

Interdefect correlation during thermal recovery of *EL2* in semi-insulating GaAs: Proposal of a three-center-complex model

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Time evolution of *EL2* thermal recovery has been investigated in detail by a piezoelectric photothermal method. Results showed a simple saturating behavior for $T > 120$ K and a sigmoid-function-like behavior for $T < 120$ K, which were both quantitatively analyzed with an autocatalytic-reaction rate equation. The latter recovery mode indicates correlation between defects, for which recovery promotion by charge transfers from recovered to unrecovered *EL2* defects can be suggested. A three-center-complex model ($V_{\text{As}}\text{-As}_{\text{Ga}}\text{-Ga}_{\text{As}}$) is proposed for the microstructure of *EL2*.

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The midgap donor *EL2*, known to play a dominant role in realizing semi-insulating (SI) liquid-encapsulated-Czochralski (LEC) grown GaAs crystals,^{1,2} has been investigated extensively in 1980s, fueled partly by industrial interests in GaAs-LSI devices. To clarify the microstructure of *EL2*, many experimental and theoretical studies have focused on the photoquenching of *EL2*, a metastable transition in which all the optical and electrical properties of *EL2* are extinguished when a LEC grown GaAs sample is exposed to ~ 1.1 -eV light at low temperatures ($T < 130$ K).³ By the end of 1980s, it had been established that *EL2* at least contains arsenic antisite (As_{Ga}),^{4,5} and its metastable transition is caused by the As atom movement of a few angstrom.⁶⁻¹⁰ Still to be understood, however, were whether the defect is an isolated As_{Ga} center⁴⁻⁷ or a complex with other defects such as arsenic vacancy (V_{As})^{11,12} and arsenic interstitial (As_i), or an aggregate of various electron traps (“*EL2* family”).^{15,16} Unfortunately, this identification problem has been left unsolved to date. Recently, however, *EL2*-like deep defects are playing an important role in low-temperature-grown GaAs layers,¹⁰ which are being applied in buffer layers for GaAs-based devices, and in other compound semiconductor layers.^{17,18} Photoquenching is also given a position as a typical example of the photoinduced atomic movement in semiconductors, which is now widely observed in various semiconductors including amorphous Si,¹⁹ ZnSe,²⁰ and GaN.²¹ In this situation, clarifying the *EL2* microstructure and mechanism of the photoquenching, an old but long-standing problem, still retains its importance. In this paper, we describe our detailed experiments on the thermal recovery of *EL2*, and propose a model for the microstructure of *EL2* based on the result.

Photoquenched *EL2* (*EL2*^{*}) recovers to its normal state (*EL2*ⁿ) in 5 min by being annealed at 130 K, but it takes as long as 200 min at 110 K.²² The reason why the thermal recovery requires such a long time is not understood. The idea that each *EL2*^{*} defect slowly recovers to *EL2*ⁿ spending 200 min may not be relevant because the essential part of the *EL2* recovery is the atomic movement of a few angstrom.⁶⁻¹⁰ The other, and more probable possibility is that individual *EL2*^{*} defect recovers in an instant, but the

ensemble of the defects as a whole takes 200 min to recover due to scattered recovery time among defects. For this, however, we must ask what makes the difference between defects when time constants should range between orders. A hint to solve this puzzle is provided by a neat inspection on the time evolution of the *EL2*ⁿ near-infrared (NIR) photoabsorption coefficient by Fischer²² showed a twofold behavior: a monotonically saturating recovery at high annealing temperatures ($T \sim 130$ K) and a delayed recovery with an incubation time at low annealing temperatures ($T \sim 110$ K). The presence of the incubation time implies presence of a “nucleation” or “excitation” stage that triggers the recovery, whose understanding could be a key to clarifying the microstructure of this defect. In NIR measurements, however, the free carriers created during the measurement may alter the recovery kinetics. It is for this reason that we have adopted piezoelectric photothermal (PPT) method to obtain the *EL2*ⁿ concentration.²³ By monitoring nonradiative transitions of electrons generated by optical absorption in semiconductors, PPT detects processes with very small optical absorptions, which allows us accurate evaluation of *EL2* concentration using a very low light intensity ($\sim 10^{-3}$ mW/cm²).²⁴

Time evolutions of the *EL2*ⁿ concentration during isothermal annealing were obtained at $110 \leq T_m \leq 130$ K. The sample ($1 \times 1 \times 0.05$ cm³) was cooled down to 80 K in the dark and its *EL2* defects were photoquenched by a 3-min illumination of a quenching light ($h\nu = 1.12$ eV, 0.3 mW/cm²). The sample temperature was then rapidly increased to a selected annealing temperature T_m within 2 min, where the probing light ($h\nu = 1.12$ eV, 10^{-3} mW/cm²) was shed onto the sample. The PPT signal intensity (1.12-eV PPT signal intensity) was detected with a disk-shaped piezoelectric transducer attached to the rear surface of the sample via silver conducting paste. The intensity of the probing light was sufficiently weak that no photoinduced changes occurred during the measurements. The photon energy of the probing light, which happened to be identical with that of the quenching light, was chosen so that the optical absorption coefficient is proportional to the total *EL2* concentration.²⁵ After

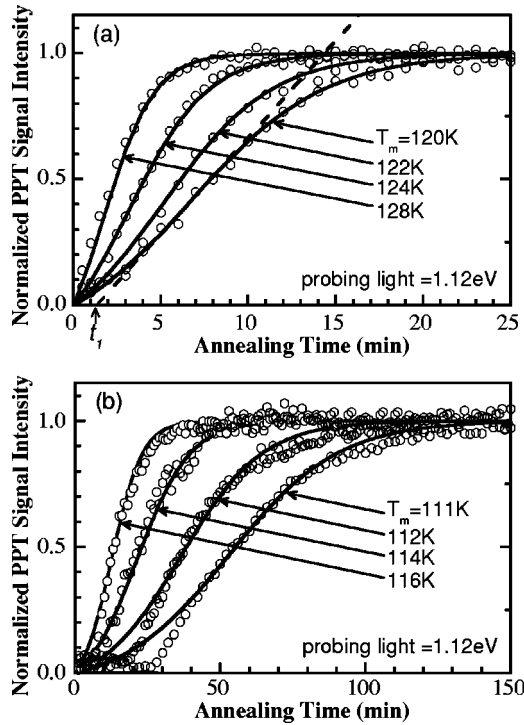


FIG. 1. Time evolutions of the thermal recovery of $EL2$ for (a) higher temperatures ($T_m = 120, 122, 124,$ and 128 K) and (b) lower temperatures ($T_m = 111, 112, 114,$ and 116 K), respectively. All the data were normalized at its saturation value. The solid curves are a fitting with Eq. (2).

obtaining the time evolution of the $EL2^n$ concentration until saturation, we annealed the sample at 150 K for 5 min to fully recover the remaining $EL2^*$ defects.

The open circles in Figs. 1(a) and 1(b) show the thermal recovery of $EL2$ for (a) high temperatures ($T_m = 120, 122, 124,$ and 128 K) and (b) low temperatures ($T_m = 111, 112, 114,$ and 116 K), respectively. Note the time-scale difference between the two figures. All the recovery curves were normalized at its saturation value. At high temperatures [Fig. 1(a)], the 1.12-eV PPT signal intensities increase immediately after the start of the annealing, and its differential recovery rate monotonically decreases until it vanishes (simple saturating). At low temperatures [Fig. 1(b)], the initial intensities scarcely increase during incubation time, after which the recovery rate suddenly increases and decreases again until saturation (sigmoid-function-like). This kind of transition from the simple saturating to sigmoid-function-like behavior can be most simply described with an autocatalytic-reaction (ACR) model.²⁶ The ACR from A to B is a reaction whose rate is proportional to the concentrations not only of the reactant A but also of the product B . Assuming that the thermal recovery of $EL2$ is an ACR from $A = EL2^*$ to $B = EL2^n$, we obtain the following equation:²⁷

$$\frac{d\theta}{dt} = \frac{1}{\tau_0\theta_0}(1-\theta)(\theta_0+\theta). \quad (1)$$

Here θ is the fractional concentration of $EL2^n$, or the normalized 1.12-eV PPT signal intensity, t is the annealing time,

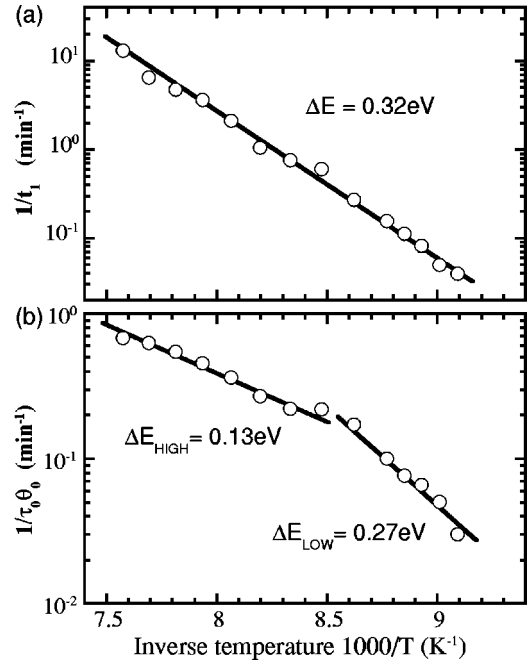


FIG. 2. Arrhenius plots of (a) $1/t_1$ and (b) $1/\tau_0\theta_0$. The former characterizes the recovery rate in the slow recovery stage, while the latter is related with the rapid recovery stage.

and τ_0 and θ_0 are the parameters that control the line shape. Equation (1) has an analytical solution,

$$\theta(t) = \theta_0 \frac{1 - e^{-\kappa t/\tau_0}}{\theta_0 + e^{-\kappa t/\tau_0}} \quad (2)$$

with $\kappa = (\theta_0 + 1)/\theta_0$. The time evolution $\theta(t)$ becomes simple saturating for $\theta_0 \gg 1$ and sigmoid-function-like for $\theta_0 \ll 1$, covering the whole range of the time evolutions. Mathematically, τ_0^{-1} is the initial slope of $\theta(t)$ and θ_0 is the critical θ at which the sudden increase of θ onsets. Also, $(4\tau_0\theta_0)^{-1}$ is roughly the steepest gradient during the time evolution. The solid curves in Figs. 1(a) and 1(b) indicate the fits by Eq. (2). Except for slight deviations in the very initial part of the low-temperature recoveries, the overall behavior of the time evolutions is well described with the single rate equation containing only two fitting parameters. The incubation time separates the thermal recovery into a pair of stages: a slow recovery stage before the incubation time and a rapid recovery stage after the incubation time. To characterize the former, the incubation time t_1 was defined, as shown for $T_m = 120$ K in Fig. 1(a), as the temporal intersect of the steepest tangential line of the fitted curve. Figure 2(a) shows the Arrhenius plot of $1/t_1$ thus obtained. All the data line up along a single straight line and the thermal activation energy was obtained to be 0.32 eV. Figure 2(b) shows the Arrhenius plot of $1/\tau_0\theta_0$, which is related to the highest recovery rate in the rapid recovery stage. In contrast to the slow recovery stage, the recovery rate in the rapid recovery stage showed a twofold behavior: the low-temperature region with a thermal activation energy of 0.27 eV ($110 \leq T_m < 120$ K) and the high-temperature region with 0.13 eV ($120 \leq T_m \leq 130$ K).

The presence of the incubation time, within a framework of “recovery as an ensemble,” implies that the thermal recovery of *EL2* is correlated among defects, i.e., recovery of one defect is accelerated by recovery of other *EL2* defects. How, then, do they communicate with each other? A one-to-one direct communication between defects is unlikely because the interdefect distance is $\sim 10^2$ atoms in typical LEC grown GaAs crystals containing $\sim 10^{16} \text{ cm}^{-3}$ defects. Some indirect, nonlocalized interactions must be considered. Phonons, emitted during the lattice relaxation associated with the recovery, are ruled out because their emission rate is proportional to the concentration of *EL2*^{*}, not of *EL2*ⁿ as predicted in the ACR model. Memory of early recovery should be stored as a state variable within the system to promote recovery of other defects.

A most probable mechanism in this respect is a charge transfer from recovered *EL2*ⁿ to unrecovered *EL2*^{*}. Benchiguer *et al.*^{28,29} have proposed a charge-transfer model for *EL2* photoquenching, in which electrons and holes emitted optically from the $\text{As}_{\text{Ga}}^{0/+}$ defect are captured by a deep donor and an acceptor,^{30,31} where they remain trapped. This model logically necessitates a charge transfer in the reverse direction during *EL2* recovery. The sigmoid-function-like behavior is explained when we notice the decisive role of the deep acceptor in the *EL2* photoquenching/recovery. According to our previous NIR study,³² the deep acceptor, located at $E_V + (0.07-0.08) \text{ eV}$ and most probably a $\text{Ga}_{\text{As}}^{0/-}$ defect, promotes the photoquenching when it is neutral and promotes recovery when it is negatively ionized. This deep acceptor was further implied to be a part of a metastable complex involving As_{Ga} in the photoquenched state from a thermally stimulated current measurement.³³ On the other hand, it is known that the conduction is *n*-type SI in the normal state and *p*-type SI in the photoquenched state, though the detailed mechanism for the type conversion is still unresolved. Putting these two together, we attribute the present sigmoid-function-like behavior of the *EL2* recovery to interdefect correlation via electrons. As the recovery of *EL2* defects proceeds, the conduction type changes from *p*-type SI to *n*-type SI. The increased free electrons then increases the fraction of negatively ionized deep acceptors at metastable *EL2* defects, which promotes the *EL2* recovery. Actually, the rate of thermal recovery in *n*-type GaAs is proportional to the concentration of free electrons.^{34,35}

While the deep acceptor controls the metastable transitions, the deep donor is more directly involved in the metastable transition. The deep donor can be related to the *A*-peak level ($A^{0/+}$) found in our recent PPT measurement.³⁶ This peak appears in the early stage of the *EL2* photoquenching at $h\nu \sim 1.05 \text{ eV}$, moves to higher photon energies by $\sim 0.15 \text{ eV}$ with the progress of the photoquenching, and eventually disappears. The photon energy that gives the maximum PPT intensity suggests $E_V + \sim 1.1 \text{ eV}$ for the level's location. The transient appearance of the level, as well as its peak shift, implies that the level is involved in the metastable transition of the *EL2*. The most probable candidate for this level is V_{As} , located at $E_C - 0.45 \text{ eV}$ or $E_V + 1.1 \text{ eV}$.³⁷ Being positively ionized in the normal state, the

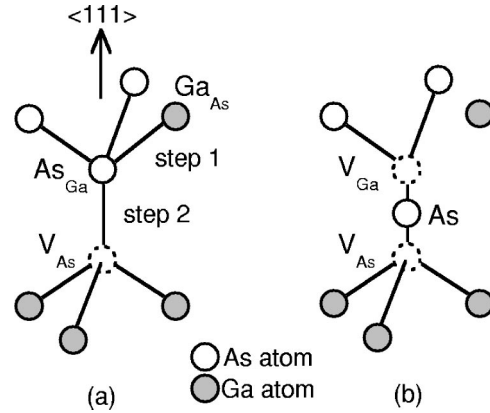


FIG. 3. A three-center-complex model for the microstructure of *EL2*: (a) normal and (b) photoquenched states.

level emits holes to the valence band by excitations with 1.1-eV photons. Theoretical calculation by Baraff and Schluter¹² predicts that the As vacancy, when combined with the As antisite to form an $\text{As}_{\text{Ga}}-\text{V}_{\text{As}}$ complex, shows a bistability; with movement of the As atom towards the vacancy along the $[111]$ direction, the complex becomes metastable and the $V_{\text{As}}^{0/+}$ level vanishes. This is consistent with the *A*-peak behavior in the PPT measurement. Presence of V_{As} in GaAs is confirmed by Dannefaer and Kerr using their positron lifetime measurement³⁸ for crystals grown under As excess atmospheres. They estimated the concentration of grown-in vacancies to be in the range of $(1-4) \times 10^{17} \text{ cm}^{-3}$. The $\text{As}_{\text{Ga}}-\text{V}_{\text{As}}$ complex well accounts for the observed increase in the *EL2* concentration with increasing As pressure during growth,³⁹ the decrease in the *EL2* concentration with increasing concentration of shallow donor dopants,³⁹ and the broad peak around 0.9 eV in the photo-induced recovery rate.³

Based on the discussions above, we here propose a three-center-complex model, $\text{V}_{\text{As}}-\text{As}_{\text{Ga}}-\text{Ga}_{\text{As}}$, as the microstructure for *EL2* (Fig. 3). The $\text{As}_{\text{Ga}}-\text{V}_{\text{As}}$ pair provides the metastability, while the charge state at $\text{Ga}_{\text{As}}^{0/-}$ controls the transition between the normal and metastable states. In the normal state (a), the Coulombic interaction between Ga_{As}^- and As_{Ga}^+ pins the As atom at its Ga site. The *EL2* photoquenching starts with a neutralization of Ga_{As}^- , which captures a hole photo-excited from As_{Ga}^+ defect to become Ga_{As}^0 .³⁰⁻³² As a result of this neutralization and/or the loss of the valence electron, the bond between As_{Ga} and Ga_{As} breaks up (step 1), and the As atom moves towards the vacancy (step 2) until the formation of a metastable complex (b). In this respect, the deep acceptor is essentially an inhibitor, rather than an actuator as addressed in previous studies.^{30,31}

This three-center-complex model for *EL2* has important implications on the interpretation of the three activation energies obtained in the ACR analysis: 0.32 eV for $1/t_1$ and 0.13 and 0.27 eV for the high- and the low-temperature region of $1/\tau_0 \theta_0$, respectively. The overall reaction of the *EL2* recovery is given by $[\text{V}_{\text{As}}-(\text{As})-\text{V}_{\text{Ga}}]-\text{Ga}_{\text{As}}^0 \rightarrow [\text{V}_{\text{As}}^+-\text{As}_{\text{Ga}}^+]-\text{Ga}_{\text{As}}^-+e^-$, which is consistent with the conduction-type conversion during the recovery. The three elementary processes involved in the process: (1) ionization

of the deep donor V_{As}^0 , (2) ionization of the deep acceptor Ga_{As}^0 , and (3) As atom movement towards the antisite position,⁴⁰ are then reasonably attributed to the three activation energies. The activation energies for the ionization processes (1) and (2) can be related to the electronic levels of the relevant defects. The electronic level for the isolated $V_{As}^{0/+}$ is reportedly $E_C - 0.45$ eV,³⁷ which, after considering possible variation during photoquenching as suggested by the PPT measurement,³⁶ can be related to the activation energy of 0.32 or 0.27 eV. As for the acceptor, the reported activation energy³² of 0.07–0.08 eV suggests 0.13 eV as the relevant activation energy. The barrier for the As atom movement, calculated to be 0.3–0.4 eV,¹² is related to 0.32 or 0.27 eV in our activation energies. Of the two, however, 0.27 eV is more likely because the charge induced atomic movement should be associated with the rapid recovery stage. From the

same reason in the reverse direction, the donor's ionization should be related to the activation energy of $1/t_1$, giving 0.32 eV.

To conclude, by using the PPT method, we have investigated the kinetics of the thermal recovery of *EL2* in detail. The presence of the incubation time, as well as the self-promoted behavior of the recovery, suggests interdefect correlation during recovery, which is consistently explained considering a charge transfer between defects. Three activation energies obtained through the analysis with the autocatalytic-reaction model can be related to the three elementary processes suggested by the charge-transfer model. A three-center-complex model has been proposed for the microstructure of *EL2* based on the result.

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- ⁴⁰The process (1) can occur only after the process (3) evolves when the $V_{As}^{0/+}$ level appears.