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Photoquenching and photoinduced-recovery properties of the *EL*2 defect in GaAs: Evidence against the identification of *EL*2 with the isolated $\mathrm{As_{Ga}}$ defect

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Photoquenching of the stable state and photoinduced recovery from the metastable configuration of the *EL*2 defect in semi-insulating GaAs grown by liquid-encapsulated Czochralski technique were studied by use of the infrared absorption technique concurrent with monochromatic light irradiation in the energy range of $0.7 \le h\nu \le 1.5$ eV. The monochromatic light intensity was ≤ 2 mW/cm^2. The photoquenching data show two peaks at 1.125 and 1.30 eV while the photoinduced recovery data exhibit a complex structure consisting of a broad band around 0.9 eV and a set of multiple sharp peaks between 1.44 and 1.5 eV. The present results cannot be explained in terms of the available calculations and predictions reported for the isolated arsenic antisite when it undergoes a symmetry-distortion transition.

It is well recognized that one of the keys to reaching a clearer understanding of the nature of the *EL*2 defect in GaAs is to understand its metastable state ($EL2^*$). $EL2^*$ apparently exhibits no experimentally observed properties of its own. Conflicting and controversial issues, both experimental and theoretical, concerning the *EL*2 atomic structure, the transformation of *EL*2 from its normal state ($EL2^0$) to $EL2^*$, and the recovery from $EL2^*$ back to $EL2^0$ dominate the current literature. The most active controversy involves identification of the atomic structure of *EL*2 and how its constituent atom(s) rearrange during the $EL2^0 \leftrightarrow EL2^*$ transformation in response to electronic transitions under photoexcitation with certain photon energies (for a review see Refs. 1-3).

Since $EL2^*$ is experimentally inaccessible, we are reduced to constructing our knowledge of this state by indirect methods. One approach is to observe its recovery back to the normal state ($EL2^* \rightarrow EL2^0$). It is well known that such recovery can occur thermally by heating the sample to about 140 K or higher for a short period of time. Recovery can also be induced optically by irradiating the sample with photons of appropriate energy.

A few attempts have been made recently to transform the *EL*2 defect from $EL2^*$ to $EL2^0$ by photon irradiation. Such photoinduced recovery has been reported for photoluminescence,[4] photoconductivity,[5] photocapacitance,[6] infrared (ir) absorption,[7-10] and electron paramagnetic resonance.[11] Even though all these studies have established that the optical recovery of $EL2^*$ can be induced, they disagree on some important aspects such as the amount of optical recovery and the spectral dependence of the recovery. The reason for these disagreements is usually not obvious, but it is known that in at least some cases the results are highly dependent on parameters such as temperature, the history of the sample, the technique employed to study the recovery, and the intensity of the irradiation.[10] There is also a general consensus that photons with an energy of 1.1 eV quench $EL2^0$. This has led many authors to speculate that the $EL2^0 \rightarrow EL2^*$ transformation occurs through an internal transition that leaves the electrons localized within *EL*2. This transition is believed to be responsible for the broad peak observed at 1.18 eV in the ir absorption spectrum of $EL2^0$ (see, for example, Refs. 12-14).

In this Rapid Communication we report new experimental measurements for the photoquenching of $EL2^0$ and the photoinduced recovery from $EL2^*$ by using the ir absorption technique. The present results will be tested against the existing models proposed for *EL*2. We will show that the photoquenching and optical recovery data cannot be explained in terms of the available calculations and predictions reported for the isolated $\mathrm{As_{Ga}}$ defect[12] when it undergoes a symmetry-distortion transition.

Several semi-insulating GaAs samples (doped and undoped) grown by the liquid-encapsulated Czochralski (LEC) technique and obtained from several manufacturers were investigated. In the present paper, we report the measurements that were obtained for an undoped and annealed sample which shows the typical characteristics of *EL*2 such as thermal stability, photoquenching with white light or 1.1-eV monochromatic light, thermal recovery from $EL2^*$, and the concentration ($\sim 1.55 \times 10^{16}$ cm^3). Infrared absorption measurements were made with a Cary 2300 spectrometer. Its probing light is weak enough that no observable photoquenching or photoinduced recovery occurs during long sample exposure times in the beam (~ 18 h). A separate monochromator with an external 100-W quartz-halogen lamp provided the irradiation light. A wide range of photon energies (0.7-01.51 eV) was available with this monochromator. A cutoff filter with 50% transmittance at 1.46 eV and zero transmittance at 1.515 eV was placed at the output of the monochromator to prevent illumination with photon energies larger than the band gap. The intensity of the monochromator output was measured with a calibrated thermopile and it was kept constant (~ 1.9 mW/cm^2) by adjusting the voltage on the light source at each photon energy over the range of 0.7-1.4 eV. The intensity decreased from 1.9 mW/cm^2 at 1.4 eV to ~ 0.4 mW/cm^2 at 1.50 eV.

The photoquenching data were collected as follows.

The sample was cooled in the dark to 9 K by using a closed-cycle refrigerator. The ir absorption spectra were taken before (S_1) and after (S_2) photoquenching of $EL2^0$ using $h\nu = 1.125$ eV. The residual absorption, S_2, was subtracted from S_1 and from all other spectra taken during either the quenching or recovery process. The difference between S_1 and S_2 was taken in order to calculate the absorption coefficient, α_0, at 1.18 eV from which $[EL2^0]$ was calculated by using Martin's criterion.[15] Then the sample was heated to 150 K for several minutes to recover $EL2^*$. The sample was then cooled to 9 K and $EL2^0$ was photoquenched with various monochromatic light energies in the range of $0.7 \leq h\nu \leq 1.51$ eV for 50 sec. The absorption coefficient, α, was calculated from the ir spectrum at 1.18 eV for each photon energy and compared to α_0 as shown in Fig. 1. The sample was again heated to 150 K and then cooled to 9 K for each run cycle.

The photoinduced-recovery ($EL2^* \rightarrow EL2^0$) data were collected according to the following procedure. After a complete photoquenching of $EL2^0$ at 9 K using 1.125 eV light, the sample was heated to 77 K and illuminated with monochromatic light in the 0.7–1.51-eV range for a specific period of time. The sample was then cooled to 9 K again to collect the ir absorption spectrum from which the absorption coefficients, α, were determined at the 1.18- and 1.40-eV positions. These absorption coefficients were compared to α_0 which was also measured at 1.18 and 1.40 eV. The above procedure was repeated for each run and each run was repeated at least three times. The results are shown in Fig. 2. A few points should be noted here. First, the 1.18- and 1.40-eV positions were chosen to calculate the absorption coefficient because two broad peaks were obtained at these positions when a base line correction was made (see Refs. 1 and 16). Second, thermal recovery is insignificant[17] ($< 1\%$) at 77 K for the illumination period of 25 min used in this study. Third, an illumination time of 25 min was used because it was long enough to permit significant optical recovery while still short enough to collect a reasonable number of data points in a day's time. Fourth, optical recovery was observed at 9 K but with a slower rate as compared to the recovery rate at 77 K using 1.46-eV monochromatic light (see Ref. 10).

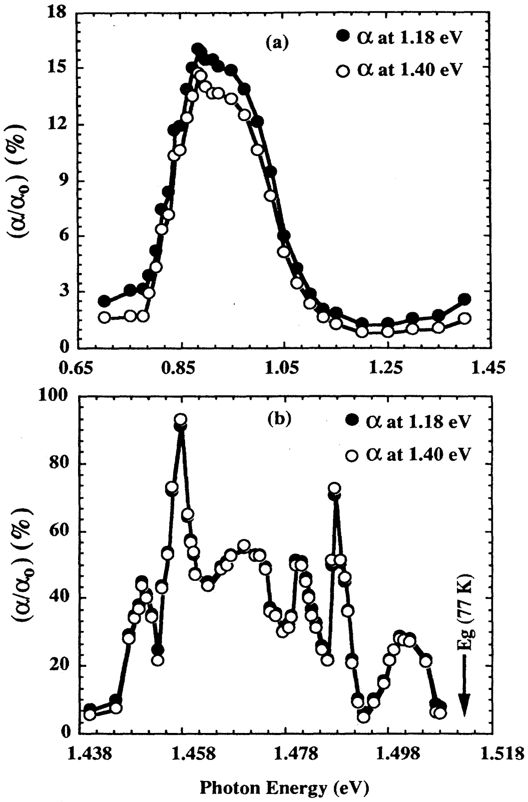

FIG. 2. Photoinduced $EL2^* \rightarrow EL2^0$ recovery for the same sample as in Fig. 1 as a function of photon energy (a) in the 0.7–1.4-eV range and (b) in the 1.44–1.51-eV range. The optical recovery was determined at both the 1.18 eV (●) and 1.40 eV (○) energy positions in the ir absorption spectrum after illumination for 25 min with monochromatic light of energy indicated by each pair of data points. Sample was illuminated at 77 K then cooled to 9 K to measure the absorption coefficients.

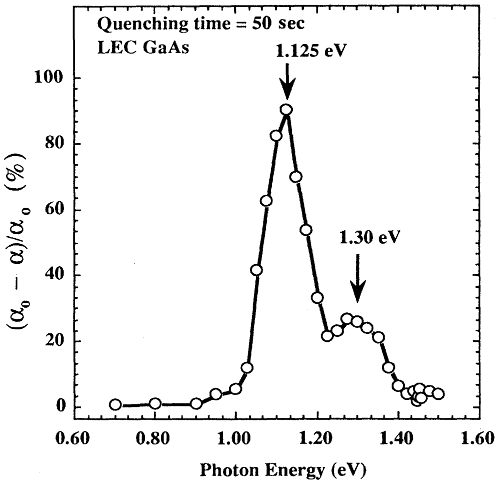

FIG. 1. The ir absorption photoquenching data for LEC semi-insulating GaAs as a function of photon energy. Both absorption coefficients, α and α_0, were obtained from the $EL2^0$ ir absorption spectrum at 1.18 eV. The spectra were collected at 9 K and $EL2^* \rightarrow EL2^0$ was thermally regenerated at 150 K before each run.

There have been recent theoretical developments toward identifying $EL2$ with the isolated $\mathrm{As_{Ga}}$ defect. Exciting results were reported by Dabrowski and Scheffler[12] (DS) who performed parameter-free, self-consistent Green's function calculations of the electronic structure, total energy, and forces of $\mathrm{As_{Ga}}$ and found that the defect can in fact possess a metastability. According to Fig. 2 of the DS paper, electrons can be promoted from the normal state (F) to an excited state (E) within $\mathrm{As_{Ga}}$ and can then decay to the metastable state (M). The $F \rightarrow E$ transition was calculated to be 0.97 eV and DS made an attempt to identify this transition with the broad peak (BP) observed at 1.18 eV in the $EL2^0$ ir absorption spectrum.[18] This attempt was made under the assumption that the zero-phonon line (ZPL) observed at 1.039 eV and BP belong to the same transition, i.e., $F \rightarrow E$ transition. Figure 1 seems to be in conflict with the DS model for the following reasons. First, two peaks were observed at 1.125 and 1.30 eV in Fig. 1 suggesting that $EL2^0 \rightarrow EL2^*$ transformation occurs through two paths. Second, the 1.125-eV peak is in disagreement with the BP and ZPL energies. This disagreement may suggest that the $EL2^0 \rightarrow EL2^*$ transformation does not occur through the BP. Third, the calculated energy of 0.97 eV is in good agreement with the ZPL energy, but a wide range of monochromatic light energies can photoquench $EL2^0$ in a way that the calculated energy of 0.97 eV is meaningless when one compares it to the experimental observation as shown in Fig. 1. Fourth, $EL2^0$ was found to be photoquenched by using 0.8 or 1.4 eV after an illumination time longer than 25 min. The photoquenching of $EL2^0$ at the above energies and illumination time was found to be complete especially for unannealed doped or undoped semi-insulating GaAs. It was also noted that the latter samples were found to photoquench completely with $1.4 \leq h\nu \leq 1.5$ eV monochromatic light. Fifth, the 1.30-eV peak in Fig. 1 was observed in all samples that were tested. The quenching time at this energy was found to be sample dependent. There is also experimental evidence that the ZPL and BP belong to two different transitions.[19,20]

Although the DS model provides a good description of an Auger-type recovery under electron injection, it does not give any information about the photoinduced recovery of $EL2^*$, a process that was found to occur with various techniques as mentioned earlier. The optical recovery as shown in Fig. 2 is still unexplained. One possible explanation of the recovery data is that the peaks observed in Fig. 2 represent energy levels of a defect(s) that is not part of $EL2$ from which free electrons were excited and then captured by $EL2^*$ causing an Auger-type recovery. This explanation, however, is ruled out easily by our discovery that photons in the energy range of $1.4 \leq h\nu \leq 1.51$ eV were found to quench $EL2^0$ for an illumination time ≥ 25 min. Again, this illumination time was found to be sample dependent.

According to Fig. 2, we found that the recovery obtained when using photons of about 0.9 eV energy is only about 16% [Fig. 2(a)] and that the band seems to be composed of two peaks. On the other hand, the recovery in Fig. 2(b) is about 93% at 1.46 eV. The amount of recovery in both Figs. 2(a) and 2(b) was found to be sample dependent and shows a more complex structure in unannealed doped or undoped semi-insulating GaAs. It is noted that (α/α_0) measured at 1.40 eV is larger than (α/α_0) measured at 1.18 eV only when the magnitude of the recovery is larger than 50%.

The recovery data in Fig. 2 were tested against the well-known models proposed for the metastable $EL2$ defect, namely, arsenic antisite-gallium vacancy,[12] arsenic split-interstitial,[21] arsenic antisite-arsenic vacancy,[22] and arsenic antisite-divacancy[23-25] (gallium vacancy-arsenic vacancy). It appears that one point defect which has electronic energy levels which coincide with the peaks observed in the recovery data (Fig. 2) is the arsenic vacancy (V_{As}). The V_{As} was found[26-28] to possess an s-like energy level near or above midgap and a p-like energy level close to the conduction band. These energy levels may be shifted due to other point defects present in the vicinity. It is not the purpose of this paper to show how much the levels shift or in which direction this shift may occur, but rather to show qualitatively that the present optical recovery data support the models that involve V_{As}. Thus, V_{As} may act as an actuator for the $EL2^* \rightarrow EL2^0$ transformation.

The question of whether the peaks observed in Fig. 2 are due to splitting in the V_{As} energy levels or to the fact that $EL2$ is a family of slightly different levels is still open. However, the presence of what appears to be two peaks around 0.9 eV in Fig. 2(a) and the fact that an s-like energy level (a_1) does not split under crystal or strain fields may suggest that the data in Fig. 2 are due to both splitting in the p-like levels and the existence of a family of levels. Additional results, analyses, and interpretations will be presented elsewhere.

In conclusion, we have presented novel experimental measurements in which two peaks were observed in the photoquenching data of the normal state of $EL2$ and a complex structure in the photoinduced-recovery data from the metastable configuration. An optical recovery has been observed for the first time in the 1.4–1.5-eV region. The recovery in this region is more efficient and more complex than that previously reported for the 0.9-eV region. As shown elsewhere, the recovery characteristics are also very temperature dependent.[10] In general, the lower the temperature the smaller the amount of recovery. The photoquenching and photoinduced-recovery data cannot be explained in terms of the isolated arsenic antisite when it undergoes a symmetry distortion transition as described by Dabrowski and Scheffler.[12] The peaks in the optical recovery data are coincident with the arsenic vacancy energy levels. Hence, the present results support the complex models involving an arsenic vacancy which have been proposed for $EL2$. Both photoquenching and optical recovery were found to be sample dependent.

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