Identification of a defect in a semiconductor: $EL2$ in GaAs

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We present here a complete set of experimental results, obtained by electron paramagnetic resonance (EPR) and deep-level transient spectroscopy (DLTS), on the so-called $EL2$ defect in GaAs. It is obtained on semi-insulating materials and specially doped materials grown as semi-insulating ones, which have been submitted to electron irradiation, thermal treatments, and annealing followed by a quench. First, we show that there are two types of defects which give rise to the same EPR spectrum associated with the antisite As_{Ga}: the one associated with $EL2$, since it presents its well-characterized metastable property, and another one associated with the isolated As_{Ga}, which is not metastable. Second, we demonstrate that an $EL2$ defect can be transformed into an isolated As_{Ga} by a thermal treatment. Third, we describe how $EL2$ defects can be regenerated by a low-temperature treatment in materials which have been annealed and quenched. These results, together with considerations on self-diffusion in GaAs, allow us to conclude that $EL2$ is a complex formed by an isolated As_{Ga} and an intrinsic interstitial defect, namely As_i or Ga_i. Finally, we studied the kinetics of $EL2$ regeneration by DLTS in quenched material; since this regeneration occurs through the interstitial mobility and since the associated activation energy is similar to the one found for As_i mobility in electron irradiated p-type material, we deduce that $EL2$ is the complex $As_{Ga} + As_i$. All these results, as well as the ones provided by the literature, can be understood if the stable state of $EL2$ corresponds to As_i in second-neighbor position of As_{Ga} while the metastable state corresponds to As_i in first-neighbor position.

I. INTRODUCTION

Defect identification is very important in semiconductors because all the electronic and atomic transport properties of the material depend on the presence of defects (if one includes the doping impurities as a class of defects). Indeed, the electrical properties are directly related to the concentration of the defects, the positions of their various associated energy levels in the forbidden gap, and the corresponding capture cross sections for minority and majority carriers; as to the atomic transport properties, migration and diffusion, they are also related to defect total energies, i.e., migration and formation energies and entropies.

It has been hardly recognized that this problem of defect identification is not an easy one. In many cases the electron paramagnetic resonance (EPR) technique has proven to be essential for the establishment of the microscopic structure of the point defects such as, for instance, the cases of the vacancy and simple vacancy complexes (divacancy, A and E centers) in Si, group-III and -V sub-

stitutional impurities in group-IV materials, and transition-metal ions and anion antisite defects in the III-V compounds. However, in the case of GaAs, the interpretation of the EPR observations is rendered more difficult due to the presence of unresolved superhyperfine interactions leading to strongly broadened spectra.

The defects can also be studied by a number of complementary techniques, electrical [conductivity, Hall effect, deep-level transient spectroscopy (DLTS)] and optical (luminescence and absorption) which provide some of their characteristical properties: concentrations, energy levels, carrier capture cross sections, Franck-Condon shifts, optical cross sections, and sometimes the nature of the impurity (if any) involved through the detection of vibrational modes. However, none of these techniques, applied separately, is able to provide the complete nature of the defect, i.e., its atomic configuration including relaxation and distortion of the lattice around it. In order to identify the defect, one should rely on a combination of all these techniques, coupled with polarized excitations (photons, stress, etc.) and applied on samples having re-

ceived various types of treatments (annealing, diffusion, quenching, irradiation, etc.). Then, after long work and luck, a firm identification can sometimes be made.

This is the picture we shall present here for the defect called *EL* 2 in GaAs. This defect is famous because it is present in all bulk materials with relatively large ($\sim 10^{16}$ cm^{-3}) concentrations and in epitaxial layers with low ($\sim 10^{14}$ cm^{-3}) concentrations. It compensates the free carriers in undoped or lightly doped materials resulting in their semi-insulating property. This defect has been extensively studied because of its technological importance (active layers are grown epitaxially on semi-insulating substrates) but also because it presents a peculiar behavior: under a low-temperature photoexcitation it transforms into a different configuration. All the studies which have been performed on this defect will not be described in detail here because they have been the subject of several reviews (see, for instance, Ref. 1). Below we shall briefly recall its main characteristics.

(i) DLTS indicates that the associated energy level is located around $E_c - 0.8$ eV.[2] The emission rate of an electron into the conduction band is sensitive to the electric field,[3] suggesting a Franck-Condon shift of 130 ± 10 meV confirmed[4] by deep-level optical spectroscopy; the optical cross sections have also been determined.[4] The "signature" of the defect, i.e., the variation of the electron emission rate with the inverse of temperature differs with the authors because very often the experimental conditions in which the DLTS technique is applied are not correct. Most of the studies have been performed in semi-insulating materials in which the free-carrier concentration N_D is not large enough compared to the defect concentration N_T, leading to nonexponential transients (because the space-charge region varies as the emission proceeds[5] and also because of series-resistance effects).[6] Other reasons are, firstly, the effect of the electric field on the emission rate, and secondly (which will be cleared up in this paper) related to the fact that the emission observed originates from more than one energy level. For these reasons here we have applied DLTS on special materials grown like semi-insulating ones but specially doped so that N_T/N_D, of the order of 0.5, becomes less than 0.1 after thermal annealing.

(ii) Its concentration is dependent upon the mode of growth (type of epitaxy, stoichiometry of bulk material); it increases with the [As]/[Ga] ratio.[7−10]

(iii) It is found to anneal above 600 °C;[11] this annealing is related to a diffusion process since after annealing the concentration exhibits a profile, with a minimum concentration near the surface. The associated diffusion coefficient has been reported to depend on the type of material and on the method of encapsulation (for a review see Ref. 12). From its variation with temperature (see Fig. 1) an activation energy of ~ 4 eV is derived.[11] Actually, most of the results have been obtained by profiling with the DLTS technique and the results are often unreliable[13] because the DLTS analysis made does not take into account all the corrections[14] which are then necessary (variation of the space-charge region during the emission, trap-filling occupation versus applied reverse bias, series-resistance effects, etc.).
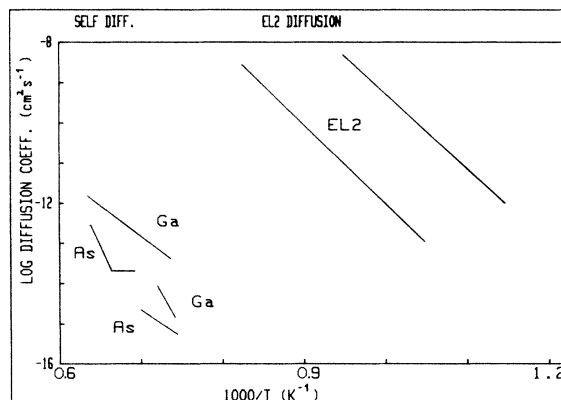

FIG. 1. Arrhenius plot of the self-diffusion coefficients for As and Ga in GaAs according to Refs. 53 and 54 showing the range in which the diffusion associated with *EL* 2 annealing occurs.

(iv) As already indicated, photoexcitation at 1.0−1.3 eV at low temperature transforms the defect into a new configuration (which apparently cannot be detected either by DLTS or by EPR); the 1.1-eV excitation is said to be due to an intracenter transition.[15] The new state is metastable: annealing above 140 K regenerates the initial state, the associated activation energy being 0.34 eV.[16] This regeneration process can be accelerated by the presence of electrons:[16] This reflects an electron capture with a cross section thermally activated (0.1 eV). This metastable behavior is observed through many photoelectronic properties.[17−20]

(v) Recent EPR studies have shown that the arsenic antisite defect, As$_{Ga}$, is present in doped or undoped high-resistivity materials[21−24] and that its intensity is proportional to the EL 2$^+$ (defect in its single positive charge state) concentration. Photoquenching and enhancement of the antisite spectrum show clear similarities with the optical cross sections of EL 2,[23] providing a further link between EL 2 and As$_{Ga}$.

Thus EPR observations provide a first step towards the identification of EL 2. Although several authors[25−27] suggested that EL 2 is the isolated antisite, this is not easily accepted for several reasons, one of them being that it is difficult to conceive that the isolated antisite can present a metastable state under 1-eV excitation. The other reasons will be developed here. One is related to the annealing behavior of the defect: The temperature at which it occurs excludes the possibility of the migration of a substitutional impurity. The other is that when EL 2 is said to anneal, i.e., when its electronic behavior disappears, its EPR signature is not modified. Thus, because of the existence of the metastable state, the EL 2 defect is rather expected to be a complex involving As$_{Ga}$, as suggested by electron-nuclear double resonance[24] studies. Indeed, EPR-tagged magnetic circular dichroism measurements show the different intracenter electronic transitions for the isolated As$_{Ga}$ and EL 2.[28] Identification of EL 2 therefore consists in the demonstration that EL 2 is a complex involving As$_{Ga}$ and in the determination of the entity X involved in this complex: As$_{Ga} + X = EL$ 2. This

is done in this paper using correlated DLTS and EPR measurements, coupled with optical excitation, in a large set of materials obtained in various growth conditions and submitted to various treatments (annealing, quenching, and irradiation). The final attribution is made possible by comparing the behavior of the entity X with those of defects created in electron-irradiated materials.

We proceeded in several steps. The first one consists of getting a method that allows one to detect $EL\,2$ and As_{Ga} *independently* (the notation As_{Ga} will be used only for the *isolated* antisite), thus verifying that the spectrum associated with the antisite detected by EPR can be associated with As_{Ga} as well as with $EL\,2$. This method is described in Sec. II where we show that EPR measurements, coupled with 1.1-eV photoexcitation, in semi-insulating materials containing As_{Ga} created by electron irradiation, are able to differentiate two types of defect in the spectrum associated with the antisite: one stable under photoexcitation created by the irradiation, i.e., As_{Ga}, and another one metastable i.e., $EL\,2$ preexisting in the material. The second step consists in dissociating the complex $EL\,2$ into its components As_{Ga} and X. This is done in Sec. III through thermal annealing at 850 °C followed by a quench: in unirradiated semi-insulating material the metastable character of the antisite spectrum is found to disappear. The third step consists in verifying that the material, once annealed and quenched, contains distributions of As_{Ga} and X by the search of a low-temperature thermal treatment allowing us to regenerate $EL\,2$, knowing that this regeneration should occur through the mobility of X since we know that As_{Ga} antisite defects are stable at least up to 900 °C (as expected for a substitutional atom). We indeed demonstrate in Sec. IV that the regeneration of $EL\,2$ occurs around 130 °C, and we present an extensive study, using DLTS, of the associated kinetics. The last step, the subject of Sec. V, consists in identifying the entity X from its thermal behavior (mobility); this is done by a comparison with the thermal behavior of several defects which have been extensively studied and identified in electron-irradiated materials. The entity X is attributed to an intrinsic interstitial, which we deduce to be the As interstitial, and we finally show in Sec. VI that this attribution is in agreement with all the observations concerning $EL\,2$. We also explain quite simply, in terms of a Coulomb interaction between As_{Ga} and the As interstitial, how the metastable character of $EL\,2$ can be understood and why the EPR spectra associated with As_{Ga} and $EL\,2$ cannot be distinguished.

II. DISTINCTION BETWEEN $EL\,2$ AND THE ISOLATED ANTISITE

EPR measurements were performed, in the range 4—290 K, using an X-band spectrometer, on various slices taken from liquid encapsulated Czochralski-grown (LEC) GaAs materials grown in BN boats. In situ photoexcitations were realized by a monochromator (8400 Å to 2 μm) and a 100-W quartz halogen lamp.

These semi-insulating materials exhibit the spectrum associated with As_{Ga}^{+} (Ref. 21) shown in Fig. 2. The concentration of this defect, on the order of 10^{15}—10^{16} cm^{-3},
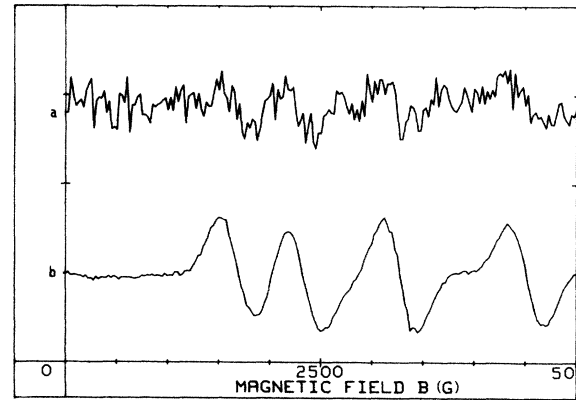

FIG. 2. Antisite-associated EPR spectrum observed in (a) semi-insulating and (b) electron-irradiated materials.

varies from sample to sample. Actually, the detected concentration is not the total defect concentration because only a fraction of the defects is in the $+$ paramagnetic charge state, the Fermi level E_F being located near the level E_T associated with the transition $+\rightarrow 0$. This is demonstrated by the influence of near-band-gap illumination, which increases the intensity of the EPR spectrum in a fashion that depends on the position of E_T as compared to E_F. The EPR spectrum must be associated with $EL\,2$ since it presents the characteristic photoquenching behavior of this defect: As shown in Fig. 3 the signal is fully and persistently quenched under 1.1-eV photoexcitation and is thermally regenerated at 140 K.

In order to get samples containing both $EL\,2$ and As_{Ga}, to demonstrate that $EL\,2$ can be distinguished from As_{Ga}, we used electron irradiation. Indeed, electron irradiation is known to introduce antisite defects.[29-31] The introduction rate of these defects is strongly dependent on the doping concentration, increasing in a nonlinear fashion with this concentration.[29] In the case of Fig. 4 a semi-insulating undoped material is irradiated with 7×10^{17} 1-
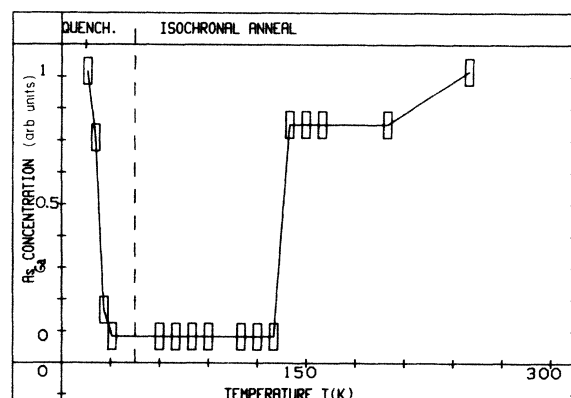

FIG. 3. Variation of the antisite concentration induced by 1.1-eV photoquenching and subsequent thermal annealing in a semi-insulating material.

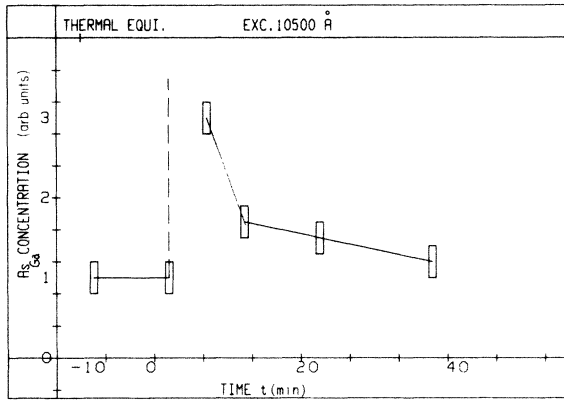IDENTIFICATION OF A DEFECT IN A SEMICONDUCTOR: . . .

FIG. 4. Variation of the antisite concentration versus time in a semi-insulating, irradiated, material following 1.1-eV photoexcitation.

MeV electrons per cm^{-2}, resulting in an introduction of $\sim 10^{16}$ cm^{-3} As_{Ga}. As shown in this figure, 1.1-eV photoexcitation induces a sharp increase of the As_{Ga}^{+} EPR spectrum, which subsequently returns toward its equilibrium value. This behavior is interpreted in the following way. The irradiated material contains $EL\,2$ and As_{Ga} defects; in thermal equilibrium at 4 K only the irradiation-induced As_{Ga} are detected by EPR, because after the irradiation E_F still lies above the $EL\,2$ (0/ +) level, but below the As_{Ga} (0/ +) level. The effect of illumination at 1.1 eV at time $t=0$ is to depopulate the $EL\,2$ levels, resulting in the sharp increase of the EPR spectrum; but due to their photoquenching behavior, these defects are subsequently transformed into their metastable states and the EPR signal intensity returns to the value it had prior to illumination. This therefore demonstrates that As_{Ga} and $EL\,2$ defects can be differentiated using photoexcitation. This method will be used in the following sections to distinguish $EL\,2$ from As_{Ga}.

III. DISSOCIATION OF $EL\,2$: CONVERSION INTO As_{Ga}

The following experiments have been performed on specially grown samples in order to allow coupled EPR and DLTS measurements on the same samples. The samples are selected from ingots grown in BN boats in a way identical to the growth of semi-insulating materials, but with the incorporation of Si in the melt (under dry B_2O_3 encapsulation) in such a way that we were able to select slightly n-type doped (in the range of $10^{15}-10^{16}$ cm^{-3}) slices in the ingots. After the annealing treatments described below, these samples are well adapted to quantitative DLTS measurements, the concentration of deep levels being at most 10% of the free-carrier concentration. For EPR measurements, they are irradiated with a low dose of 1-MeV electrons $(2 \times 10^{15}$ $cm^{-3})$ to make them semi-insulating; it has been verified that this low does does not introduce any detectable EPR signal.

The samples are submitted to a thermal treatment in H_2

atmosphere at 850 °C for 10 min with Si_3N_4 encapsulation (this encapsulation is equivalent to a thermal treatment of 450 °C for 10 min), followed by a quench. The quenching procedure consists simply in abruptly removing the samples from the oven and allowing them to cool down to room temperature in air atmosphere; it is therefore not well controlled. The DLTS measurements are made on Al Schottky barriers deposited at room temperature after the encapsulation has been removed; the surface is not etched before deposition. As to the Ohmic contacts, they are made prior to the Schottky barriers by evaporation of Au and In (2000 Å), followed by a 400- °C annealing for 10 min under N_2 atmosphere.

In these samples the As_{Ga}^{+} EPR spectrum is detected at 16 K; its concentration at thermal equilibrium varies from sample to sample in the range $10^{15}-10^{16}$ cm^{-3} and is photoquenchable; i.e., all the defects associated with the spectrum are related to $EL\,2$. After annealing and quenching, the samples still exhibit the As_{Ga}^{+} spectrum but now *it can no longer persistently be quenched* by 1.1-eV illumination.

DLTS observations are performed using a double lock-in amplifier to analyze the transient; typically, the spectra are recorded at 35 Hz, with a pulse width of 1 ms, a pulse amplitude of 3 V, and a reverse bias of -3 V. This way the concentration of defects measured is the average concentration in the depth $0.1-1$ μm. The $EL\,2$ defect gives rise to a peak situated at ~ 70 °C for a rate window set at 50 s^{-1}. Depending on the samples, the initial $EL\,2$ concentration is $(1-3) \times 10^{15}$ cm^{-3}; the encapsulation procedure (450 °C, 10 min) reduces this concentration in the range $(0.5-1) \times 10^{15}$ cm^{-3}; after 850 °C (10 min) the remaining concentration is $(0.5-5) \times 10^{14}$ cm^{-3}.

Typical profiles of $EL\,2$ obtained after 450 °C and 850 °C annealings are shown in Figs. 5 and 6. It appears that the $EL\,2$ concentration remains practically constant in the depth studied $(0.6-1.5$ $\mu m)$, while other authors[11] have observed large variations (by nearly two orders of magnitude) in the same region. Obviously, this is due to the conditions (type of encapsulation, nature of the atmo-
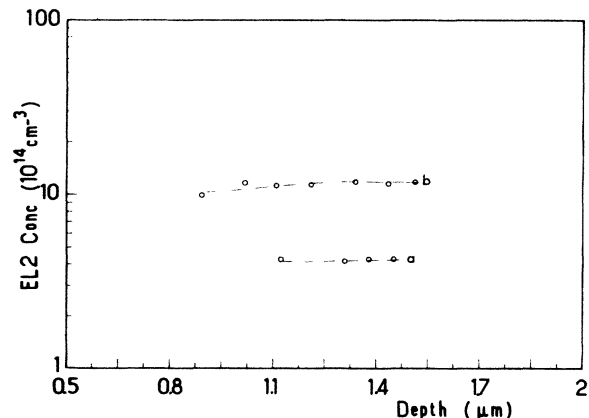

FIG. 5. $EL\,2$ concentration versus depth in specially doped semi-insulating material after (a) 450 °C annealing and (b) 450 °C annealing followed by a regeneration treatment at 130 °C.
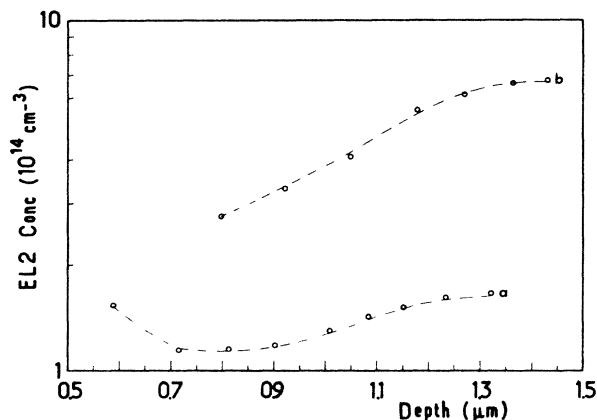
FIG. 6. *EL* 2 concentration versus depth in specially doped semi-insulating material after (a) 850-°C annealing and (b) 850 °C annealing followed by a regeneration treatment at 130 °.

sphere), in which the annealing is performed.[11]

These DLTS measurements are therefore in agreement with similar results described in the literature: apparently, *EL* 2 has been partially ($\sim$90%) annealed by the 850 °C treatment. However, the EPR observations demonstrate that, the concentration of antisite-related defects is unchanged but their nature is changed. We can conclude that *the effect of thermal treatment is to break the complex* $As_{Ga}+X$, since the remaining defects are isolated antisites not photosensitive.

IV. REGENERATION OF *EL* 2

On the 850 °C thermally annealed and quenched samples, subsequent annealing steps in the range from 50 °C to 250 °C were performed in He or N_2 atmosphere with the encapsulation removed.

The EPR observations show that the effect of such annealing induces at approximately 140 °C the reverse transformation: The nonphotosensitive As_{Ga}^+ spectrum becomes again photosensitive, i.e., a 140-°C annealing has partly regenerated *EL* 2 defects.

DLTS observations show that the *EL* 2 peak increases versus time during annealing treatments in the range from 90 °C to 130 °C. These observations are performed in the following way. Once the *EL* 2 spectrum has been recorded at approximately 70 °C (corresponding to the remaining defects left by the 850-°C thermal treatment), the temperature is still increased in the range from 90 °C to 150 °C at which the sample is kept for a given time (typically few minutes); the temperature is then reduced to record again the *EL* 2 spectrum. The accuracy of the measurements is not very good because the *EL* 2 spectrum is observed at a temperature close to the temperature at which the process takes place. An increase, by a factor 1.1 to approximately 4, depending on the sample, in the amplitude of the spectrum is observed. Such scatter in the result is not surprising in view of the facts that the initial concentration of *EL* 2 varies from sample to sample and that the thermal procedure they received—especially the quenching step—
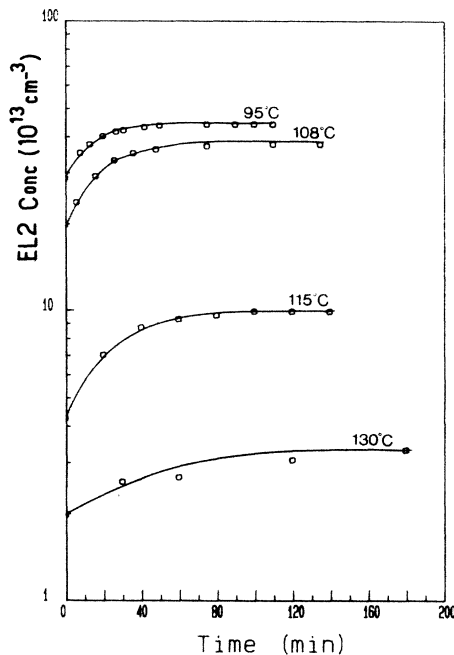

FIG. 7. Variation of the *EL* 2 concentration versus time at different temperatures in a semi-insulating material which has been submitted to an annealing at 850 °C followed by a quench.

can be slightly different from sample to sample.

The kinetics of growth of the *EL* 2 concentration has been studied using isothermal runs at 95 °C, 108 °C, 115 °C, and 130 °C. The results are shown in Fig. 7. For a process involving the formation of *EL* 2 defects (in concentration n_t) through the interaction of mobile entities X, in concentration small compared to the concentration of antisites n_a, with the antisites, the kinetics are expected to follow the law

$$n_t(t)=(n_0-n_i)[1-\exp(-Kn_at)]+n_i \ ,$$

where n_0 and n_i are the final and initial concentrations of *EL* 2. It can be seen in Fig. 8 that the kinetics observed
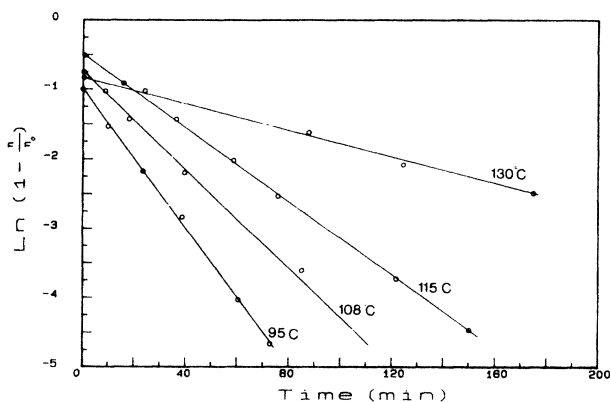

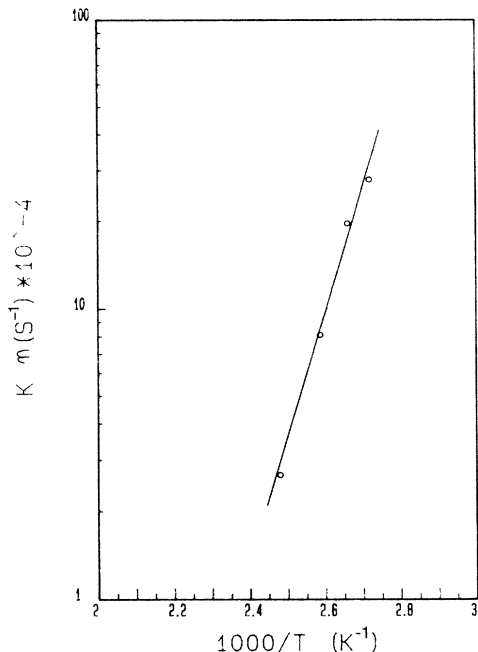FIG. 8. Regeneration kinetics of *EL* 2 deduced from the data of Fig. 5.

FIG. 9. Arrhenius plot of the regeneration rate of $EL\,2$ deduced from the kinetics of Fig. 6.

FIG. 10. Shape of the DLTS spectrum associated with $EL\,2$ in 850 °C annealed and quenched material after thermal treatment at 85 °C or above, showing the two components A and B of the spectrum.

verify this law and, from the variation versus temperature of the slope of $\ln(1 - n_t/n_0)$ versus time, the activation energy E_a associated with the process, i.e., the activation energy for the mobility of X, is deduced (Fig. 9): $E_a \sim 0.7 \pm 0.08$ eV.

A careful examination of the shape of the $EL\,2$ spectrum during the regeneration shows that it is actually composed of two distinct spectra. This is clearly seen in some cases, such as the one depicted in Fig. 10. The change of the shape of the spectrum results from a modification of the relative amplitudes of the two components of the spectrum. When the temperature decreases and when the reverse bias is applied, the low-temperature component (A) increases and the high-temperature component (B) decreases. The appearance of the component A is observed only with the reverse bias applied and if the temperature reached is high enough (approximately 90 °C); heating without bias or below 85 °C does not result in the appearance of component A.

Because the component A appears only when the reverse bias is applied, it is possible to study the kinetics of the transformation $B \rightarrow A$ by measuring the amplitude of A at various temperatures versus the time during which the reverse bias is applied. The results are not very accurate because, the two components overlapping, their absolute amplitudes are difficult to obtain. From the variations of the A amplitude versus time at 104° and 94 °C an activation energy of 0.65 ± 0.15 eV has been deduced.

The A component is not stable: It disappears with time and the component B increases correlatively. The rate of annealing is dependent on the bias: With a reverse bias applied, the rate decreases by a factor of approximately 2. The creation and disappearance of the component A can
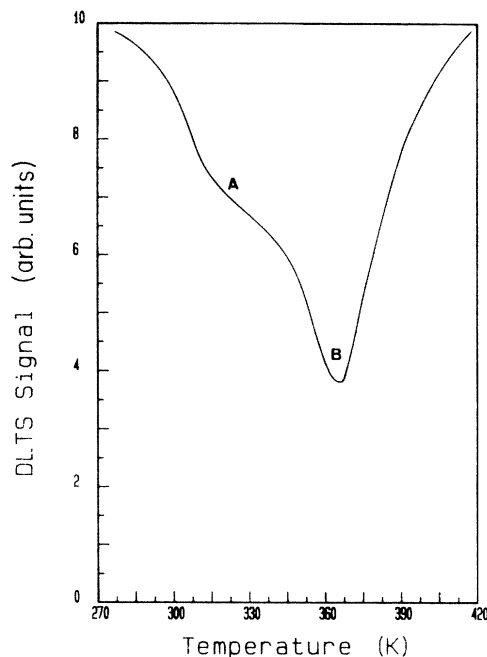
be reproduced indefinitely, since after annealing it can be reproduced by the application of temperatures (90 °C) and bias.

Such behavior strongly suggests that there are two different configurations for $EL\,2$: one stable, corresponding to the component B and the other, unstable, corresponding to the component A which is produced by the application of the reverse bias when the temperature exceeds 90 °C. Once the unstable configuration has been created it relaxes towards the stable one with an activation energy equal (within the experimental accuracy) to the one associated with the X mobility. The two configurations correspond obviously to two different positions of X in the neighborhood of the antisite.

The variation of the emission rate e_n with temperature (the signature) has been studied for the two components A and B. It shows (see Fig. 11) that the B component is $EL\,2$ (similar signature) and that the A component corresponds to an ionization energy about half of that of $EL\,2$.

All these observations are consistent with the ones described in the previous sections. The annealing at 850 °C breaking the complexes $As_{Ga} + X$, the expected result after quenching is a distribution of As_{Ga} and X. The entity which moves in order to make the dissociation effective is obviously X because antisites should behave like substitutional impurities, i.e., they become mobile only in the same high-temperature range, where self-diffusion occurs, since, in order to move, a substitutional impurity needs the formation of vacancies. As shown in Fig. 1, the diffusion coefficient deduced from the variation of $EL\,2$ profiles at different temperatures is several orders of mag-
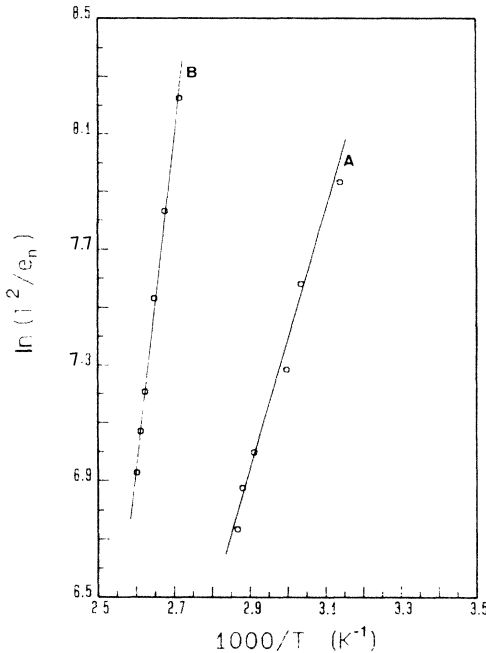
FIG. 11. Variation of the emission rate of components A and B versus the inverse of the temperature.

nitude larger than the self-diffusion coefficients in the As or Ga sublattices. Thus X is the moving entity, and from the $EL\,2$ annealing results we expect it to be of *interstitial type;* the activation energy associated with its mobility is ~ 0.7 eV.

The thermal treatment around 140 °C can therefore be understood as a regeneration of the complexes by the mobility of X at this temperature. The kinetics is first order because it corresponds to a diffusion of the entities X distributed at random, towards As_{Ga} sites in a concentration large compared to the X concentration. The region where the regeneration is observed is the junction space charge, i.e., a region close to the surface (1 μm or less) where the concentration of X is small compared to the initial $EL\,2$ concentration because a fraction of X is lost on the surface. The faster rate at short times reflects the fraction of X which are close to As_{Ga}.

The existence of the two components A and B in the spectrum of $EL\,2$ suggests that there are two possible trapping sites for X in the vicinity of As_{Ga}, one of which being more stable. By using a combination of temperature and electric field (induced by a reverse bias) it is possible to change the relative populations of these two sites. Such a conclusion is therefore consistent with the suggestion, often repeated, that $EL\,2$ is not a single trap but that there is a family of $EL\,2$ traps. This could explain some observations such as the fact that two regimes of formation kinetics of $EL\,2$ are found depending on the range of growth temperature.[8]

V. IDENTIFICATION

It remains to determine the nature of the entity X. It can be of intrinsic or extrinsic origin. An intrinsic X can *a priori* be a vacancy: V_{Ga} or V_{As} or an interstitial As_i

or Ga_i. Of extrinsic origin, it will be an interstitial impurity since we have shown in Sec. IV that the temperature at which the regeneration of $EL\,2$ (through the mobility of X) occurs eliminates the possibility of a substitutional impurity.

From one important observation obtained on $EL\,2$ it seems natural to eliminate V_{As}, V_{Ga} and Ga_i. Indeed, the $EL\,2$ concentration increases with the ratio [As]/[Ga] in the melt; thus, one expects As to be in excess, i.e., no presence of Ga_i, V_{Ga} (which would trap As_i to give antisite) and V_{As}. This argument rules out clearly vacancy defects but should only be considered as an indication for Ga_i since the presence of trapped Ga_i could perhaps be possible even in As-rich materials. It remains to consider As_i; since the excess of As would result in As precipitation in the form of aggregates, the existence of As_i is quite natural as suggested by Ikoma *et al.*[32]

Consider now the possibility of X being an impurity. Common impurities (i.e., in concentration usually larger than 10^{14} cm^{-3}) in undoped liquid encapsulated Czochralski-grown (LEC) GaAs materials are C, O, B, Si, and S. They are on substitutional sites but the possibility cannot be excluded that a fraction of their concentrations are on interstitial sites. Actually, all these impurities can reasonably be ruled out using the following arguments: (i) a comparison between the concentration of the impurity considered, C_i, and the $EL\,2$ concentration C_{EL2} (average value over the area of a given slice) in different types of materials and (ii) a correlation between C_i and C_{EL2} as a function of the position in the ingot for a given material.

First, C and O are known to exist in all types of materials with approximately the same concentrations, C_C and C_O (typically 10^{14}–10^{16} and 10^{15}–10^{16} cm^{-3}, respectively), while C_{EL2} varies from $\sim 10^{16}$ cm^{-3} (in LEC and Bridgman materials) to $\sim 10^{14}$ cm^{-3} (in vapor-phase epitaxy and metal-organic chemical-vapor disposition materials) and even to lower values ($\sim 10^{13}$ cm^{-3}) in liquid-phase epitaxy and molecular-beam epitaxy materials. Because of its segregation coefficients C_O varies from few 10^{15} cm^{-3} to a few 10^{16} cm^{-3} from the head to the tail of an ingot[33] while C_{EL2} can have the same value at both ends of the ingot.[34] It can even happen that C_O is lower than C_{EL2}. As for C_C in LEC materials it varies from 8×10^{15} cm^{-3} for ~ 50 ppm H_2O to 4×10^{14} cm^{-3} for ~ 500 ppm H_2O, while C_{EL2} remains in the range of 10^{16} cm^{-3}.

As to other impurities, except B, their concentrations are always less than 10^{15} cm^{-3}, i.e., far lower than C_{EL2}. As for B, its concentration varies sharply with the humidity of B_2O_3, from 10^{14} to 10^{17} cm^{-3},[34–41] and is uncorrelated with C_{EL2}.

We are thus led to examine in more detail the possibility that X is an intrinsic interstitial, i.e., As_i or Ga_i. For this we can only use the known characteristics of X, namely, that it is mobile around 140 °C with an associated activation energy of ~ 0.7 eV. Fortunately, the atomic behavior of As_i is known from the extensive studies which have been performed on the defects produced by electron irradiation in n- and p-type GaAs. Electron irradiation produces vacancy-interstitial pairs in the As and Ga sublattices. It is now understood[42] that in n-type

GaAs following irradiation (from 4K to room temperature) with a light electron dose [such as the one used for DLTS studies for which a defect concentration small compared to the free-carrier concentration must be introduced] the remaining defects are related to a distribution of vacancy-interstitial pairs in the As sublattice; the pairs in the Ga sublattice are not observed. These V_{As}-As$_i$ pairs correspond to the DLTS peaks labeled $E1$ to $E5$. However, when the dose of irradiation used is high (such as the ones used for EPR or infrared (IR) absorption of local modes of vibration, which necessitate a compensation of the free carriers), there is an interaction of the created defects with impurities, leading to the formation of complexes. The reason is that some mobility of As$_i$ is induced by the presence of the electron-hole pairs produced by the irradiation (presumably this mobility is driven by the energy liberated by the recombination of electron-hole pairs on the site of As$_i$). When the duration of irradiation is large enough, the diffusion length of As$_i$ becomes sufficient to allow interaction of As$_i$ with several types of impurities: Antisite defects are created,[29−31] as well as C and B complexes with As$_i$,[43] detected by EPR and IR absorption, respectively.

Thus, the thermal behavior of V_{As}-As$_i$ pairs and of C-As$_i$ and B-As$_i$ complexes can provide information on the mobility of As$_i$. The vacancy-interstitial pairs annihilate at approximately 200 °C with an associated activation energy of 1.5 eV through the As$_i$ mobility since we know from EPR measurements that V_{As} is stable above this temperature.[44] Such activation energy is higher than the one associated with the mobility of the entity X. This difference can be understood, however, if the recombination process is limited by the barrier for the recombination of As$_i$ with V_{As} and not by the As$_i$ mobility. We therefore turn to C-As$_i$ and B-As$_i$ complexes. They are known to dissociate at approximately 130 °C and 200 °C, respectively.[43,45] This difference in the annealing temperatures means that the dissociation energy is lower in case of C and therefore that the mobility of As$_i$ occurs near 130 °C, temperature at which we observe the mobility of X. In conclusion, the behavior of As$_i$ in electron-irradiated n-type GaAs is consistent with the attribution of X as being As$_i$ but constitutes only an indication. The evidence comes from the behavior of As$_i$ in p-type material. Indeed, in this type of material As$_i$ is more mobile than in n-type material under irradiation and As$_i$-impurities complexes are easily formed.[46] These complexes (corresponding to DLTS spectra labeled H$_2$–H$_5$) anneal also in the range from 130 °C to 200 °C and the associated activation energy, related to the mobility of As$_i$ has been measured and found to be close (0.5±0.1 eV), i.e., within the experimental uncertainty, to the one associated to the X mobility.[46]

The study of irradiation-induced defects thus leads to the conclusion that X is the As interstitial. It should be noted here that the identification of As$_i$-related defects is mostly based on the fact that defects belonging to the Ga sublattice had not been observed. However, recently von Bardeleben et al.[47] have observed a new EPR spectrum, associated with the complex As$_{Ga}$-V_{As}, resulting from the transformation of an unstable V_{Ga}. Then, there are de-

fects created by irradiation in the Ga sublattice, and consequently complexes involving Ga$_i$ cannot be ruled out. In conclusion, once again the possibility that X is the Ga interstitial cannot be completely eliminated if both Ga$_i$ and As$_i$ have similar activation energies associated with their mobility.

It remains to discuss one point—that annealing at 850 °C under our condition leads to a strong reduction of the $EL2$ concentration, resulting from the separation of the $EL2$ complex into its constituents As$_{Ga}$ and As$_i$ and that consequently after such treatments the material contains isolated antisites. This is apparently in contradiction with the often reported observation that different high-temperature annealing—in particular close-contact annealing under As atmosphere—do not change the mean bulk $EL2$ concentration significantly. The $EL2$ concentration is normally deduced from the optical-absorption coefficient at 1.1 eV as described by Martin.[48] Two aspects have to be considered, however; first, the optical-absorption spectrum of the isolated As$_{Ga}$ defect has not been studied up to now and then it cannot be excluded that both $EL2$ and As$_{Ga}$ give rise to a similar near-band-gap absorption. Second, low-temperature optical absorption measurements can be used to distinguish the two defects by their metastable behavior. However, it is not sufficient to observe the quenching of the absorption spectrum below 140 K. The temperature dependence of the thermal recovery has to be studied to separate metastability and shift of the Fermi-level effects.

This is illustrated (see Fig. 12) by EPR observation. It shows that the photoquenched EPR spectrum does not recover at 140 K as it should do if associated with $EL2$, but at a higher temperature (∼250 K). The reason for such behavior is the following. The material contains isolated As$_{Ga}^+$, not $EL2$, which, under illumination, transform into As$_{Ga}^0$ or As$_{Ga}^{2+}$ states, no more observable by EPR, the carriers being transferred from the antisite into other deep traps. When the carriers are thermally released from
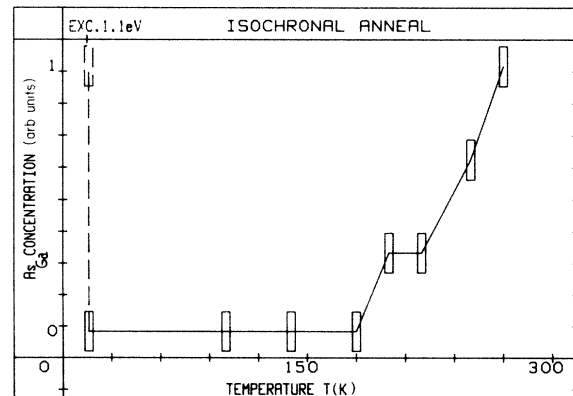

FIG. 12. Variation of the antisite concentration induced by 1.1-eV photoquenching and subsequent thermal annealing 850-°C annealed semi-insulating material.

these traps, the antisite + charge state is repopulated and the EPR signal regenerated. Thus, care must be taken when trying to detect the presence of $EL\,2$ defects using IR absorption.

VI. MODELS OF METASTABILITY

In the preceding section we have shown that the attribution of $EL\,2$ as a complex involving As_{Ga} and As_i is in agreement with most of the observations which have been performed on $EL\,2$, As_{Ga}, and As_i. However, we have still to demonstrate that this identification is consistent with the photoquenching behavior, i.e., with the existence of a metastable state. The photoquenching behavior has been first described using the configuration coordinate diagram[4] model, which implies that a large lattice distortion is associated with $EL\,2$, whereas for the isolated antisite theory predicts small lattice relaxation and distortion.[49] However, more recently a more specific model has been presented[50] in which the structural rearrangement of the defect is driven by electrostatic forces and lattice strain, controlled by the charge states of the elements of the complex.

The models we shall consider here will be deduced from the present results, keeping the idea of the existence of a charge-state-controlled dipolar structure. Indeed, we have demonstrated that the $EL\,2$ is a complex of two entities As_{Ga} and As_i and that the perturbation of As_i on the As_{Ga} electronic states corresponding to the stable state of $EL\,2$ is small since it cannot be detected by EPR. We shall therefore try to account for the electronic as well as atomic perturbations that As_i induces on As_{Ga} using a simple picture of Coulomb interaction.

The first possible model we examine is the following. The stable state of $EL\,2$ is composed of the As antisite with an As_i in close (let us say first-neighbor) position. This complex is formed during cooling of the material which, because it is As rich, contains stable isolated As_{Ga} and mobile As_i. The association is a consequence of the trapping of As_i by the strain field of As_{Ga}. A Coulomb attraction does not seem reasonable since, from the theory, we expect the charge states of both entities to be neutral or positive.[51] The interaction results in shifts of the As_{Ga} (A_1) and As_i (T_2) level with a splitting of the T_2 level into E and A_1 levels (Fig. 13).

In semi-insulating materials we know that the $EL\,2$ $(0/+)$ level is close to the Fermi level E_F, usually slightly below (when no EPR signal is observed without photoexcitation). The charge-state picture is therefore that of a complex As_{Ga}^0 with As_i^+ (As_i^0 cannot be ruled out *a priori* since we do not have an idea of the shift of the As_i level due to the interaction; however, this charge state would not explain the metastability of the defect as we shall see now).

In order to account for the optically induced metastability of $EL\,2$ one has to consider that 1.1-eV photoexcitation induces charge-state changes of one or both elements of the complex in such a way, that a Coulombic repulsion occurs, resulting in the jump of As_i, from a first-neighbor position to, for example, a second-neighbor position. This can be achieved for instance through a photo-induced
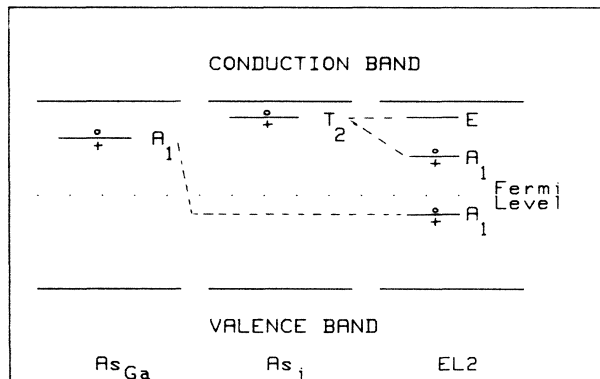

FIG. 13. Schematic representation of the energy levels associated with the isolated antisite and As interstitial and their variation when they are in interaction to form $EL\,2$.

charge of As_{Ga}^0 into As_{Ga}^+. After the optical excitation is turned off, the two entities are expected to recover their original charge state (As_{Ga}^0, As_i^+).

The return of the metastable (As_i in second neighbor) to the stable state (As_i in first neighbor), through thermal excitation or electron injection can be easily understood. Due to thermal excitation (140 K), the As_i is able to jump in first-neighbor position over a barrier (0.1 eV) to recover its stable position. Due to electron injection, electron trapping is possible on the site of As_i; this electron, releasing its energy into phonons, allows equally the jump of As_i.

Such model, although it explains most of the observations, is apparently unable to account for two observations: (1) that the optical excitation inducing the metastable state corresponds to a center of T_d symmetry; (2) that the EPR spectrum associated with As_{Ga} disappears when $EL\,2$ is in its metastable state. Indeed, one expects the wave function associated with As_{Ga} in slight interaction with As_i to be similar to the one of isolated As_{Ga} and strongly modified, to become similar to the one of isolated As_i, when the interaction is strong (i.e., in case of the stable position where As_i is in first-neighbor position). In the same way, the optical T_d symmetry is expected for an isolated or only slightly disturbed point defect.

For these reasons we are led to consider a second model, "inverse" of the first one. In this model the stable position corresponds to the slight interaction between As_{Ga} and As_i (As_i in second-neighbor position) and the metastable position to the large interaction (As_i in first-neighbor position). In this second model, the formation of $EL\,2$ results, as in the first one, in the trapping in a second-neighbor position, of As_i by the strain field of As_{Ga}. Since there are many such positions, this allows to understand that there exists a distribution of $EL\,2$ defects corresponding to slightly different energy levels.[52] This also explains the fact that we observe two different levels in the DLTS spectrum related to $EL\,2$. Since the interaction is rather weak, the shifts of the levels $(0/+)$ associated to isolated As_{Ga} and As_i due to the formation of the complex are expected to be small, implying that the As_{Ga}

$(0/+)$ level is not far from $E_c - 0.7$ eV (the $EL\,2$ level), i.e., the complex is (As^0_{Ga}, As^+_i). The wave function of As_{Ga} is only slightly perturbed and the corresponding EPR spectrum is not changed (the change induced by the presence of As_i cannot be detected due to the large linewidth of the spectrum).

This expected position of the $0/+$ level of the isolated As_{Ga} is confirmed by an attempt made to locate it by EPR measurements; it demonstrates that it is situated between 0.30 and 0.76 eV. This attempt has been performed in the following way. With increasing irradiation doses, the Fermi level E_F moves deeper and deeper from the shallow donor level on the well-known $E\,2$, $E\,3$, $E\,4$ and $E\,5$ defects.[42] The energy levels of these defects being known, it is possible to locate the $0/+$ As_{Ga} level with respect to them. One finds that when E_F is quenched on the $E\,3$ level (0.30 eV) the As_{Ga} spectrum is not observed, which means that this defect is in its 0 charge state (i.e., the $0/+$ level is below the $E\,3$ level). When E_F is quenched on the $E\,4$ level (0.76 eV) the spectrum is observed that is the $0/+$ level is above the $E\,4$ level.

The optical excitation resulting in the transformation of the stable to the metastable configuration now must be understood in term of charge-state changes inducing a Coulomb attraction. The As_i jumps closer to As_{Ga}, i.e., into a first-neighbor position. Under photoexcitation (1.1 eV) free electrons are created and subsequently captured by the neutral As_{Ga}, which changes its charge state to $-$, giving rise to a Coulomb attraction for the As^+_i ion. This optical excitation reflects a T_d symmetry, because again the perturbation induced by As_i is small, when it is in second-neighbor position.

The EPR spectrum associated with this new metastable configuration is no more a spectrum similar to the one of As_{Ga}. The wave function of the complex is rather expected to look like the one of As_i (perturbed by the presence of As "impurity" in first neighbor). This explains why the As_{Ga} ESR spectrum is no more observed.

As to the return from the metastable state to the stable state it can be understood in a fashion similar to the one depicted in the first model.

The existence of two different configurations for $EL\,2$, detected through the two components A and B in the DLTS spectrum of $EL\,2$ can be easily understood in the second model. Indeed, if As^+_i in second-nearest-neighbor position of As^0_{Ga} is the stable position of $EL\,2$ (the B configuration) it is obvious that the application of the reverse bias will transform this pair into the pair $As^+_{Ga}\text{-}As^+_i$ and the Coulomb repulsion will induce the jump of As^+_i in third- or fourth-nearest-neighbor position (the A configuration) when the temperature is high enough. This explains the reason why both reverse bias and temperature are necessary to induce the transition $B \rightarrow A$ and the reversibility of this process. The A configuration corresponds to an $EL\,2$ defect in which the antisite is only slightly perturbed by the As interstitial. As a result the ionization energy of the A configuration should be close to the one expected for As_{Ga}. The energy value (~ 0.40 eV) we obtain from Fig. 11 is indeed in agreement with the indirect determination of the $0/+$ As_{Ga} level we have made previously.

VII. CONCLUSION

We have described a set of experiments which clearly demonstrates that the $EL\,2$ defect is not the isolated As antisite but a complex involving As_{Ga} and an interstitial defect. We have also shown that the interstitial defect is of intrinsic nature, i.e., is As_i or Ga_i. Finally, we have deduced from a comparison between the atomic behavior of this interstitial defect with the one of irradiation-induced defects, that it is most presumably As_i. All the experimental results described here as well as those provided by the literature, including the metastable character of the $EL\,2$ defect, can be understood if this defect corresponds to an $As_{Ga}\text{-}As_i$ complex, with As_i in second-neighbor position for the stable state and with As_i in first-neighbor position for the metastable state.

ACKNOWLEDGMENTS

[1]S. Makram-Ebeid, P. Langlade, and G. M. Martin, in *Proceedings of the Third Conference on Semi-Insulating III-V Materials*, edited by D. C. Look and J. S. Blakemoore (Shiva, Nantwich, England,1985), p. 184.

[2]G. M. Martin, A. Mitonneau, D. Pons, A. Mircea, and D. W. Woodward, J. Phys. C 13, 3855 (1980).

[3]S. Makram-Ebeid and M. Lannoo, Phys. Rev. B 25, 6406 (1982).

[4]A. Chantre, G. Vincent, and D. Bois, Phys. Rev. B 23, 5353 (1981).

[5]D. Stievenard, M. Lannoo, and J. C. Bourgoin, Solid State Electron. 28, 485 (1985).

[6]A. Broniatowski, A. Blosse, P. C. Srivastava, and J. C. Bourgoin, J. Appl. Phys. 54, 2907 (1983).

[7]L. Samuelson, P. Omling, H. Titze, and H. G. Grimmeis, J. Cryst. Growth 55, 164 (1981).

[8]M. D. Watanabe, A. Tanaka, T. Udagawa, T. Nakanisi, and Y. Zohta, Jpn. J. Appl. Phys. 22, 923 (1983).

[9]P. K. Bhattacharya, J. W. Ku, S. T. J. Owen, V. Aebi, C. B. Cooper, and R. L. Moon, Appl. Phys. Lett. 36, 304 (1980).

[10]M. D. Miller, G. H. Olsen, and M. Ettenberg, Appl. Phys. Lett. 31, 538 (1977).

[11]S. Makram-Ebeid, D. Gautard, P. Devillard, and G. M. Martin, Appl. Phys. Lett. 40, 160 (1982).

[12]G. M. Martin and S. Makram-Ebeid, Acta Electron. **25**, 2 (1983).

[13]F. Hasegawa, N. Yamamoto, and Y. Nannichi, Appl. Phys. Lett **45**, 461 (1984).

[14]D. Stievenard and D. Vuillaume (unpublished).

[15]M. Kaminska, M. Skowronski, J. Lagowski, J. M. Parsey, and H. C. Gatos, Appl. Phys. Lett. **43**, 302 (1983).

[16]A. Mitonneau and A. Mircea, Solid State Commun. **30**, 157 (1979).

[17]L. Lin, E. Omelianovskii, and R. H. Bube, J. Appl. Phys. **47**, 1852 (1976).

[18]G. Vincent, D. Bois, and A. Chantre, J. Appl. Phys. **53**, 3643 (1982).

[19]A. L. Lin and R. H. Bube, J. Appl. Phys. **47**, 1859 (1976).

[20]G. Vincent and D. Bois, Solid State Commun. **27**, 431 (1978).

[21]R. J. Wagner, J. J. Krebs, G. H. Strauss, and A. M. White, Solid State Commun. **36**, 15 (1980).

[22]K. Elliott, R. T. Chen, S. G. Greenbaum, and R. J. Wagner, Appl. Phys. Lett. **44**, 907 (1984).

[23]M. Baeumler, U. Kaufmann, and J. Windscheif, Appl. Phys. Lett. **46**, 781 (1985).

[24]D. M. Hofmann, B. K. Meyer, F. Lohse, and J. M. Spaeth, Phys. Rev. Lett. **53**, 1187 (1984).

[25]M. Kaminska, M. Skowronskii, and W. Kuszko, Phys. Rev. Lett. **55**, 2204 (1985).

[26]E. R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982).

[27]E. J. Johnson, J. Kafalas, R. N. Davies, and W. A. Dyes, Appl. Phys. Lett. **40**, 913 (1982).

[28]B. K. Meyer, J. M. Spaeth, and M. Scheffler, Phys. Rev. Lett. **52**, 851 (1984).

[29]H. J. von Bardeleben and J. C. Bourgoin, J. Appl. Phys. **58**, 1041 (1985).

[30]N. K. Goswami, R. C. Newman, and J. E. Whitehouse, Solid State Commun. **40**, 473 (1981).

[31]R. B. Beall, R. C. Newman, J. E. Whitehouse, and J. Woodhead, J. Phys. C **17**, 2653 (1984).

[32]T. Ikoma, M. Taniguchi, and Y. Mochizuki, in *Proceedings of the 11th International Symposium on GaAs and Related Compounds,* edited by B. de Cremoux (Adam Hilger, Bristol, 1985), p. 65.

[33]A. M. Huber and G. Morillot, Revue Technique Thomson—CSF, 1985 (unpublished).

[34]J. B. Clegg, J. Appl. Phys. **53**, 5972 (1982).

[35]D. E. Holmes, R. T. Chen, K. R. Elliott, C. G. Kirkpatrick, and P. W. Yu, IEEE Trans. Electron Dev. **29**, 1045 (1982).

[36]K. Shikano, K. Kobayashi, and S. Miyazawa, Appl. Phys. Lett. **46**, 391 (1985).

[37]K. Kuramoto, M. Nakajima, T. Kikuta, F. Orito, H. Emori, and K. Ishida, Proceedings of the 4th International Conference on Secondary Ion Mass Spectroscopy, Osaka (unpublished).

[38]J. R. Oliver, R. P. Fairman, R. T. Chen, and P. W. Yu, Electron Lett. **13**, 839 (1981).

[39]A. T. Hunter, K. Kimura, J. P. Baukus, H. W. Winston, and O. J. Marsh, Appl. Phys. Lett. **44**, 74 (1984).

[40]T. Kobayashi and J. Osaka, J. Cryst. Growth **71**, 240 (1985).

[41]A. M. Huber, N. T. Linh, M. Valladon, J. L. Debaun, G. M. Martin, A. Mitonneau, and A. Mircea, J. Appl. Phys. **50**, 4022 (1979).

[42]D. Pons and J. C. Bourgoin, J. Phys. C **18**, 3839 (1985).

[43]F. Thompson, S. R. Morrison, and R. C. Newman, in *Radiation Damage and Defects in Semiconductors,* edited by J. E. Whitehouse (IOP, London, 1972), p. 371.

[44]H. J. von Bardeleben and D. Stievenard (unpublished).

[45]M. R. Brozel and R. C. Newman, J. Phys. C **11**, 35 (1978).

[46]D. Stievenard, X. Boddaert, and J. C. Bourgoin, Phys. Rev. B **34**, 4048 (1986).

[47]H. J. von Bardeleben, J. C. Bourgoin, and A. Miret, Phys. Rev. B **34**, 1360 (1986).

[48]G. M. Martin, *Proceedings of the Conference on Semi-Insulating III-V Materials,* edited by G. J. Rees (Shiva, Nantwich, England, 1980), p. 13.

[49]G. B. Bachelet and M. Scheffler, *Proceedings of the 17th International Conference on Semiconductors, San Francisco, 1984,* edited by J. D. Chandi and W. A. Harrison (Springer, New York, 1985), p. 755.

[50]M. Levinson, Phys. Rev. B **28**, 3660 (1983).

[51]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 2340 (1985).

[52]T. Taniguchi and T. Ikoma, J. Appl. Phys. **54**, 6448 (1983).

[53]N. Arnold, R. Schmittk and K. Heime, J. Phys. D **17**, 443 (1984).

[54]H. D. Palfrey, M. Brown, and A. F. W. Willoughby, J. Electron. Mater. **12**, 863 (1983).