

Carrier capture on defects in multiband semiconductors

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We analyze electron capture on a defect that exhibits no electron-phonon interaction. In this case, capture occurs by a cascade mechanism via the defect excited states. In direct-band-gap materials, when the temperature is too high to allow the filling of the Γ excited states at the bottom of conduction band, capture takes place via the excited states of a higher band, provided that they are deep enough. Experimental evidence for capture via the excited states of the L and X bands is provided for several defects or impurities in InP, GaAs, and related alloys.

Carrier capture on defects in semiconductors occurs through the so-called multiphonon-emission process or the cascade capture mechanism (for tutorial treatments see Ref. 1) depending on the magnitude of the electron-phonon interaction. When lattice distortion is present around the defect as a manifestation of an electron-phonon interaction, the nonadiabaticity operator,² treated by time-dependent perturbation theory, leads to a capture probability which is thermally activated, at least in a given temperature range

$$\sigma_{mpe} = K \exp \left[-\frac{B}{kT} \right]. \quad (1)$$

The energy B can be viewed classically³ as a barrier the electron has to overcome in order to recombine on the defect site with a cross section K (the expression of K can be found in Ref. 1). A number of defects have been found to exhibit such barrier for capture in particular in GaAs and GaP.³ Generally this barrier is rather small and defined in a limited temperature range which strongly limits the accuracy with which it is known.

When the electron-phonon interaction is negligible, capture with multiphonon emission is impossible (this can be classically viewed as a very high value of B) and the cascade process dominates. In this process electrons are first trapped on excited states of the defect and decay from an excited state to another deeper one by emitting a phonon. Then the capture cross section can be written as a sum over all excited orbitals i of the capture cross section on the excited orbital σ_i , times a sticking coefficient S_i which expresses the probability for the electron not to be reemitted,

$$\sigma_c = \sum_i \sigma_i S_i. \quad (2)$$

S_i is of course non-negligible only for excited states which exhibit a binding energy larger than kT . Evidence for the existence of this capture mechanism is provided by the giant cross sections ($\sigma_c \sim 10^{-12} - 10^{-14} \text{ cm}^2$) of shallow donors and by their temperature dependence.⁴

For shallow donors whose excited states lie within ~ 1 meV below the bottom of the conduction band, the mechanism is operative at low temperature (typically below 10

K) since at a higher temperature an electron cannot be trapped on an excited orbital. However, for other defects, depending on the relative contributions between the short-range central potential and the Coulombic tail, some of the excited states can lie at an energy larger than kT below the conduction band. Consequently, for such defects the cascade capture can, in principle, be operative at moderate temperatures. The aim of this communication is to demonstrate that this is indeed the case and leads to an unexpected but typical behavior of σ_c versus temperature in covalent semiconductors.

The lowest part of the conduction band in a tetrahedral semiconductor is composed of several valleys, eventually degenerated of symmetry $\Gamma(1)$, $L(4)$, and $X(3)$ with very different effective masses (commonly $m_\Gamma^* \sim 0.1m_X^*$ and $m_L^* \sim m_X^*$). Thus a defect possesses three different sets of excited states, each one associated to a band, whose sequence in energy depends on m^* . Owing to the relative values of the effective masses we expect the Γ associated set to lie closer (within an energy labeled e_Γ) from the bottom of the Γ band than the $L(X)$ associated excited states, lying within $e_L(e_X) \gg e_\Gamma$ from the $L(X)$ bottoms.

Now we consider a direct gap material, such as GaAs or an alloy such as $\text{Ga}_{1-x}\text{Al}_x\text{As}$ (for $x < 0.4$), for which the Γ band lies below the L and X bands. We assume that it contains a defect characterized by a negligible electron-phonon interaction. Then electron trapping on this defect must occur by the capture of an electron located in the bottom of the Γ band through a cascade mechanism. Experimentally, this capture is obtained from the capture kinetics measured through electron emission (see, for instance, Ref. 1), i.e., typically in a moderate temperature range Te where electron emission can be monitored. If kTe is larger than e_Γ but smaller than e_L (or if the material is degenerate for the Γ band) the sticking coefficient is nonzero only for the L excited states. In other words capture can only take place through the excited states of the L band, and the capture cross section is given by

$$\sigma_c = \sigma_0 \exp \left[-\frac{\Delta_{L\Gamma}}{kT} \right], \quad (3)$$

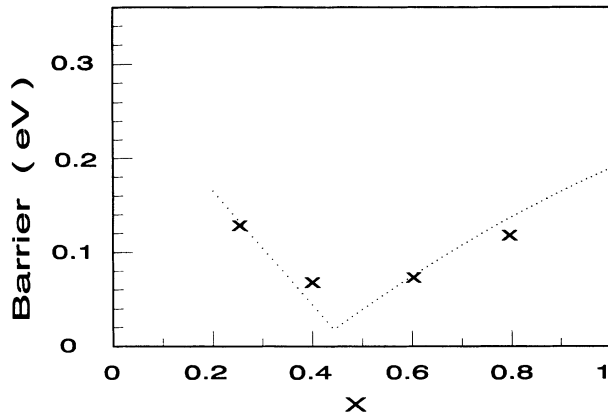


FIG. 1. Variation of the barrier for electron capture on the *DX* center in Te-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ vs the alloy composition x (corrected for band filling). The dashed line corresponds to the energy difference between the *L* (or *X*) band and the Γ band.

where $\Delta_{L\Gamma}$ is the energy difference between the *L* and Γ bands, the exponential term expressing the probability for an electron in the bottom of the Γ band to reach the *L* excited states.

It is possible to select the defects for which such capture processes occur through the measurement of the associated barrier which must be equal to the energy difference between the *L* (or *X*) band and the bottom of the (Γ) conduction band. Such defects can indeed be found in GaAs, InP, and related alloys. The ones we have found^{3,5-8} are listed in Table I, together with the references in which the corresponding measurements are described. The energy level E_T associated with the ground state is obtained from the temperature variation of the free-carrier concentration while the barrier B is deduced from capture kinetics using deep-level transient spectroscopy (DLTS) (which also provides the ionization energy E_i equal to $E_T + B$). As is shown in the table, for these defects the experimental value of B is equal to the energy difference between the *L* (or *X*) and Γ bands,

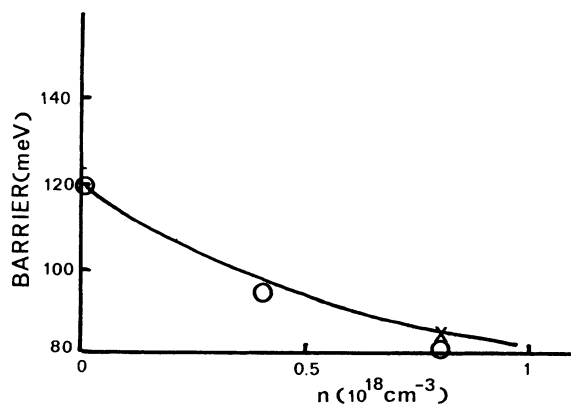


FIG. 2. Variation of the barrier for electron capture on the *DX* center in Te-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ vs electron concentration in the Γ band, obtained from capacitance transients (\circ) and DLTS (\times). The full line represents the calculated variation.

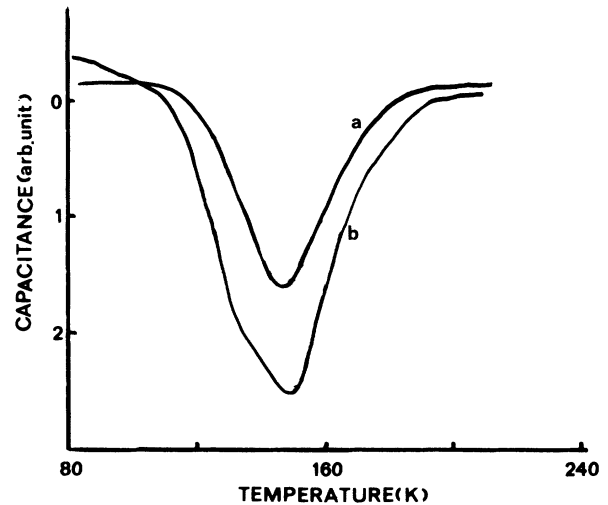


FIG. 3. DLTS spectra of the *DX* center in Te-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ for alloy compositions (b) $x=0.50$ and (a) $x=0.25$.

within the experimental accuracy. In these cases the barriers are large enough (0.3–0.4 eV) to be determined with a reasonable accuracy (of the order of 30 meV). In GaAs the electron cross sections of the acceptor defects (at 0.71, 0.52, and 0.79 eV above the valence band) correspond to electron capture by a neutral center. These cross sections are practically identical although the defects have quite different energy levels. Note that the hole capture cross sections of the $E_v + 0.52$ eV and $E_v + 0.79$ eV (related³ to Fe and Cr impurities, respectively) do not exhibit any significant temperature variation⁹ which confirms that capture does not take place by multiphonon emission and thus that these defects exhibit a negligible electron-phonon interaction.

The case of defects in alloys such as $\text{Ga}_{1-x}\text{Al}_x\text{As}$ is not mentioned in Table I although they also contain at least one defect having an electron cross section characterized by Eq. (3). This is the well-known *DX* center

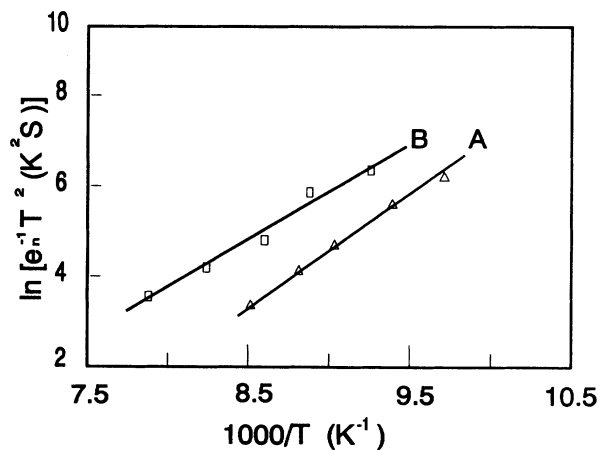


FIG. 4. Variation of the emission rates vs temperature for the two components *A* and *B* exhibited by the DLTS spectrum of Fig. 3(b).

TABLE I. Electron or hole ionization energy (relative to the conduction E_C and valence E_V bands), energy level E_T (obtained from the variation of the free-carrier concentration vs temperature), capture cross section σ_0 , and barrier B associated with electron capture for comparison with the energy difference $\Delta_{L\Gamma}$ between the L and Γ bands.

| | E_i (eV) | $E_C - E_T$ (eV) | σ_0 (cm ²) | B (eV) | Δ_{LG} (eV) | Refs. |
|------|---------------|---------------------|----------------------------------|-------------|-----------------------|-------|
| GaAs | $E_C - 0.83$ | 0.53 | 1.8×10^{-14} | 0.29 | 0.29 | 7,8 |
| | $E_V - 0.71$ | | $\sim 10^{-15}$ | 0.26 | | 3 |
| | $E_V - 0.52$ | | $\sim 10^{-15}$ | 0.26 | | 3 |
| | $E_V - 0.79$ | | $\sim 10^{-15}$ | 0.26 | | 3 |
| InP | $E_C - 0.59$ | 0.20 | 2×10^{-12} | 0.39 | 0.39 | 5,6 |
| | $E_C - 0.63$ | | 3×10^{-15} | 0.39 | | 5,6 |

directly associated with the donor impurity (for a description of the properties of this center see Ref. 10). For the DX center associated with substitutional impurities (Se,Te) on As sites, the barrier associated with electron capture varies, as shown in Fig. 1,¹¹ with the alloy composition x as

$$B(x) = \Delta_{L\Gamma}(x) - \delta, \quad (4)$$

where δ is the filling level of electrons in the Γ band (see Fig. 2). We do not consider here the case of Si-associated DX centers for which $B(x)$ is given by expression (4) in which a constant (~ 200 meV) has to be added.^{7,12} Here we present a direct evidence that capture is occurring through the excited states of a higher band by showing that it can also occur via both the L and X bands, provided the X band is not far in energy from the L one. For this we monitored the DLTS spectrum of the Te-associated DX center in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ having an alloy composition $x = 0.40$, in which the L and X bands are

separated by ~ 10 meV. As shown in Fig. 3 the DLTS spectrum contains two components A and B , while for other x values it contains only one component. Analysis of the spectrum (variation of the emission rate and of the peak amplitude versus temperature) provides the ionization energies (E_i) and capture barriers (B) associated with each component (see Figs. 4 and 5). As shown in Table II these barriers correspond to the energy differences between the X or L bands and the Γ band, as expected.

The DX center is commonly interpreted as being an isolated donor accompanied by a large lattice distortion (for a recent discussion on DX models see Ref. 13). This model is deduced from several experimental observations, one of which is precisely the fact that the capture barrier B can be very large. However, this model is unable to explain the variation of B versus the alloy composition x : the barrier being typical of the defect configuration must not depend on x . Since B is equal to the energy difference between the L band and the bottom of the conduction band, the interpretation in terms of a cascade mechanism is straightforward. This implies that the DX center must exhibit only a small, if any, lattice distortion. Note that the fact that the hole capture cross section presents practically no temperature dependence¹⁴ confirms our interpretation.

In conclusion, there is a category of defects for which the energy barrier associated with the capture cross section is equal to the difference between the bottom of the conduction band (Γ) and a higher band (usually L). We have demonstrated that this behavior is simply charac-

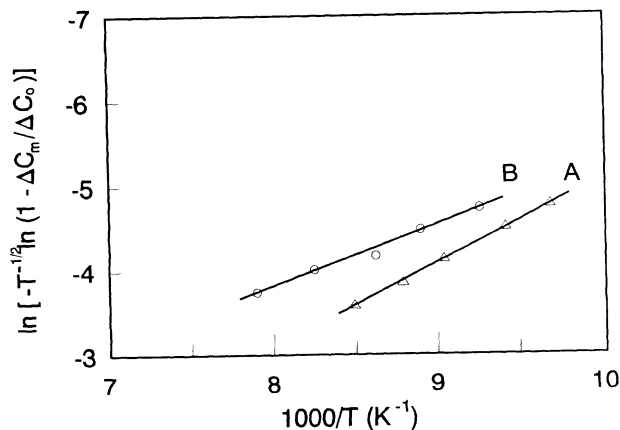


FIG. 5. Variations of the quantity $(1 - \Delta C_m)/\Delta C_0$ vs temperature, whose slope provides the capture barriers, for the two components A and B exhibited by the DLTS spectrum of Fig. 3(b).

TABLE II. Ionization energy (E_i) and capture barrier (B) associated with the two components of the DLTS spectrum associated with the DX center in Te-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ ($x = 0.50$). The difference in barriers between the A and B components is equal to the energy difference between the X and L bands ($\Delta_{X\Gamma} - \Delta_{L\Gamma}$) ~ 10 meV demonstrating that A (B) components correspond to electron capture via the excited states of the L (X) bands.

| Component | E_i (eV) | B (eV) | $\Delta_{L\Gamma}$ (eV) | $\Delta_{X\Gamma}$ (eV) |
|-----------|---------------|-------------|----------------------------|----------------------------|
| A | 0.205 | 0.075 | 0.050 | |
| B | 0.175 | 0.065 | | 0.040 |

teristic of an electron capture via a cascade mechanism, thus implying that the corresponding defect exhibits no electron-phonon interaction. This appears to be the case, for instance, for Fe and Cr impurities in GaAs and to the donor-associated defect (labeled *DX*) in $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

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