New Configuration-Coordinate Model for the Ground, Excited, and Metastable States of $EL2$ in GaAs

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A new configuration-coordinate model for $EL2$, where the excited state has asymmetrical dual minima, is proposed to explain the oscillatory spectrum of transition rate obtained by a novel spectral photocapacitance transient analysis measurement. The model claims that an electron in the excited state of $EL2$ has a probability of relaxing both to the conduction band and to the metastable state. It can explain a Gaussian shape of the photoquenching spectrum which cannot be interpreted with the conventional scheme. The proposed model suggests that $EL2$ in GaAs originates from a complex defect of arsenic antisite with arsenic interstitial atom(s).

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A main midgap level called $EL2$ in GaAs plays an important role in the compensation mechanism in undoped semi-insulating crystals which are used for very high-speed large-scale-integrated devices. Therefore, it is urgent to elucidate the atomic structure and origin of $EL2$. Kaminska *et al.*[1] reported a Gaussian-type spectrum of internal electron excitation to the excited state at $EL2$, and a zero-phonon line (ZPL) with its phonon replica at 1.039 eV. They further found[2] that the transition is from A_1 to T_2 states and identified $EL2$ to be an isolated arsenic antisite (As_{Ga}). On the other hand, $EL2$ has a peculiar optical property of photoquenching[3] a transition to the metastable state. This kind of metastability is difficult to explain by assumption of an isolated As_{Ga} from the theoretical calculation.[4]

So far the photocapacitance transient spectra have been measured point by point and a fine oscillatory structure has been missed, although Skowronski, Lagowski, and Gatos[5] reported an enhancement of photoquenching rate near the zero-phonon transition energy. In the present study a novel technique named spectral photocapacitance transient analysis (SPTA)[6,7] is applied to investigate optical transition characteristics at $EL2$ in GaAs. In this Letter we propose a new configuration-coordinate diagram model for $EL2$ based on the SPTA measurement. The atomic structure of $EL2$ is also discussed.

In the SPTA measurement, the time derivative of a photocapacitance transient is measured on a logarithmic scale as a function of photon energy to obtain a continuous spectrum of the optical cross sections. When illumination starts at $t=0$, the capacitance transient is written[3] as

$$C(t)=C_0[\exp(-b_2t)-\exp(-b_1t)], \quad (1)$$

where

$$b_1=(\sigma_n^0+\sigma_p^0)\Phi, \quad (2)$$

$$b_2=[\sigma_p^0\sigma_*^0/(\sigma_n^0+\sigma_p^0)]\Phi, \quad (3)$$

and C_0 is the total capacitance change as a result of the photoionization of $EL2$. In (2) and (3), σ_n^0 and σ_p^0 are photoionization cross sections for electrons and for holes, respectively, and σ_*^0 is the cross section for optical transition of electrons from the normal state to the metastable state. Φ is the photon flux. Therefore, b_1 expresses the photoionization rate while b_2 corresponds to the transition from the normal state to the metastable state. Although the transient is expressed with two time constants, it is possible to determine b_1 and b_2 separately since b_1 is much larger than b_2 for $EL2$.

The sample used was an n-type GaAs wafer grown by metal-organic vapor-phase epitaxy (MOVPE) and contained $EL2$ as a dominant electron trap. Schottky diodes with Au electrodes were employed for photocapacitance measurements.

The inset in Fig. 1 shows a photoquenching rate (b_2) spectrum measured at 24 K. The spectrum consists of a broad Gaussian shape and an oscillatory structure near the threshold energy. The Gaussian spectrum is in good agreement with the photoquenching spectra previously

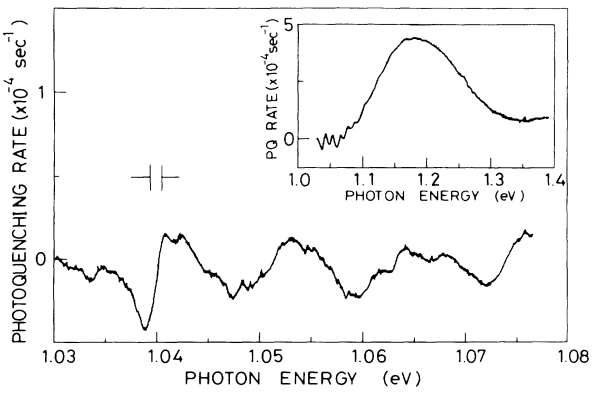

FIG. 1. Oscillatory spectrum of photoquenching rate measured with SPTA at 22 K. Inset: The overall spectrum of photoquenching rate.

reported.[3,8] The oscillatory structure was observed for the first time in the photocapacitance transient spectrum. The fine structure measured with a higher resolution (1.6 meV) is shown in Fig. 1. The spectrum consists of a ZPL at 1.039 eV and an oscillation at its higher-energy side with an interval of about 11 meV. The b_1 spectrum measured with the same resolution has no oscillatory structure in the same energy range. The oscillation in b_2 became weak as temperature was raised and disappeared above 63 K.

The most important feature is that the ZPL at 1.039 eV has a negative direction in the SPTA spectrum. The negative peak corresponds to a sweep-out of electrons from the space-charge region, thereby indicating that the final state of electron transfer should be the conduction band. Here, the validity of SPTA data is examined. If a nonexponentiality in photoquenching or photoionization is not negligible, b_1 and/or b_2 would become time dependent. However, in the present measurement the photocapacitance transient measured at 1.17 eV was purely exponential with a single time constant ($1/b_2$). More generally speaking, even when the transient was nonexponential, the SPTA spectrum taken in a limited range of photon energy could give a correct fine structure since the initial stage of the transient is of primary interest. The term $d(\log C_0)/dt$ appearing in the SPTA spectrum gives a dc contribution and no effect is expected on the oscillation since this term is a function of σ_n^0 and σ_p^0 which vary slowly within the photon energy of our interest. Therefore, it is concluded that the oscillatory fine structure really reflects a sharp change of the optical transition rate itself.

In the SPTA measurement, $(db_2/d\lambda)(d\lambda/dt)$ can contribute to the spectrum. However, this effect was confirmed to be negligibly small in the present measurement since the ZPL spectrum was almost independent of scanning direction and speed.

The Gaussian peak in the SPTA spectrum of Fig. 1 is very similar to that obtained in Ref. 3 and also to that of the intracenter absorption spectrum obtained by Kaminska *et al.*[1] Therefore, it should be regarded as of the same origin. Vincent, Bois, and Chantre proposed a simple configuration-coordinate (CC) diagram to explain the Gaussian spectrum. However, by use of their CC diagram with more quantitative consideration, some inconsistencies arise. One of them is that the observed FWHM (150 meV) is too small to be explained by a Franck-Condon shift of approximately 1 eV. Furthermore, the coincidence in shapes between the intracenter absorption and the photoquenching spectrum has led us to suspect the attribution[3] that the Gaussian photoquenching spectrum should be a direct transition process to the metastable state. Instead, as already suggested by Kaminska *et al.*,[1] this spectrum should be regarded as due to the transition from the ground state to the excited state. Electrons once transferred to the excited state eventually relax to the metastable state. This excited state should have a relatively large Huang-Rhys factor (>6) so as to give rise to a broad line shape.

The ZPL and the following oscillatory structure in the SPTA spectrum are considered to be due to transition to the excited state. As stated before, these transitions have a final state in the conduction band. This situation is clearly understood when the SPTA spectrum is compared with the absorption[9] and photocurrent[10] spectra as shown in Fig. 2. At the energies where the absorption and photocurrent show peaks, the SPTA spectrum has dips. Thus, it is pointed out that the excited state must be resonant with the conduction band. Furthermore, the clear ZPL and phonon replica show that the electron-lattice coupling should be weak with a small Huang-Rhys factor. Therefore, this excited state is different from the one which couples to the metastable state and gives rise to the Gaussian peak. This suggests that two different excited states should be present.

The present result on the ZPL is not in agreement with that by Skowronski, Lagowski, and Gates,[5] who observed only the ZPL and no clear oscillatory structure by a point-by-point measurement. The negative peak of the present ZPL is opposite to their positive peak. As is easily seen in Fig. 1, however, the energy interval in the point-by-point measurement must be as small as 1 meV to determine clearly the shape of the ZPL and subsequent fine structure. Therefore, it is very difficult to use a point-by-point measurement in order to determine the fine structure. In fact, they did not succeed in observing the whole shape of the fine structure.[5] There is no artificial factor in the SPTA measurement to introduce a negative peak as analyzed by the theory and also evi-

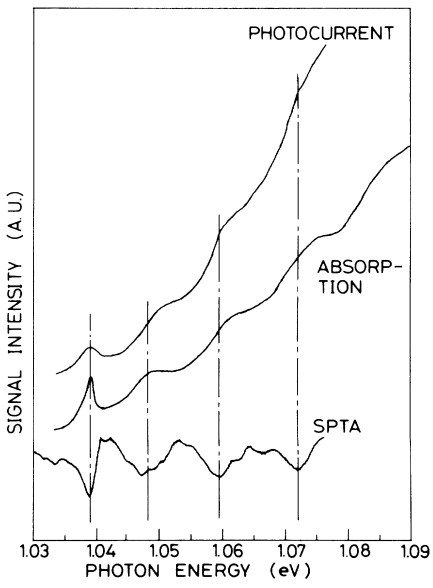

FIG. 2. Fine structures in the SPTA spectrum compared to those in the absorption (Ref. 9) and photocurrent (Ref. 10) spectra.

denced by the experiments performed under different scanning speeds and directions. We are convinced that the ZPL in the present spectrum clearly indicates an enhancement of electron transfer to the conduction band at this energy.

Now we construct a new CC model for the ground state, the excited states, and the metastable state of $EL2$, based on the aforementioned results together with the experimental facts so far reported and summarized as follows: (1) The photoquenching spectrum has a Gaussian-type shape with a maximum around 1.18 eV and FWHM of 0.15 eV. (2) In addition, the photoquenching rate again increases at higher energies than 1.3 eV.[8] (3) The ground state of $EL2$ is 0.74 eV below the conduction-band edge with an activation energy of 80 meV in the electron-capture cross section.[11] (4) Thermal recovery from the metastable state to the normal state has a potential barrier of 0.30 eV.[3] From the experimental observations (1), (3), and (4), we could draw a simple CC diagram as proposed in Ref. 3 in the framework of the harmonic and linear electron-lattice coupling approximations. However, we face inconsistency as pointed out above and also by Mochizuki and Ikoma.[12] Furthermore, such a simple CC diagram cannot explain the observation (2), either. An Auger-type process proposed in Ref. 10 is not applicable to the present case because in the present experiment what is accessed is the space-charge region where free electrons are swept out and shallow levels cannot be neutralized.

Now we draw a new CC diagram as shown in Fig. 3. Here, two branches of the excited states, Ex_1 and Ex_2, are featured. One of them is resonant with the conduction band and the other couples with the metastable state with a larger lattice relaxation. In the model, the metastable state is drawn in such a way that it crosses the excited state Ex_2 at the bottom and has an 0.30-eV thermal barrier for recovery. Ex_2 has a Franck-Condon shift of 0.14 eV while Ex_1 should have a small lattice displacement, with the Huang-Rhys factor of less than 1, to account for the rather well-observed ZPL and phonon replica.

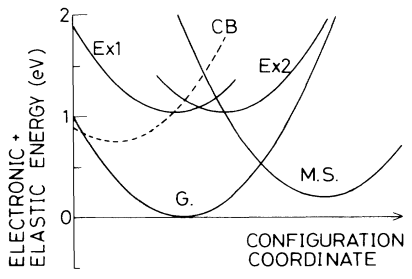

FIG. 3. A proposed CC model for $EL2$, showing the ground state (G.), the excited states (Ex), and the metastable state (M.S.). Broken curve (CB) corresponds to the conduction band.

The photoquenching takes place through Ex_2 and therefore the photoquenching spectrum reflects the Franck-Condon shift of Ex_2 (0.14 eV). With the assumption of this value, the half-width of the Gaussian spectrum (150 meV) is explained with a reasonable phonon energy of 29 meV. On the other hand, the electron transfer to the conduction band follows the excitation to Ex_1 which has a small lattice relaxation and gives rise to the negative ZPL in the SPTA spectrum. If we assume the phonon energy of 11 meV, a Huang-Rhys factor as small as 0.52 is possible for Ex_1 to maintain the resonant condition. The total SPTA spectrum is conceived as the convolution of these transitions. However, the line shape of the fine structure cannot be predicted by the simple theory.[13] This may be due to the resonant nature of Ex_1 or an oversimplified treatment of the system.

In the new CC diagram, the bottom of the metastable state is higher than that of the ground state, and therefore the metastable state has a "metastability." This was not so in the old scheme.[12] The fact that the photoquenching effect is also observed[8] at energies higher than 1.3 eV is explained by the new diagram as a direct transition to the metastable state peaked at 1.9 eV. It is expected that a tail of the transition becomes observable around 1.4 eV because of the large lattice relaxation, and the photoquenching rate increases with photon energy up to the band-gap energy.

The present CC model gives an insight into the atomic structure of $EL2$. First of all, it is suggested that $EL2$ should be a complex defect. The Ex_1 branch has a small lattice relaxation, indicating the involvement of a rigidly bonded defect. On the other hand, the large lattice relaxation required for the Ex_2 branch suggests the involvement of a soft-bonded defect that can be easily relaxed. Among many possible models, we propose that $EL2$ should be an As_{Ga} associated with arsenic interstitial(s), which is consistent with our previously proposed model.[14] The associated As atoms may be more than one since we have observed that in liquid-encapsulated Czochralski-grown GaAs, the detailed shape of the SPTA spectrum is different from that measured in metal-organic vapor-phase epitaxially grown GaAs, although it maintains the major feature.

A similar CC diagram has been predicted by Figielski, Kaczmarek and Wosinski,[15] who assumed that $EL2$ should be a double antisite arsenic defect, $(As_{Ga})_2$, or a nine-arsenic cluster. However, their consideration results in a symmetrical branch for the excited state when coupling with a single phonon mode is assumed. Although such a scheme can account for existence of the excited state resonant with the conduction band as well, the Franck-Condon shift for Ex_1 seems to become too large. Therefore, it is more appropriate to assume an As_{Ga}-related complex defect other than the double antisite, $(As_{Ga})_2$.

More recently, von Bardeleben *et al.* proposed an identification of $EL2$ as a complex of As_{Ga} with As_I.[16]

Our present model is in good agreement with their model although the two approaches to reach this model are different. An asymmetry in the CC model prefers an asymmetrical bonding model as proposed by them.

A recent calculation[17] for $V_{As} \leftrightarrow As_{Ga} + V_{As}$ indicates that the nature of the metastability is similar to the present experimental observation. This strongly suggests that $EL2$ is an association of As_{Ga} with another simple defect such as a vacancy or an interstitial atom. Actually, the complex, $As_{Ga} + As_I$, is also predicted to have a metastability.[18] An involvement of an interstitial As was proposed in our previous paper,[19] where As_I should play an important role in the formation of $EL2$ centers. Although we have no quantitative evidence, a tetrahedral As_I has a similar atomic arrangement to that of As_{Ga} and is expected to have a similar energy in its antibonding state (Ex_2).

In conclusion, a new CC model for $EL2$, including two asymmetrically located excited states with different degrees of lattice relaxation, is proposed to explain the oscillation and Gaussian spectrum observed with the novel SPTA technique. The model explains the experimental observation that an electron at the excited state of $EL2$ has a probability of relaxing both to the conduction band and to the metastable state. It can explain the line shape of the SPTA spectrum as well as the onset of photoquenching rate above 1.3 eV which cannot be interpreted with the conventional model. The new CC model suggests that $EL2$ in metal-organic vapor-phase epitaxially grown GaAs originates from a complex defect of As_{Ga} and As_I.

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