RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 5 15 FEBRUARY 1987-I

Fourier-transform infrared-absorption studies of intracenter transitions in the $EL2$ level in semi-insulating bulk GaAs grown with the liquid-encapsulated Czochralski technique

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(Received 12 November 1986)

The intracenter transitions that are responsible for the characteristic absorption band of $EL2$ in the spectral region of 8060–10 500 cm^{-1} were studied using a high-resolution Fourier-transform infrared spectrophotometer. The results show that the zero-phonon line observed at 8379 cm^{-1} has a complex structure and therefore cannot be assigned to a unique center. The phonon replicas associated with the zero-phonon line indicate that couplings other than transverse-acoustic phonon may exist. A group-theoretical analysis of the present results shows that the $EL2$ center has a symmetry lower than that of T_d suggesting that $EL2$ can be identified as a pair defect which involves an arsenic antisite with a vacancy or interstitial.

The midgap level referred to as $EL2$ in As-rich melt-grown GaAs has a most profound potential importance in solid-state electronics and optoelectronics. It is considered to be responsible for the semi-insulating (si) behavior of undoped GaAs. In spite of intensive characterization efforts to control the concentration and uniformity of this deep level, the problem of establishing the nature of $EL2$ is yet a matter of controversy.

After the attribution of $EL2$ to oxygen[1] had been found to be untenable,[2] attempts were made to assign $EL2$ to the isolated As_{Ga} antisite defect.[3–5] Meyer and Spaeth[6] and Meyer, Spaeth, and Scheffler[7] studied $EL2$ absorption properties using magnetic circular dichroism (MCD) and concluded that $EL2$ cannot be associated with the isolated As_{Ga} antisite. It has been shown that the simplest complex that can be identified with $EL2$ will consist of the arsenic antisite with an interstitial[8,9] or a vacancy[10,11] defect.

The absorption spectrum of undoped bulk GaAs attributed to $EL2$ contains a band of intracenter transitions with a zero-phonon line (ZPL).[4,12] The zero-phonon line was found to split under uniaxial stress applied in a certain crystallographic direction.[5] This splitting was interpreted to be an A_1 to T_2 transition.[4] The above interpretation was based on the assumption that the zero-phonon line is assigned to a unique center under no stress. However, the fine structure of the zero-phonon line observed in the present measurements indicates for the first time that the intracenter transitions arise from more than one center and therefore $EL2$ can be identified as a pair defect.

The two single-crystal specimens of GaAs used in the present measurements were grown by the liquid-encapsulated Czochralski (LEC) technique.[13] The first crystal was cut into a $9\times9\times5$-mm^3 sample and the second crystal was cut into a $11\times11\times22$-mm^3 sample. For the zero-phonon line measurements, the cold finger of a variable-temperature (8–300 K) optical cryostat was used to cool the samples to 8.5 K. The optical-absorption measurements of the samples were performed along the 9-mm direction for the first sample and along the 22-mm direction for the second sample. Optical absorption spectra were acquired with a Fourier-transform infrared (FTIR) spectrometer (Bomem DA3.01) with a quartz beam splitter, a cooled InSb detector, and a quartz-halogen source to cover the spectral region of 5000–12 000 cm^{-1}. Wafers of GaAs and Si were used at room temperature as filters. As judged by the comparison of consecutive absorption spectra, $EL2$ was less than 10% quenched for 12 and 90 min for GaAs and Si filters, respectively.

A typical FTIR absorption spectrum of si GaAs is presented in Fig. 1. The zero-phonon line at energy 8379 cm^{-1} and a few replicas can be clearly seen. This spectrum was obtained at 8.5 K, 2-cm^{-1} resolution using strong apodization,[14] and smoothed by a degradation factor of 2. The structure of the $EL2$ absorption in Fig. 1 shows three threshold regions at approximately 6750, 8350, and 10 500 cm^{-1}. This is in good agreement with previous optical-absorption measurements.[12,15]

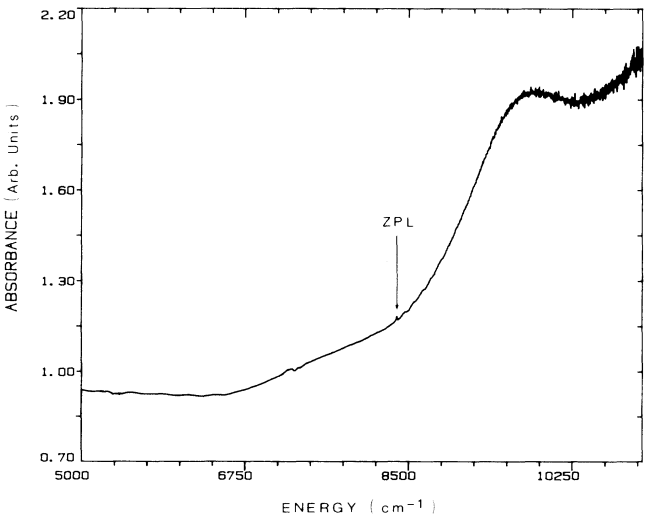

FIG. 1. Optical absorption of $EL2$ as a function of photon energy in si LEC GaAs. Measurements (50 scans) were made at 8.5 K for the $11\times11\times22$-mm^3 sample with a resolution of 2 cm^{-1}.

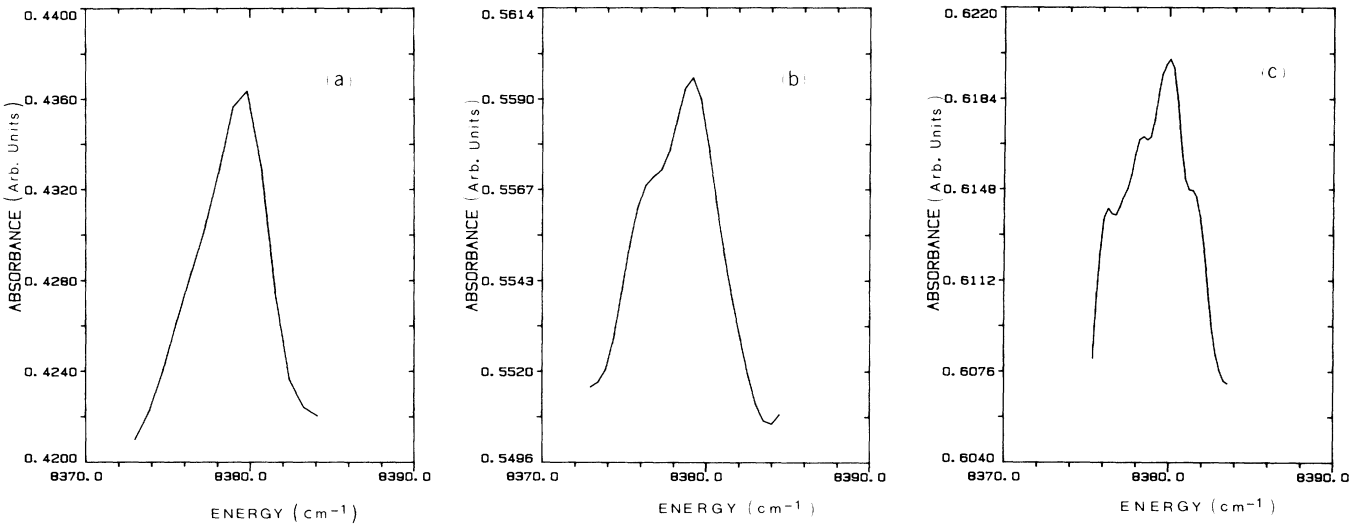

FIG. 2. Fine structure of the zero-phonon line at 8.5 K. (a) Measurements (200 scans) were made for the $11\times11\times22$-mm^3 sample with a resolution of 2 cm^{-1} using a Si filter. (b) Measurements (50 scans) were made for the $9\times9\times5$-mm^3 sample with a resolution of 1 cm^{-1} using a GaAs filter. (c) Measurements (1000 scans) were made for the $11\times11\times22$-mm^3 sample with a resolution of 0.5 cm^{-1} using a Si filter. No zero baseline correction was made for any of the spectra.

The optical absorption of the ZPL as a function of wave number is shown in Fig. 2. The absorbance scaling in Figs. 2(a), 2(b), and 2(c) is different due to the fact that no zero baseline correction was made for any spectra. A striking feature of the zero-phonon line at 2 cm^{-1} resolution [Fig. 2(a)] is its asymmetric shape. It deviates from a Lorentzian or Gaussian shape predicted for a homogeneously or inhomogeneously broadened zero-phonon line.[16] The complex structure of the ZPL is revealed as the resolution is increased. In Fig. 2(b) one can observe two peaks at approximately 8376.2 and 8379 cm^{-1}. This spectrum was taken at a resolution of 1 cm^{-1} and smoothed by a factor of 2. Two more lines appear in the ZPL spectrum as the resolution changed from 1 to 0.5 cm^{-1} (smoothed by a factor of 1.5) as shown in Fig. 2(c).

In Fig. 3, we present a spectrum for the ZPL and 8 replicas which were taken for the $9\times9\times5$-mm^3 sample at a resolution of 2 cm^{-1}. This structure is plotted after the baseline correction was made. The positions, relative areas, and full widths at half maximum are summarized in Table I. The replicas are displaced from each other by an average interval of 11.5 ± 0.8 meV.

The fine structure of the zero-phonon line shown in Fig. 2(c) indicates that four transitions contribute to the observed infrared absorption. The present observation is consistent with the models proposed by Bardeleben, Steivenard, Bourgoin, and Huber[9] and Baraff and Shluter[10] in which the $EL2$ center has C_{3v} symmetry and is in disagreement with the assignment of $EL2$ to an isolated As_{Ga} antisite defect.[4,5,17] As mentioned earlier, the simplest complex of the $EL2$ center that gives a C_{3v} symmetry consists of an As_{Ga} antisite with an As interstitial or As vacancy. Green's-function calculations[10] predict that C_{3v} splits into an A level which lies in the band gap and an E level which is resonant with the conduction band. Including spin, the E state gives rise to four degenerate energy levels. Under crystal-field and spin-orbit (SO) coupling, E should split into four energy levels.

The four peaks in Fig. 2(c) are separated by approximately 2 cm^{-1} (0.25 meV), which is very small when compared to the 10-meV splitting for the crystal field and 0.2–0.3 eV for SO splitting in III-V semiconductors as calculated from tight-binding,[18] pseudopotential,[19] and Green's-function models.[20] The latter predicts that the SO splitting is of the order of 5–10 meV for GaAs. A

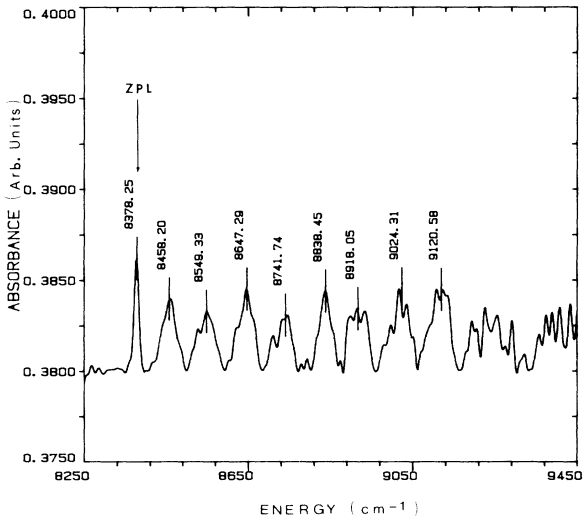

FIG. 3. Fine structure of the zero-phonon line and its replicas at an average energy interval of 11.5 ± 0.8 meV at 8.5 K after baseline correction was made. Measurements (40 scans) were obtained for the $9\times9\times5$-mm^3 sample with a resolution of 2 cm^{-1} and smoothed by a degradation factor of 5. The filter was a GaAs wafer.

TABLE I. Spectroscopic parameters of the zero-phonon line and its associated replicas.

Line	Position (cm^{-1})	Position (eV)	(Replica's area)/(ZPL area)	Full width (cm^{-1})
0 (ZPL)	8378.25	(1.0387)	0.0954 ± 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
8	9120.58	(1.1308)	2.694 ± 0.021	59 ± 7

[a]This is the absolute value of the ZPL area in absorbance cm^{-1} after smoothing by a factor of 5.

qualitative comparison between the experimental results[21] of ZPL in Zn:GaAs, which has an absorption spectrum similar to the present measurements, shows that the peaks observed in the ZPL spectrum are separated by approximately 1.5 meV, which is in fair agreement with the present ZPL measurements.

We have shown that the present measurements provide evidence that $EL2$ is a complex defect. However, we still have to explain the fine structure of the zero-phonon line. The static crystal field and spin-orbit splitting may not account for such structure. Indeed, a recent model was proposed by Bardeleben *et al.*,[22] which, based on the structural arrangement of the defect, may have the capability of explaining the existence of a group of $EL2$ levels. According to this model, the stable state of the defect corresponds to the As_{Ga} antisite and the As interstitial in a second-neighbor position, and the metastable state corresponds to the As_{Ga} antisite and the As interstitial in a first-neighbor position. Thus, the formation of $EL2$ results from the trapping in a second-neighbor position of the As interstitial by the strain field of As_{Ga}. Since there are many such positions, it is possible that there exists a group of similar $EL2$ defects with slightly different energy levels. Taking the above model into consideration, the simplest way to account for the four peaks in the zero-phonon line is to assume they result from the contributions from four different but similar centers, each with one ZPL. A group of $EL2$ levels has been reported earlier[23] which is in good agreement with the present measurements.

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[21] and other semiconductors,[24,25] but are in-band resonant modes associated with local vibrations of the absorption center. Similar behavior is observed in silicon doped with copper.[26] This assumption is based on the fact that the areas under the replicas in Fig. 3 are not decreasing with increasing photon energy (see Table I), and that they do not follow the selection rules for coupling electronic transitions to multiphonon modes in the GaAs lattice.[27] The average displacement of the replicas from each other, 11.5 ± 0.8 meV, is in good agreement with previous measurement[12] of 11 ± 1 meV. This separation is slightly larger than the transverse-acoustic phonon[28] which is approximately $(2.36 \pm 0.015) \times 10^{12}$ cps or 9.76 ± 0.06 meV.

The four peaks observed in the ZPL optical absorption as illustrated in Fig. 2(c) and the anomalous behavior of the associated replicas shown in Fig. 3 are strong evidence that the $EL2$ center in si bulk GaAs is a complex defect, most likely a pair defect composed of the As_{Ga} antisite with an arsenic vacancy or arsenic interstitial. The presence of a vacancy or interstitial as a nearest neighbor to the As_{Ga} antisite will change the binding forces from those found in the perfect lattice. Therefore, it should be possible to measure the local vibrational modes (LVM) of this complex using a high-resolution FTIR spectrophotometer. Additional experiments are needed and should be directed toward studying the LVM of the As defect in GaAs. According to the present measurements (Fig. 3), we predict that the arsenic defect LVM should lie in the wave number range of 80–100 cm^{-1}.

In conclusion, we provide for the first time an FTIR absorption spectrum showing the structure of the intracenter transitions in $EL2$. Based on this structure we identify four different but similar $EL2$ centers each with a ZPL. We also observed coupling of $EL2$ to the local vibrational modes of an As defect in GaAs.

We are thankful to Dr. D. N. Talwar and Dr. G. A. Baraff for many useful discussions and Morgan Semiconductor for providing the GaAs samples. This work is supported by a Texas Advanced Technology grant, Sam Houston State University, and the Air Force of Scientific Research Contract No. F-49620-85-0013.

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