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Charge-state-controlled structural relaxation of the *EL* 2 center in GaAs

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Existing approaches are unsuccessful in explaining the anomalous persistent photocapacitance quenching effect associated with the *EL* 2 center in GaAs. Here a model is presented which invokes a simple physical mechanism to account in a consistent way for all aspects of this behavior. The model consists of a charge-state-controlled, electrostatic and lattice-strain driven, structural rearrangement of a defect complex. This rearrangement results in two defect configurations, each with distinct electronic and optical properties. It is proposed that this type of configurational instability may be common, but rarely detected, in covalent semiconductors.

The *EL* 2 center is responsible for the dominant deep level in melt-grown undoped GaAs. Its identity (it was formerly believed to be due to oxygen) and relation to crystal-growth parameters have been the subject of active investigation, in part because the deep level it introduces has been associated with the semi-insulating nature of this material.[1-5] *EL* 2 is also very unusual in that it has been shown to exhibit anomalous optical properties at $T \lesssim 100$ K, including those of absorption,[6] photoconductivity,[7] and most notably the persistent photocapacitance quenching (PPCQ) effect.[8-11]

These anomalous properties have been attributed to a configurational instability, which was described with the help of configuration coordinate diagrams.[8,9,11] While this approach is helpful in visualizing the defect properties in an empirical way, the nature of the electron-lattice interaction, which provides the driving force for configurational change, is not well defined.[12] In addition, for the *EL* 2 center this model is incapable of explaining one important property, that of the free-electron or "Auger" deexcitation of the photocapacitance quenching.[10,11]

In this Rapid Communication we propose a new model which for the first time uses a simple physical mechanism to account in a consistent way for all the properties of the *EL* 2 center associated with the PPCQ effect. These properties may be summarized as follows[8-11]:

(1) The junction capacitance of an *n*-type GaAs diode containing *EL* 2 is monitored at $T < 100$ K, in darkness, with applied reverse bias, after a zero-bias trap filling pulse. If the sample is now illuminated with $0.9 \lesssim h\nu \lesssim 1.35$ eV, the capacitance first increases as expected for trap emptying, but then decreases almost to its initial value. This decrease is the PPCQ effect.

(2) The "quenched" condition is persistent at low temperature. However, the initial "unquenched" state may be regenerated, with no change of capacitance (if the light is off), by increasing the temperature. The thermal regeneration rate was found to be

$$R^r_{\rm th} \sim 10^{11} \exp(-0.3\ \text{eV/kT})\ \text{sec}^{-1} \ . \qquad (1)$$

(3) The initial state may also be regenerated by the introduction of free electrons. The regeneration rate $R^r_{\rm elec}$ appears to reflect electron capture with a thermally activated cross section

$$\sigma \approx 10^{-13} \exp(-0.108\ \text{eV/kT})\ \text{cm}^2 \ . \qquad (2)$$

However, there is again no change in the depletion layer capacitance, and thus no change in total defect charge after the capture and regeneration process. This is the "Auger" deexcitation effect.

(4) The sample is cooled in darkness under reverse bias from $T \geqslant 320$ K, so that the 0.75-eV state[13-15] associated with *EL* 2 is empty due to thermal emission. At low temperature, where the Auger regeneration capture expressed by Eq. (2) is negligible, a trap filling pulse is applied. Illumination now produces photocapacitance quenching, revealing that after the filling pulse the defect was in the unquenched condition.

The present model is similar to one which has been shown to explain the behavior of another anomalous defect, the *M* center in InP.[16,17] The model consists of a charge-state-controlled electrostatic interaction between two or more defects in a complex. The minimization of electrostatic and lattice-strain energy gives rise to structural rearrangements which correspond to transformations between two possible configurations of the complex. Each configuration has distinct electronic energy levels and optical properties. Proposed energy-level diagrams for both configurations are shown in Fig. 1.

We refer to the two configurations as O and O^*, in accordance with previous nomenclature.[9,11] However, in the present model we contend that O^* does not only appear under certain special conditions (those of the PPCQ effect), but occurs whenever the defect charge is made sufficiently positive. Nevertheless, the existence of O^* is only detected via the PPCQ effect because of the particular properties of the defect in each configuration.

We assume for simplicity that the complex consists of two defects: a shallow donor D and a multiply charged defect C. When C is negative the two are bound by electrostatic attraction. This is configuration O. As C becomes positive, O^* is formed as

$$\begin{aligned} (C^- D^+)^0 &\rightarrow (C^0 D^+)^+ + e^- \\ &\rightarrow (C^+ D^+)^{+2} + 2e^- \\ &\overset{R^f}{\rightarrow} C^+ + D^+ + 2e^- \ . \end{aligned} \qquad (3)$$

The first electron is lost from level O_1, which is ~ 0.025 eV below the conduction band. Evidence for the existence

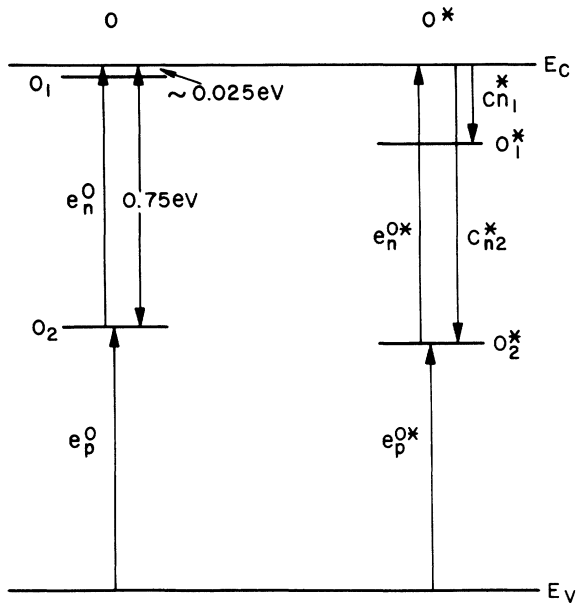

FIG. 1. Proposed energy-level diagram for configurations O and O^*. The level positions of O are based on experimental data. Those of O^* are only qualitative.

of this level has come from Hall[5] and photoluminescence[18] measurements. Because the level is shallow, it may be empty at moderate temperatures. However, if it is empty, the defects remain paired in order to minimize lattice-strain energy. The second electron emission, from level O_2, is that of either the ~ 0.82-eV thermal emission[13–15] characteristic of $EL2$, or an optical ionization e_n^O (Fig. 1). With the loss of the second electron, O transforms to O^* as electrostatic repulsion promotes the separation of the two defects at a rate, R^f. Nevertheless, the two defects remain sufficiently close together that they may reassociate under the proper conditions.

The reverse transformation $O^* \rightarrow O$ can take place in one of two ways: first, if O_2^* becomes occupied, C and D reassociate to minimize lattice strain, as

$$C^+ + D^+ + 2e^- \rightarrow C^0 + D^+ + e^- \xrightarrow{R_{\rm th}^r} (C^0 D^+)^+ + e^- \ . \quad (4)$$

In this case, there is a thermal activation barrier for atomic displacement, so this process does not occur at low temperature.

Secondly, if both O_2^* and O_1^* are filled, repairing occurs by electrostatic attraction:

$$C^+ + D^+ + 2e^- \rightarrow C^0 + D^+ + e^- \rightarrow C^- + D^+ \xrightarrow{R_{\rm elec}^r} (C^- D^+)^0 \ . \quad (5)$$

Here the atomic displacement activation barrier is overcome by the electrostatic potential.

Using this model, the PPCQ effect may now be explained in detail. With the sample at zero bias in darkness, $EL2$ is occupied and thus in configuration O, which is stable regardless of the occupation of level O_1. When a reverse bias is applied, O_1 empties thermally but configuration O remains metastable at temperatures below that of the ~ 0.82-eV thermal emission from level O_2. With illumination at the appropriate wavelength, O_2 empties at a rate e_n^O resulting in an increased capacitance, and configuration O transforms to O^* at a rate R^f [Eq. (3)]. We assume $R^f >> e_p^O$, so that O_2 disappears as $O \rightarrow O^*$ before it can be refilled from the valence band. e_p^O is therefore essentially inoperative.

The defect is now in configuration O^* where $e_p^{O^*} >> e_n^{O^*}$. Level O_2^* therefore becomes occupied and the capacitance decreases. At low temperatures where thermal regeneration is negligible [Eqs. (1) and (4)], a steady state is reached with O_2^* occupied, and the capacitance is near to its initial value. The defect is now in O^*, with O_2^* occupied and O_1^* empty. This is the quenched condition.

The transformation $O \rightarrow O^*$ occurs when level O_2 empties, and $O^* \rightarrow O$ takes place by thermal regeneration when O_2^* is occupied. Therefore, the rate equations governing the PPCQ describe the occupation of levels O_2 and O_2^*, and include the transformation rates R^f and $R_{\rm th}^r$. Assuming carrier capture rates are negligible,

$$\begin{aligned}
\frac{dN}{dt} &= -e_n^O N + e_p^O n + R_{\rm th}^r N^* \ , \\
\frac{dn}{dt} &= e_n^O N - e_p^O n - R^f n \ , \\
\frac{dN^*}{dt} &= -e_n^{O^*} N^* - R_{\rm th}^r N^* + e_p^{O^*} n^* \ , \\
\frac{dn^*}{dt} &= R^f n + e_n^{O^*} N^* - e_p^{O^*} n^* \ , \\
N_T &= N + n + N^* + n^* \ ,
\end{aligned} \quad (6)$$

where N and N^* are the number of occupied states of O_2 and O_2^*, respectively, and n and n^* are similarly the number of unoccupied states. N_T is the total number of $EL2$ defects. We assume e_p^O and $e_n^{O^*}$ are negligible, and the solution of (6) is greatly simplified by considering low temperatures where $R_{\rm th}^r \approx 0$. An additional simplification is obtained with the assumption that $R^f >> e_n^O$ and $R^f >> e_p^{O^*}$. With $N = N_T$ and $n = N^* = n^* = 0$ at time $t = 0$, the total number of unoccupied states, and thus the increase in positive charge $P(t)$ is

$$\begin{aligned}
P(t) &= n(t) + n^*(t) \\
&= N_T \frac{e_n^O}{e_n^O - e_p^{O^*}} [\exp(-e_p^{O^*} t) - \exp(-e_n^O t)] \ .
\end{aligned} \quad (7)$$

The capacitance change ΔC is proportional to $P(t)$. Equation (7) thus predicts an increasing, then decreasing capacitance change, as is observed. It is similar in form to an equation previously proposed for this effect,[11] but in this case its derivation is based on a specific physical mechanism. Rather than describing an optically induced transition to a special "metastable" state, this equation is derived from a charge-state-dependent structural rearrangement of the defect which results in altered electronic and optical properties, in particular, $e_p^{O^*} >> e_n^{O^*}$.

The thermal regeneration process is just that described by Eq. (4). The rate is expressed in Eq. (1), which is seen to be consistent with a single diffusionlike atomic displacement characterized by a vibrational attempt frequency of $\sim 10^{11}$

$\sec^{-1}$ and an activation barrier of ~ 0.3 eV.

The free-electron or "Auger" regeneration takes place as follows: In the quenched condition the defect is in configuration O^* with O_2^* occupied and O_1^* empty. Free electrons are captured into O_1^* at a rate $c_{n_1}^*$ with the thermally activated cross section of Eq. (2). Immediately, $O^* \rightarrow O$ because the displacement activation barrier has been overcome by the Coulombic potential [Eq. (5)]. The captured electron is now in shallow level O_1, and is reemitted by thermal or optical excitation. Therefore the charge at the defect is the same as before capture, but the defect is now in configuration O.

If the defect is in configuration O^* with O_2^* unoccupied, free electrons are captured into both O_1^* and O_2^*. If however, the temperature is such that $c_{n_1}^*$ is negligible [Eq. (2)], the transformation $O^* \rightarrow O$ may still proceed in a slightly different way. Electrons are captured ($c_{n_2}^*$) into O_2^* by a multiphonon emission process, which transfers the energy difference $E_c - E(O_2^*)$ to the lattice at the defect. This energy is sufficient to overcome the 0.3-eV activation barrier and so the transformation $O^* \rightarrow O$ proceeds according to Eq. (4). This accounts for the property number (4) above, and is an example of a recombination enhanced reaction.[19]

The present model thus accounts for the anomalous behavior associated with the photocapacitance quenching, and is also consistent with the other reported anomalous optical properties. It is interesting to note that this model indicates that care is required in the interpretation of experiments involving this defect. For example, deep-level transient spectroscopy (DLTS) measurements of the 0.75-eV level associated with $EL2$,[14,15] would show the electron emission behavior of level O_2, but the capture properties of O_2^*. This occurs because when O_2 emits its electron, it disappears as $O \rightarrow O^*$. The empty level that captures a free electron is O_2^*, which then itself disappears as $O^* \rightarrow O$. In the same way, the presence of level O_1^* can only be deduced indirectly by the electron capture associated with the "Auger" deexcitation effect. Deep levels are normally identified by the detection of a carrier emission from the level. However, O_1^* disappears upon electron capture, so no reemission occurs to be observed.

More definitive information as to the nature of the structural relaxation might be gained using a structure-sensitive technique such as electron paramagnetic resonance. Spectra could be compared for both configuration O with O_2 occupied, and O^* with O_2^* occupied. The latter would be prepared at low temperature by sufficient illumination (~ 1 h with a tungsten source and monochromator) at the proper wavelength.

We have shown how charge-state-controlled structural rearrangement accounts for the unusual behavior of $EL2$. This model requires that $EL2$ consist of a defect complex rather than an isolated point defect, such as the arsenic antisite, as has been proposed.[2-5] The PPCQ effect reflects both the existence of the configurational transformation, and the particular properties of the defect in each configuration. With the right combination of defect properties, the transformation would be much more easily observed. This is the case with the M center in InP.[16,17] On the other hand, with a less fortuitous set of properties ($e_n^{O^*} > e_p^{O^*}$, for example), the transformation would remain undetected. Because defect complexes are common in elemental and III–V compound semiconductors, it is possible that there are many other instances of just such undetected charge-state-dependent configurational changes.

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