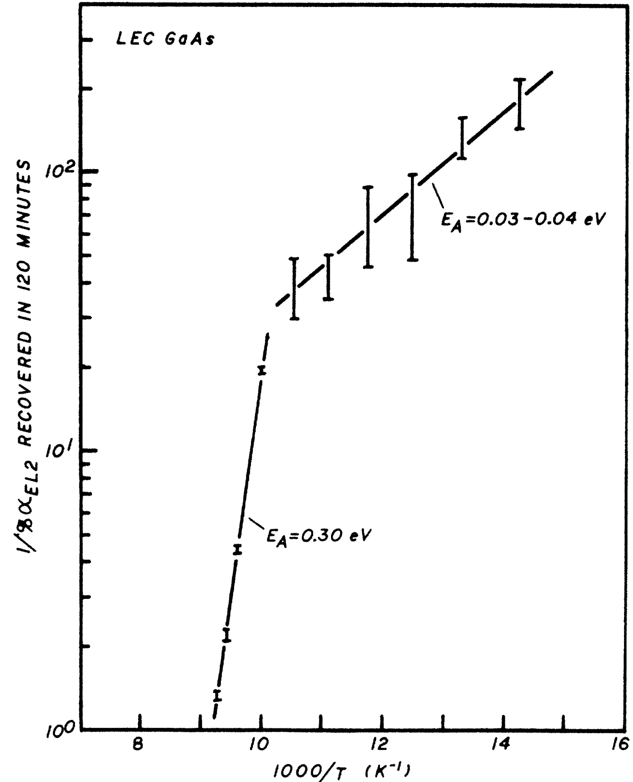

FIG. 5. Plot of logarithm of reciprocal of percentage $EL2$ absorption recovered in 120 min vs $1000/T$ for temperature range 70 K $\leq T \leq$ 108 K.

The amount of $EL2^* \rightarrow EL2^0$ absorption recovery was measured for specific time increments of 1, 2, 3, and 4 h for the temperature range 70 K $\leq T \leq$ 106 K. Results of the 2-h recovery measurements for sample R103 are shown in Fig. 5. The data points for $T > 100$ K fall on a straight line of slope 0.30, as expected (see Fig. 4). Below 100 K, however, the behavior changes considerably. The data points not only deviate significantly from the 0.30-eV slope, but they exhibit a rather large variation in recovery from run to run. The error bars in Fig. 5 show the range of values obtained for each data point for four separate runs on this one sample. For $T > 100$ K, the data are very reproducible. For $T < 100$ K the scatter is obvious. Let us assume that these data points for $T < 100$ K fall more or less along a straight line. Given the scatter in data, there will be a range of line slopes to which these points could be fit. In this case, the range corresponds to an activation energy somewhere between 0.03 and 0.04 eV. It is noted that the LO-phonon energy[23] (0.036 eV) falls in this range, so such an activation energy may not be unreasonable.

IV. SUMMARY AND CONCLUSIONS

The $EL2^* \rightarrow EL2^0$ thermal recovery of the $EL2$ infrared absorption in LEC GaAs was studied for 70 K $\leq T \leq$ 150 K. Different activation energies were found to dominate over different temperature ranges. In the

range 100 K $\leq T \leq$ 120 K, the absorption recovery agrees quite well with previously reported photocapacitance recovery. One sample exhibited an activation energy of 0.30 eV, while a second one showed an activation energy of 0.25 eV over the same temperature range. The different observed energies seem to support the view that $EL2$ is not a single defect, but rather a family of defects with different family members exhibiting different thermal barrier energies. It is believed that the barrier corresponds to the energy required to thermally excite an electron from $EL2^*$ to the conduction band.[21] The family concept is more understandable if $EL2$ is considered to be an As_{Ga} complex rather than an isolated As_{Ga}.[1,2]

For temperatures outside the 100 K $< T <$ 120 K region, the thermal recovery of $EL2$ absorption exhibits different activation energies than any previously reported. At $T <$ 100 K, an activation energy of 0.03 to 0.04 seems to dominate. Most surprisingly, an activation energy of 0.07 eV becomes apparent for $T >$ 120 K. It was noted that these two energies corresponded to one and two times the LO-phonon energy, respectively. Nevertheless, it is not clear why the 0.07-eV activation should dominate over the 0.3-eV thermal barrier activation at $T >$ 120 K for the absorption but not for the photocapacitance.

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