Infrared-absorption properties of *EL*2 in GaAs

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The optical properties of semi-insulating bulk GaAs, grown with the liquid-encapsulated Czochralski techniques, were studied in the spectral region of 5000–11 150 cm^{-1} using a high-resolution Fourier-transform infrared spectrophotometer. The zero-phonon line associated with the intracenter transitions, observed at 1.039 eV and at temperatures less than 12 K, was found to exhibit a complex structure. This structure indicates that the *EL*2 center is composed of different but similar energy levels, each with one zero-phonon line. The intracenter transitions responsible for the absorption band between 1.03 and 1.27 eV show a structure involving phonon replicas at an average energy interval of 11.5±0.8 meV, which is larger than that of transverse-acoustic phonons suggesting that other couplings may exist.

I. INTRODUCTION

Although GaAs may not replace silicon technology completely, important advantages that it has over silicon have motivated the research community to turn to GaAs several times during the past two decades. Since the early 1980s, the development of high-speed integrated circuits fabricated from GaAs has placed strict requirements on the quality of substrate materials. An understanding of the defect species present in the substrate is crucial to such development. A deep center referred to as *EL*2 in GaAs is believed to be responsible for the semi-insulating (si) properties of undoped materials grown by the liquid-encapsulated Czochralski (LEC) techniques.

The search for the structure of *EL*2 is still in progress. Several models have been proposed to account for the nature of *EL*2. Most rely on the atomic displacement near the defect when a transition between a normal and a metastable state occurs. The simplest models consist of an As_{Ga} antisite defect with a vacancy[1,2] or an interstitial.[3–5] More complicated models such as an As_{Ga} with a divacancy,[6] clusters of antisites,[7] families of *EL*2 levels,[8] and a complex center involving As_{Ga} antisites and C_{As} antisites that leads to a strong lattice relaxation[9] were proposed.

The microscopic model proposed by von Bardeleben *et al.*[5] seems to account for much of what is known experimentally, but it is not without crucial problems.[10] One key factor necessary for the validity of the model of von Bardeleben *et al.* is the existence of an acceptor level associated with the normal state of *EL*2. Their model is that *EL*2 has a normal state $EL2^0$ and a metastable state $EL2^*$. The normal state corresponds to an As_{Ga} antisite with an arsenic interstitial (As_i) in the second-neighbor position and the metastable state corresponds to an As_{Ga} antisite with an As_i in the first-neighbor position.

The optical absorption spectrum shows a spectacular quenching behavior which corresponds to the transformation of the $EL2^0$ configuration to $EL2^*$. Nothing is known about the structure of $EL2^*$. This is because the $EL2^*$ state gives rise neither to levels in the gap nor to an EPR spectrum. However, it has been speculated[11] that $EL2^*$ is finalized through the intracenter transition which is degenerate with the conduction band.

In this paper, we present the experimental results of infrared absorption properties of $EL2^0$ and show the structure of the zero-phonon line (ZPL) associated with the intracenter transitions. From the complex structure of the ZPL, we infer that *EL*2 is composed of different but similar levels. Also we report on the phonon replicas and their behavior as a function of the quenching process. The structure of the replicas indicates that coupling other than transverse acoustic phonons may exist.

II. EXPERIMENTAL TECHNIQUE

Single crystals of semi-insulating GaAs have been studied by infrared absorption with a high-resolution Fourier-transform spectrophotometer (Bomem DA3.01). The samples were cut into $9\times9\times5$-mm^3 and $10\times12\times19$-mm^3 specimens. The first and second samples were grown with medium- and high-pressure LEC, respectively. The optical-absorption measurements were performed along the largest dimensions of the samples. The samples were chemically polished with 3% bromine in methanol and lightly etched in $2NH_3OH{:}1H_2O{:}1H_2O_2$ solution. A cold-head closed-cycle refrigerator and a helium cryostat were used to cool the samples to 8.5 and 4.2 K, respectively. A quartz beam splitter, an InSb detector cooled to liquid-nitrogen temperature, and a quartz-halogen source were employed to cover the spectral limits 4000–12000 cm^{-1}. Wafers of silicon and GaAs were used as filters and were kept at room temperature. All runs were made after cooling the samples in the dark.

III. RESULTS

A series of consecutive optical-absorption spectra of si-GaAs obtained in the spectral region 5000–11000 cm^{-1} is shown in Fig. 1. The spectra were taken approximately 4 min apart with a resolution of 4 cm^{-1} and with a GaAs filter. The spectrum labeled *A* was obtained after 121

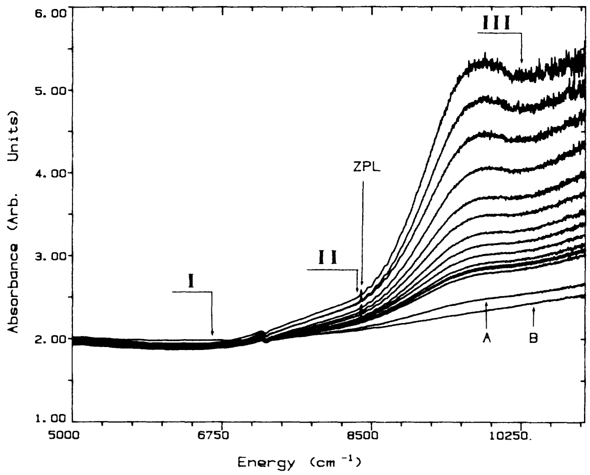

FIG. 1. A series of consecutive optical absorption spectra of $EL2$ as a function of photon energy in high-pressure LEC si-GaAs. Measurements (200 scans for each run) were made at 4.2 K for the $10\times10\times19$-mm^3 sample with a resolution of 4 cm^{-1} using a GaAs filter. Spectrum A was taken after 121 min and spectrum B was taken after 135 min after the sample was illuminated with white light during the period from 125–132 min. The filter was removed during this period. The three threshold regions are denoted as I, II, and III.

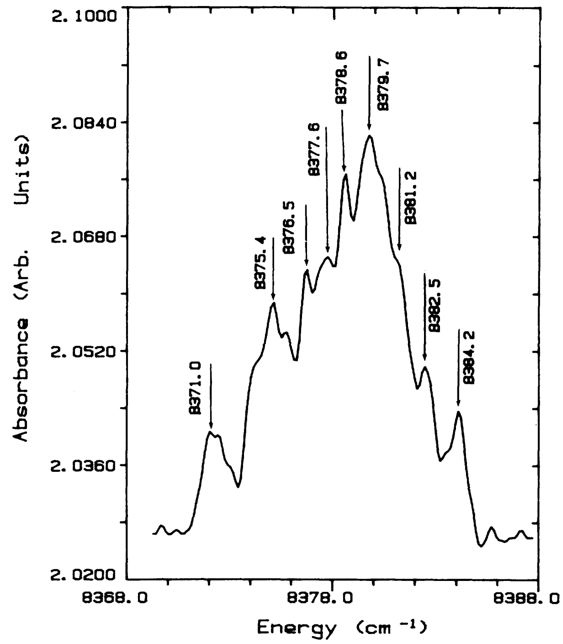

FIG. 2. Fine structure of the ZPL at 4.2 K. Measurements (200 scans) were made for the $10\times12\times19$-mm^3 sample. The resolution was 0.25 cm^{-1} with a silicon filter.

min and the spectrum labeled B was taken after 135 min. In spectrum B, the filter was removed for a period of 7 min and the sample was exposed, during this period, to the light source with the aperture opened to its maximum size (10 mm in diameter). A complete quenching (100%) was not achieved even after exposing the sample to the white light for a few hours. An anomalous structure is observed at 7250 cm^{-1} (0.9 eV). This structure did not disappear after the maximum quenching is reached. Therefore, it is possible that this structure is noise. The ZPL, observed at 8379 cm^{-1} (1.039 eV) and at temperatures less than 12 K, and a few replicas can be clearly seen in most of the spectra.

The optical absorption of the ZPL was studied as a function of resolution at 4.2 K. Nine peaks were observed at a resolution of 0.25 cm^{-1} as shown in Fig. 2. The GaAs sample used for the ZPL studies was grown by high-pressure LEC to ensure that a very high concentration of $EL2$ exists. The spectrum in Fig. 2 was plotted after a base-line correction was made.

Although no more than nine peaks were observed at a resolution of 0.25 cm^{-1}, the peaks observed below 8378.6 cm^{-1} seem to have a complex structure. The intensities of these peaks vary with respect to each other as the time increased during the photoquenching. On the other hand, the peaks observed above 8378.6 cm^{-1} including the peak at 8378.6 cm^{-1} seem to be reproducible, stable, and their intensities decrease approximately with the same rate.

In Fig. 3, we present spectra for the ZPL and its associated replicas. The spectrum in Fig. 3(a) was taken for the $9\times9\times5$-mm^3 sample at 8.5 K and a resolution of 2 cm^{-1}. The sample was exposed to the white light with a GaAs filter for 1 min. The spectra taken for the $10\times12\times19$-mm^3 sample at 4.2 K are shown in Figs. 3(b) and 3(c). The resolutions were 4 and 6 cm^{-1}, respectively. The sample was illuminated with GaAs-filtered white light for 4 [Fig. 3(b)] and 0.5 min [Fig. 3(c)].

IV. DISCUSSION

A careful examination of the optical-absorption spectra of $EL2$ in Fig. 1 shows the ZPL at 8379 cm^{-1} (1.039 eV) followed by a few replicas. The structure observed at 7250 cm^{-1} (0.9 eV) did not disappear in both normal and metastable configurations. Therefore, it is possible that this structure is noise. However, a grating-spectrometer spectrum[12] shows a structure at the same location when $EL2$ is in the metastable state $EL2^*$. Three threshold regions denoted as I, II, and III were observed at 0.82 (6620), 1.035 (8350), and 1.27 eV (10250 cm^{-1}), respectively. This structure was at first assigned to photoionization transitions from $EL2$ to the conduction-band minima at the Γ, L, and X points of the Brillouin zone.[13] Recent interpretation of the $EL2$ spectrum includes photoionization[14,15] from the $EL2$ ground state to the conduction band (region I) and intracenter transitions within $EL2$ that leave the electrons localized[16] (region II). The intracenter transitions have been interpreted as being the A_1-to-T_2 transitions of the isolated As_{Ga} antisite defect[15,17] and A-to-E transitions of a pair defect which are coupled to the activated vibrational modes of the absorbing centers.[18]

Unfortunately, no electron trapping level has yet been definitely assigned as an acceptor charge state associated with $EL2$. However, Manasreh and Covington[19] have proposed that region III observed at approximately 1.27 eV may be related to an acceptor level associated with the

*EL*2 normal state. The assignment of region III to an acceptor level is in good agreement with the theoretical predictions of Baraff and Schluter.[10] This region has been previously interpreted as a shallow excited state[20] for *EL*2 near the conduction-band minimum, an intracenter transition,[17] or a second trap[21] in *EL*2.

In Fig. 4, we plot the total integrated area of *EL*2, as calculated from consecutive spectra similar to that of Fig. 1, but with a resolution of 6 cm^{-1} in the spectral limits 6620–11150 cm^{-1}. The integrated areas of regions I, II, and III are calculated in the spectral limits 6620–8350 cm^{-1}, 8350–10250 cm^{-1}, and 10250–11150 cm^{-1}, respectively. The behavior of the data in Fig. 4 is similar to that of photocapacitance measurements reported earlier.[22] From first-order least-square fits (for time less than 22 min), the slopes were found to be -2.5×10^{-2}, -5.1×10^{-2}, -5.0×10^{-2}, and -4.3×10^{-2} for regions I, II, III, and the total area, respectively. Since the integrated area is proportional to the *EL*2 concentration, the rates of transition can be related to the slopes of the data in Fig. 4. Therefore, region I seems to have a different transition rate than regions II and III.

The data in Fig. 4 seem to deviate from exponential behavior at 22 min and tend to saturate at longer times. However, the optical absorption of *EL*2 remains observable and distinguishable from the background absorption for at least 2 h at 4.2 K. The quenching rates as well as the deviation from exponential behavior were found to depend strongly on temperature.[23] This nonexponential behavior of the optical transition from $EL2^0$ to $EL2^*$ can be interpreted by assuming a broadening of the photoquenching efficiency. This broadening suggests that *EL*2 consists of a group of distributed states. In particular, multiple metastable states are suggested to exist for the *EL*2 levels.[24] One possible explanation of the photoquenching broadening is that the *EL*2 levels have different electron-phonon couplings. This is illustrated in the complex structure of the phonon replicas presented in Fig. 3.

The fine structure of the ZPL shown in Fig. 2 indicates that *EL*2 has a complex structure which is in disagreement with the assignment of *EL*2 to the isolated As_{Ga} antisite defect.[15,25] The ZPL structure presented in Fig. 2 may not arise from the fine structure of the transition final state. This is because up to nine peaks which are separated by approximately 1 cm^{-1} (0.124 meV) were observed. The peak separation is very small compared to the 10-meV splitting for the crystal field and 0.2–0.3 eV for the spin-orbit splitting in III-V semiconductors calculated from tight-binding[26] and pseudopotential[27] models. The simplest way to account for such structures is to assume contributions from similar defects with slightly different

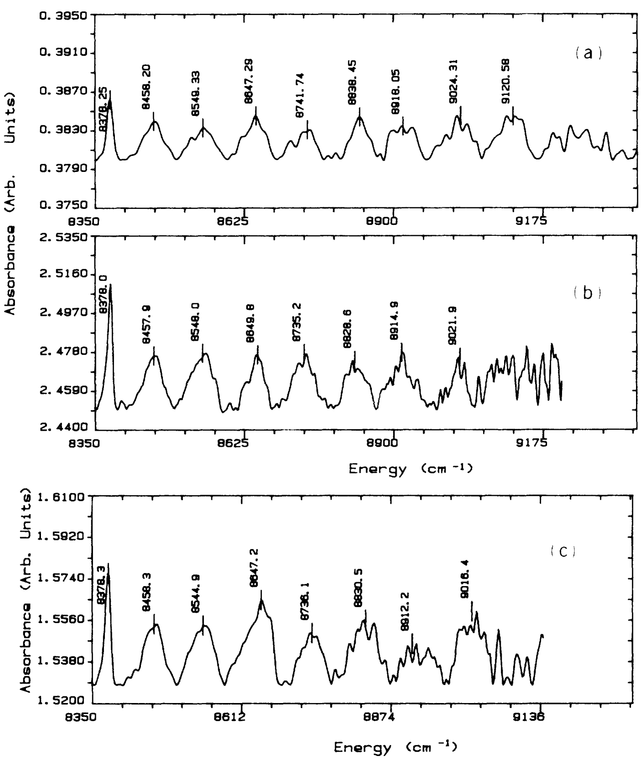

FIG. 3. Spectra of the ZPL and its associated replicas taken after the base-line correction was made. (a) Measurements (40 scans) were obtained for the $9\times9\times5$-mm^3 sample with a resolution of 2 cm^{-1} and smoothed by a factor of 5. The sample was exposed to light for 1 min at 8.5 K. (b) Measurements (200 scans) were obtained for the $10\times12\times19$-mm^3 sample with a resolution of 4 cm^{-1} and smoothed by a factor of 1. The sample was exposed to light for 4 min at 4.2 K. (c) Measurements (200 scans) were obtained for the $10\times12\times19$-mm^3 sample with a resolution of 6 cm^{-1} and smoothed by a factor of 1. The sample was exposed to light for 0.5 min at 4.2 K. In all spectra, the samples were cooled in the dark and the light exposure was made with a GaAs filter.

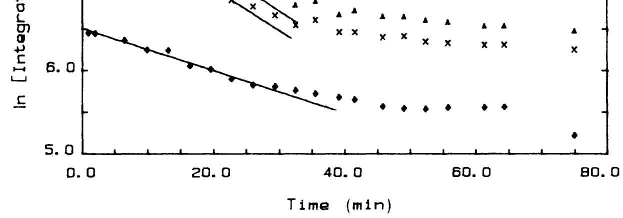

FIG. 4. The transition rate of *EL*2 to its metastable configuration is illustrated by the natural log of the integrated area versus time. The data present the total integrated area taken in the spectral limits 6620–11150 cm^{-1} (+) and region I (◆), region II (▲), and region III (×) calculated in the spectral limits 6629–8350 cm^{-1}, 8350–10250 cm^{-1}, and 10250–11150 cm^{-1}, respectively. The integrated areas were calculated from spectra similar to that of Fig. 1, but with a resolution of 6 cm^{-1}. The solid lines are the first-order least-squares fits of the data for time less than 22 min.

TABLE I. Spectroscopic parameters of the ZPL and its associated replicas reported in Fig. 3(a). The sample was exposed to light for 1 min at 8.5 K.

Line	Position (cm^{-1})	Position (eV)	Ratio of replica area to ZPL area	FWHM (cm^{-1})
0 (ZPL)	8378.25	1.0387	0.095±0.001[a]	12.2
1	8458.20	1.0486	1.792±0.002	42±3
2	8549.33	1.0600	1.698±0.002	41±3
3	8647.29	1.0721	2.055±0.003	51±3
4	8741.74	1.0838	1.499±0.016	49±7
5	8838.45	1.0958	1.698±0.004	37±3
6	8918.05	1.1057	1.897±0.016	56±7
7	9024.31	1.1188	2.317±0.021	40±7

[a]This is the absolute value of the ZPL area in absorbance per cm after smoothing by a factor of 5.

energy levels, each with one ZPL. This assumption is in excellent agreement with the microscopic model proposed by von Bardeleben *et al.*[5] As mentioned earlier, the formation of *EL*2 in this model results in the trapping of As_i in a second-neighbor position by the strain field of As_{Ga}. Since there are many such positions, there exists a distribution of *EL*2 defects corresponding to slightly different energy levels. The atomic model[6] which is based on As_{Ga} antisite with a divacancy predicts the existence of a group of identical *EL*2 levels.

Another important result of the present investigation is that the phonon replicas in Fig. 3 are not momentum conserving as in familiar optical absorption in gallium arsenide[28] and other semiconductors,[29,30] but are in-band resonant modes associated with local vibrations of the absorption center. The positions, relative areas, and full widths at half maximum (FWHM's) of the replicas presented in Fig. 3 are summarized in Tables I–III. The average displacements of the replicas from each other are 11.5±0.8, 11.4±0.9, and 11.3±1.0 meV for Figs. 3(a)–3(c), respectively. These displacements are in excellent agreement with respect to each other within the experimental error which arises from the method used to determine the peaks for broad signals. Also, the present displacements are in good agreement with previous measurements[16] of 11±1 meV and in disagreement with the transverse-acoustic phonon[31] which is approximately $(2.36\pm0.015)\times10^{12}$ cps or 9.76±0.06 meV.

A striking feature of the phonon replicas shown in Fig. 3 is the variation of their complex structure with time. As an example, the replicas in Fig. 3(b) have approximately equal intensities which change over time to a structure similar to that observed in Fig. 3(a) and 3(c). This complex structure may reflect the dynamical behavior of the defect constituent atoms during the configurational changes from the normal to the metastable states.

Since the replicas do not follow the selection rules for coupling electronic transitions to multiphonon modes in the GaAs lattice,[32] the phonon energy involved in the intracenter transitions is related to an internal Jahn-Teller effect and it is difficult to compare this phonon energy with other phonon energies involved in the multiphonon capture of electrons. In fact, the complex structure of each replica may resemble quite different local phonon modes that are involved in the intracenter transitions. The Jahn-Teller relaxation energy associated with such transitions is calculated from the difference in the ZPL (1.039 eV) and the transition maximum (1.18 eV) to be 0.141 eV. This energy is small as compared to the Franck-Condon shift (0.205 eV) calculated from the present absorption measurements (1.18 eV) and previous emission measurements[17,33] (0.77 eV).

TABLE II. Spectroscopic parameters of the ZPL and its associated replicas reported in Fig. 3(b). The sample was exposed to light for 4 min at 4.2 K.

Line	Position (cm^{-1})	Position (eV)	Ratio of replica area to ZPL area	FWHM (cm^{-1})
0 (ZPL)	8378.9	1.0388	0.795±0.003[a]	8.2
1	8457.0	1.0485	1.434±0.005	35±2
2	8548.0	1.0598	1.635±0.005	55±3
3	8649.8	1.0724	1.170±0.010	38±4
4	8735.2	1.0830	1.152±0.015	45±4
5	8828.6	1.0946	1.223±0.005	41±3
6	8914.9	1.1053	1.535±0.100	42±7
7	9021.9	1.1185	0.964±0.100	25±8

[a]This is the absolute value of the ZPL area in absorbance per cm after smoothing by a factor of 1.

TABLE III. Spectroscopic parameters of the ZPL and its associated replicas reported in Fig. 3(c). The sample was exposed to light for 0.5 min at 4.2 K.

Line	Position (cm^{-1})	Position (eV)	Ratio of replica area to ZPL area	FWHM (cm^{-1})
0 (ZPL)	8378.3	1.0387	0.750 ± 0.002[a]	10.9
1	8458.3	1.0487	1.180 ± 0.004	39 ± 2
2	8544.9	1.0594	1.270 ± 0.003	51 ± 2
3	8647.2	1.0721	1.900 ± 0.004	52 ± 3
4	8736.1	1.0831	1.010 ± 0.005	49 ± 5
5	8830.5	1.0948	1.510 ± 0.005	54 ± 7
6	8912.4	1.1049	0.990 ± 0.010	48 ± 9
7	9016.4	1.1179	1.530 ± 0.010	61 ± 9

[a]This is the absolute value of the ZPL area in absorbance per cm after smoothing by a factor of 1.

V. CONCLUSIONS

In this paper, we provide the infrared optical-absorption properties of *EL*2 in semi-insulting bulk GaAs. The results indicate that the ZPL associated with the intracenter transitions has a complex structure. This structure was revealed as the resolution increased suggesting that the *EL*2 center is composed of slightly different but similar energy levels, each with one ZPL. We have shown that the transition of *EL*2 from the normal to the metastable configurations has a nonexponential behavior which may arise from various in-band resonant modes and electron-lattice couplings. Additional work needs to be done on the activated vibrational modes associated with the absorbing centers and their effects on the relaxation energy.

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