Electronic and transformation properties of a metastable defect introduced in n-type GaAs by α-particle irradiation

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We report the electronic and transformation characteristics of an α-particle irradiation-induced defect in n-type GaAs with metastable properties, $E\alpha3$, as determined by deep-level transient spectroscopy. The $E\alpha3$, with an energy level at $E_c-0.37$ eV, captures electrons by multiphonon emission. It can be removed by hole injection and reintroduced during a first-order transformation under zero-bias annealing (activation energy $\Delta E=0.40$ eV), or during reverse-bias annealing ($\Delta E=0.53$ eV). It is suggested that $E\alpha3$ is related to a Si-impurity complex in n-type GaAs. Owing to its concentration and position in the band gap, $E\alpha3$ can significantly contribute to particle irradiation-induced carrier removal—due to its metastable properties the extent of the carrier removal may depend on bias and injection conditions.

I. INTRODUCTION

Metastable defects have been observed in as-grown GaAs,[1] as well as in hydrogen- (Ref. 2) and deuterium-passivated[3] epitaxially grown GaAs, by deep-level transient spectroscopy (DLTS).[4] Under certain experimental conditions, usually bias-on–bias-off annealing cycles, these defects are configurationally transformed to different energy states which can be detected by DLTS. A significant number of the metastable defects investigated in Si (Ref. 5) and InP (Ref. 6) were introduced by electron irradiation. It has recently been reported that electron irradiation also introduces metastable defects in GaAs;[7,8] hence it can reasonably be expected that irradiation with other particles would also introduce metastable defects in GaAs. Since a wide range of particle irradiation is encountered in radiation environments like space, and specific particle irradiation is frequently employed to controllably modify the properties of GaAs, an intimate knowledge of all particle induced defects is required. Although it has been well established that electron and heavier particle irradiation create several electron and hole defects in GaAs,[9] reports on irradiation-induced metastable defects in GaAs have only recently been forthcoming.[7,8,10]

In this paper we demonstrate that apart from electron-irradiation-induced defects and the lesser α-particle irradiation-induced defect $E\alpha8$,[10] a prominent defect in α-particle-irradiated GaAs, $E\alpha3$, is also metastable. As a result of its concentration, electronic, and metastable properties, $E\alpha3$ can significantly assist radiation-induced carrier removal and can consequently influence device operation. Furthermore, we found that bias-on–bias-off transformation cycles are not sufficient to transform $E\alpha3$, and that these cycles have to be supplemented by hole injection in order to transform this defect.

In Sec. II we briefly describe the experimental procedures involved. Section III describes the results obtained, and Sec. IV comprises a discussion, after which some conclusions are presented in Sec. V.

II. EXPERIMENTAL PROCEDURES

In our research we used Schottky-barrier diodes (SBD's) as the diode contact structure to the GaAs. Palladium SBD's on an n-type GaAs layer (doped to 1.1×10^{16} cm^{-3} with Si), grown by organometallic vapor-phase epitaxy (OMVPE) on a n^+-type GaAs substrate, were irradiated[11] with 5.4-MeV α particles at a fluence of 1×10^{11} cm^{-2}. DLTS using a lock-in amplifier-based system was used to study the defects. The bias and pulse sequence consisted of a reverse bias V_r on which pulses with amplitude V_p and frequency f were superimposed. The DLTS defect signature (energy level in the band gap, E_t, and apparent capture cross section σ_∞) were calculated from Arrhenius plots of $\ln(T^2/e)$ vs $1/T$, where e is the emission rate at the DLTS peak temperature T.

Hole injection was achieved by applying a forward current pulse at frequency f with quiescent current I_r and pulse height I_p by means of an HP3245A current source. A pulse was used instead of a constant current to minimize local heating effects in the sample that could lead to premature annealing of the defect under investigation.

III. RESULTS

Curve a in Fig. 1 is a typical DLTS spectrum of α-particle-irradiated n-GaAs, and depicts the presence of the radiation-induced defects $E\alpha1$–$E\alpha5$ and $E\alpha8$. The electronic properties of these defects have been reported previously,[11,12] and it was shown that $E\alpha1$, $E\alpha2$, and $E\alpha4$ have the same DLTS signatures as the well-known electron-irradiation-induced defects $E1$, $E2$, and $E3$,[9] respectively, which in turn are related to vacancy-interstitial pairs in the As sublattice.[9] In this study we focus on the properties of defect $E\alpha3$ that exhibits a metastable character. From DLTS Arrhenius plots for $E\alpha3$, constructed from spectra for which the maximum electric field during emission was 3.2×10^4 V cm^{-1}, we calculated $E_t=E_c-0.37$ eV and $\sigma_\infty=9\times10^{-14}$ cm^2. Due to the larger field-assisted emission[13] in the doped

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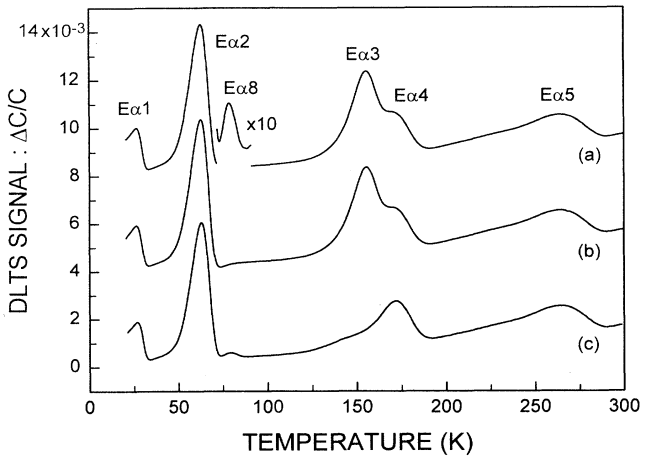

FIG. 1. DLTS spectra of α-particle-irradiated n-type GaAs ($f=1$ Hz, $V_r=2$ V, and $V_p=1.9$ V): (a) after reverse-bias (2-V) cooling; (b) after zero-bias cooling; (c) after applying a forward current density of 5.6 A cm^{-2} at 105 K for 10 s.

GaAs used in this study, this signature is slightly different from that determined for the same defect in low doped n-type GaAs.[11,12] Variable pulse-width measurements[4] (using $V_r=4$ V and $V_p=4.2$ V) revealed that the electron-capture cross section of $E\alpha3$ is temperature dependent and changes from 3.0×10^{-19} cm^2 at 150 K to 1.6×10^{-18} cm^2 at 193 K. Figure 2 shows that electron capture by $E\alpha3$ is thermally activated according to

$$\sigma(T)=\sigma_\infty \exp(-E_\sigma/kT)\ , \tag{1}$$

where k is Boltzmann's constant and E_σ is the electron-capture barrier. This temperature dependence of $\sigma(T)$ indicates that electron capture by $E\alpha3$ occurs by multiphonon emission.[13] From Fig. 2 we calculated $E_\sigma=(0.049\pm0.003)$ eV and $\sigma_\infty=(1.3\pm0.4)\times10^{-15}$ cm^2.

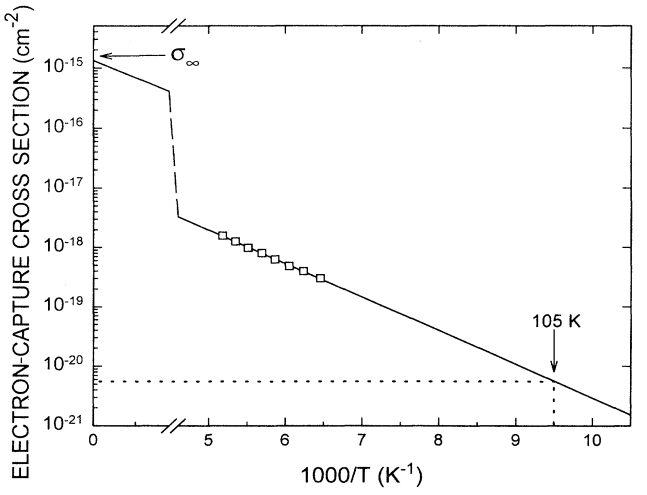

FIG. 2. Variation of $E\alpha3$ electron-capture cross-section as function of temperature. Measurement conditions: $V_r=4$ V and $V_p=4.2$ V.

The capture barrier E_σ of $E\alpha3$ is smaller than the 0.10 eV reported[13] for the $E3$ electron-radiation-induced defect which has the same DLTS signature as $E\alpha4$.[9,11] We attribute the lower value of σ_∞ calculated from Fig. 2, compared to that found from the DLTS Arrhenium plot for $E\alpha3$, to the higher maximum electric field (10^5 V cm^{-1}) present during the variable-temperature capture cross-section measurements.

In order to study metastable defect behavior, we employed DLTS in conjunction with bias-on–bias-off cooling cycles[14] and minority-carrier injection cycles: after cooling from 300 to 20 K, at a reverse bias of 2 V, a DLTS spectrum was recorded from 20 to 300 K (Fig. 1, curve *a*). Subsequently a spectrum was recorded from 20 to 300 K after cooling at zero bias (Fig. 1, curve *b*). In addition, spectra from 20 to 300 K were recorded (Fig. 1, curve *c*) after first applying a strong forward current density of 5.6 A cm^{-2} at 105 K and subsequently cooling to 20 K. These scan-up spectra indicate that the $E\alpha3$ concentration is strongly influenced by the previous scan-down bias as well as current flow at low temperatures. In contrast, the peak heights of the other defects are independent of these conditions. Specifically, curves *a* and *b* reveal that $E\alpha3$ is present after reverse-bias as well as zero-bias cooldown cycles, but that it is absent after applying a forward current density of 5.6 A cm^{-1} at 105 K (curve *c*). These bias- and current-induced transformations of $E\alpha3$ are charge state controlled and relate to a reversible disappearance and reappearance of energy levels in the band gap, thereby exhibiting charge-state-controlled metastability, as defined in Ref. 14. We assume this metastability is caused by transformation of $E\alpha3$ to and from states denoted by $E\alpha3^*$ for purposes of discussion.

IV. DISCUSSION

We consider the transformation of $E\alpha3$. The results obtained after isochronally annealing $E\alpha3$ during the flow of current are illustrated in Fig. 3. For a given

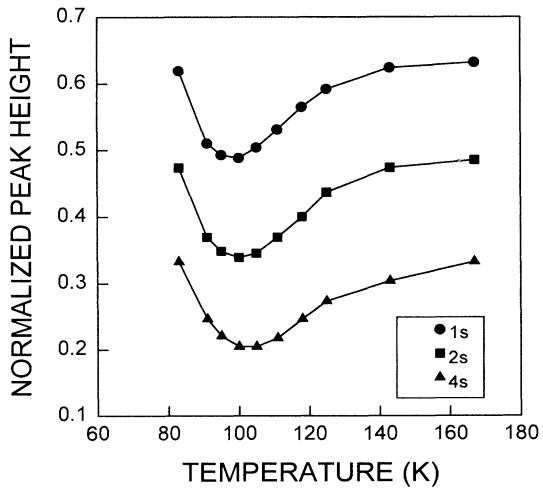

FIG. 3. Change in $E\alpha3$ peak height as a function of temperature when a forward current is applied at a current density of 1.4 A cm^{-2} for times 1, 2, and 4 s.

current density each isochronal curve shows an increasing transformation rate $E\alpha 3 \rightarrow E\alpha 3^*$ as temperature increases from 80 to 100 K. There is a clear optimum temperature, around 105 K, at which the $E\alpha 3 \rightarrow E\alpha 3^*$ transformation is most successful for a given time. As the temperature increases further, the transformation rate slows down again until it is about the same at 167 K as at 83 K.

This $E\alpha 3$ removal can be explained qualitatively in terms of hole injection: The minority-carrier injection ratio into the depletion region of a SBD is small but finite, and it increases with increasing forward current density.[15] Thus, when applying a large enough forward bias, it is possible to introduce holes into the depletion layer of a SBD. Minority-carrier injection in SBD's was used to detect hole traps in n-type GaAs (Ref. 16) by DLTS. In the present study, holes injected into the depletion region at 105 K during forward pulsing are trapped by $E\alpha 3$ or another level belonging to the same defect. At 105 K the $E\alpha 3$ electron-capture cross section is estimated from Fig. 2 as $<5\times10^{-21}$ cm^2, signifying that its electron-capture rate at 105 K is less than 2×10^2 s^{-1}. At these temperatures it seems that the ratio of hole to electron capture increases. We propose that, after hole capture, $E\alpha 3$ transforms to $E\alpha 3^*$ with an energy level different to $E\alpha 3$—illustrated by the decrease in the $E\alpha 3$ DLTS signal.

Thermally stimulated capacitance (TSCAP) curves—where the capacitance C is recorded as a function of increasing temperature T—are presented in Fig. 4. They show that the positive charge in the depletion layer is higher after the forward current pulse sequence at 105 K than after cooling to 105 K at zero bias. This indicates

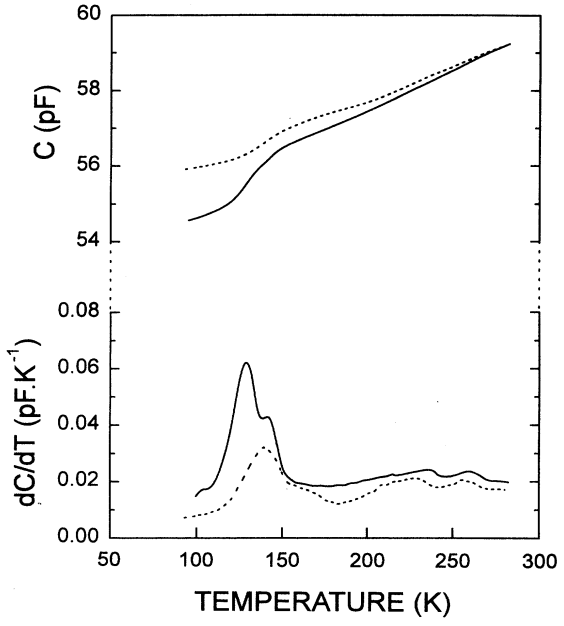

FIG. 4. TSCAP (C vs T) and dC/dT vs T of OMVPE-grown 1.2×10^{16}-cm^{-3} doped n-type GaAs, irradiated with α particles. The capacitance was recorded at a scan rate of 3 K min^{-1}. ——, zero-bias cooldown, then scan up with $V_r=4$ V. — — —, zero-bias cooldown followed by the application of an injection pulse, then scan up with $V_r=4$ V.

that either electron emission to the conduction or valence band (hole capture) takes place during the current pulse cycle at 105 K. Furthermore, during the TSCAP heating cycle, after the transformation sequence at 105 K, a decrease in $\Delta C/\Delta T$ occurs in the 107–200-K temperature range—the same range in which the $E\alpha 3^* \rightarrow E\alpha 3$ transformation occurs. A decrease in $\Delta C/\Delta T$ with increasing T can be the result of either electron capture from the conduction band or hole emission to the valence band. However, since all TSCAP curves were recorded under reverse bias, almost no free electrons are available for capture. This signifies that the decrease in $\Delta C/\Delta T$ between 170 and 200 K is caused by hole emission. Therefore, our TSCAP results imply that the $E\alpha 3$ transformations are related to hole capture and emission.

Semitransparent Au SBD's were used to qualitatively investigate the response of the $E\alpha 3$ defect to optical stimuli. The sample was illuminated through the SBD with a laser diode, energy 1.45 eV. The sample was cooled from 300 to 20 K under a reverse bias of 2 V, and a DLTS spectrum was recorded from 20 to 300 K with the light source flashing in phase with the DLTS voltage pulse V_p. The resultant spectrum showed the same main feature as Fig. 1, curve c, namely the absence of the $E\alpha 3$ peak. Holes are available via the electron-hole pairs generated by the optical pulse and are subsequently captured by $E\alpha 3$, which then transforms to $E\alpha 3^*$, disappearing from the DLTS spectrum.

The free-carrier density in the Pd-SBD sample was also determined at 140 K by capacitance-voltage (C-V) measurements before and after the current pulse sequence. From this it was found that there was an increase in free-carrier density after the current pulse sequence up to 0.8 μm from the interface. The change is free-carrier density, i.e., an increase of 2×10^{14} cm^{-3}, is very similar to the concentration of the $E\alpha 3$ defect, namely 2.4×10^{14} cm^{-3}. This further strengthens the case for hole capture by $E\alpha 3$, since the number of free carriers gained after the defect was transformed away, is the same as the number of $E\alpha 3$ defects that compensated these carriers when it was present.

As mentioned, the isochronal annealing characteristics of the transformation $E\alpha 3 \rightarrow E\alpha 3^*$ are illustrated in Fig. 3. In the temperature range 80–100 K, plots of $N_T/N(t)$ vs time (t) at different temperatures (N_T is the total $E\alpha 3$ concentration) were straight lines, indicating that the transformation obeys second-order kinetics described by

$$1/N(t)=1/N_T+\nu(T)t \ . \tag{2}$$

Here $N(t)$ is the occupied $E\alpha 3$ concentration, and $\nu(T)$ is the introduction rate constant at temperature T. From Arrhenius plots of $\ln[\nu(T)]$ vs $1/T$, the temperature dependency of the removal rates over the specified temperature range were found to obey the relation

$$\nu(T)=\nu_0\exp(-\Delta E/kT) \ , \tag{3}$$

where ΔE is the energy barrier for the $E\alpha 3$ removal. From the ν_0 and ΔE values so calculated, the $E\alpha 3 \rightarrow E\alpha 3^*$ transformation can be summarized as

$$E\alpha 3 \rightarrow E\alpha 3^*: \nu(T)=2.14\times10^4\exp(0.041/kT) \ .$$

The rate constant (2.14×10^4 s^{-1}) is much smaller than that expected for carrier capture,[17] namely $\nu_0\sim10^7$ s^{-1}. Since a capture process is the rate-limiting factor, the expression $\sigma_p p \nu_{th}$ dominates the rate constant, where σ_p is the capture cross section, p the minority-carrier concentration, and ν_{th} the hole thermal velocity. The discrepancy can then be explained by the very small minority-carrier concentration p compared to the majority-carrier concentration in the n-type GaAs.

Isochronal annealing indicated that $E\alpha3$ is reintroduced at temperatures above 160 K under zero bias, or above 190 K under reverse bias, and from isothermal annealing in these temperature ranges we obtained the $E\alpha3^*\rightarrow E\alpha3$ transformation kinetics. Plots of $\ln[\{N_T-N(t)\}/N_T]$ vs time (t) at different temperatures were straight lines, indicating that the transformation obeys first-order kinetics described by

$$N(t)=N_T[1-\exp\{-\nu(T)t\}] . \quad (4)$$

This equation has also been found to describe the introduction rates of hydrogen-related metastable defects in OMVPE-grown GaAs,[1] From Arrhenius plots of $\ln[\nu(T)]$ vs $1/T$ the temperature dependencies of the zero- and reverse-bias introduction rates were both found to obey relation (3), where ΔE is the energy barrier for the $E\alpha3$ formation. From the ν_0 and ΔE values thus calculated, the $E\alpha3^*\rightarrow E\alpha3$ transformations can be summarized as

$$E\alpha3^*\rightarrow E\alpha3:\ \nu=(6\pm2)\times10^8\exp[-(0.40\pm0.01)/kT]$$

(zero bias)

$$\nu=(6\pm2)\times10^9\exp[-(0.53\pm0.01)/kT]$$

(2-V reverse bias) .

The rate constants above are smaller than expected for carrier emission, but slightly larger than expected for carrier capture.[17] However, since the $E\alpha3\rightarrow E\alpha3^*$ process resulted from hole capture, it is reasonable to expect that the opposite process ($E\alpha3^*\rightarrow E\alpha3$) stems from hole emission, as suggested by our TSCAP data. The activation barrier for the transformation under zero bias is $\Delta E=(0.40\pm0.01)$ eV, which is lower than the $\Delta E=(0.53\pm0.01)$ eV of the process under reverse bias. The lower ΔE measured under zero bias supports the model of hole release, i.e., electron capture, since at zero type bias there is an abundance of electrons.

This phenomenon of accelerated reintroduction of a defect in the presence of electrons shows a qualitative resemblance to the so-called Auger deexcitation of the optically activated metastable state of the $EL2$ defect in n-type GaAs.[18] Here it was found that the transition from the metastable state to the stable state was much enhanced in the presence of free electrons, although in the case of $E\alpha3$ it would involve an electron-hole interaction.

A configuration-coordinate (C-C) diagram of the $E\alpha3$ defect, encompassing the results presented in this paper, is suggested in Fig. 5. The positions of the $E\alpha3$ and the $E\alpha3^*$ levels relative to conduction and valence bands are shown. The energy barrier for the transition from $E\alpha3$ to $E\alpha3^*$ is 0.04 eV and that for the reverse transition 0.40 eV. A large degree of lattice relaxation on the part of $E\alpha3^*$ is implied by the observed results.

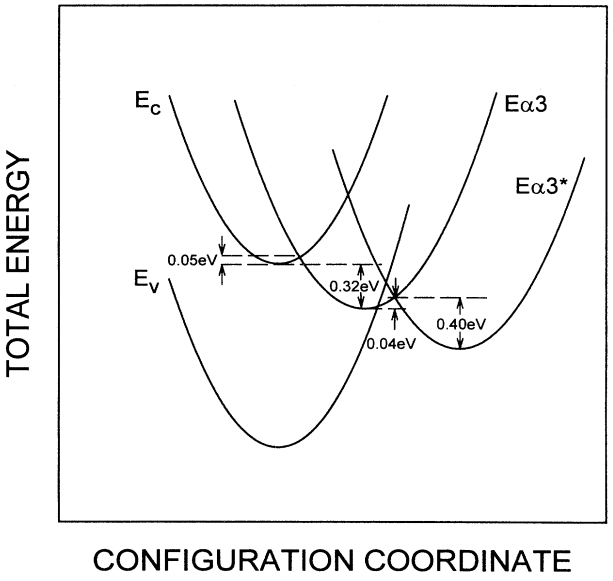

FIG. 5. Configuration-coordinate (C-C) diagram for the $E\alpha3$ defect.

Although DLTS does not provide information about the physical nature of defects, we nevertheless have two clues as to what $E\alpha3$ may consist of. First, $E\alpha3$ is present in higher concentrations in the GaAs doped to 10^{16} cm^{-3} with Si used here than in the undoped GaAs previously investigated.[18] Secondly, $E\alpha3$ has up to now been reported[18] only in α-particle-irradiated GaAs but

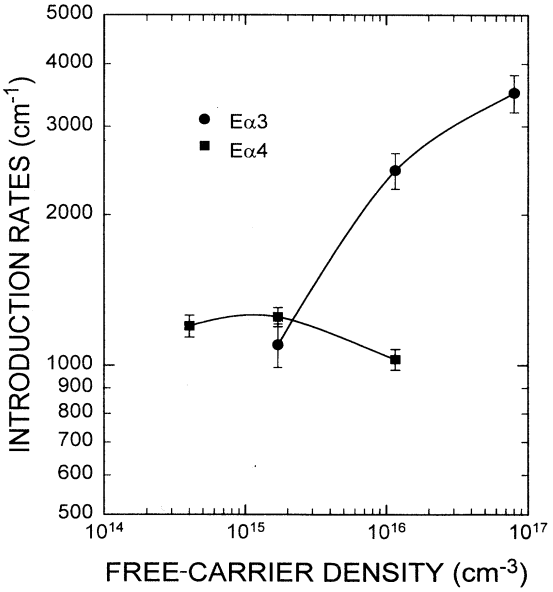

FIG. 6. Change in $E\alpha3$ and $E\alpha4$ introduction rates as a function of free-carrier concentration for Si-doped n-type GaAs.

not in electron-irradiated GaAs with the same dopant and carrier concentrations. Since an α particle can transfer much more energy to the lattice than an electron with the same kinetic energy, it is capable of forming disordered regions with a larger extent than the vacancy-interstitial pairs typically observed after electron irradiation. In Fig. 6 the relationship between $E\alpha3$ and $E\alpha4$ introduction rates and free-carrier density for Si-doped material is presented. It is clear that, for the same fluence of α particles, there is a higher introduction rate of $E\alpha3$ in material doped to a higher level, illustrating a relationship between $E\alpha3$ and Si concentrations. Introduction rates of the other defects $E\alpha1$, $E\alpha2$,$E\alpha4$, $E\alpha5$, and $E\alpha8$ stay constant with increasing free-carrier density, as typically illustrated by $E\alpha4$. The apparent decrease in the introduction rate of $E\alpha4$ for 10^{16}-cm^{-3} free-carrier density material is due to the high electric-field dependence of this defect,[19] resulting in a smaller measured peak height. It has also been found that in material doped to the same levels as in Fig. 6 with different doping materials, no presence of $E\alpha3$ could be found after α-particle irradiation. In view of these facts we suggest that $E\alpha3$ may consist of a Si atom linked to a more complex lattice defect than an As vacancy or interstitial.

V. CONCLUSIONS

In conclusion, the results presented here indicate that the α-particle irradiation-induced defect in n-type GaAs, $E\alpha3$, exhibits charge-state-controlled metastability and can be reversibly transformed using conventional bias-on–bias-off temperature cycles in conjunction with forward current hole injection pulses at specific temperatures. $E\alpha3$ has an energy level 0.37 eV below the conduction band and thermally activated capture cross section [capture barrier $E_\sigma = (0.049 \pm 0.003)$ eV], indicating that electron capture occurs by multiphonon emission. From its electronic properties and concentration it is clear that $E\alpha3$ can significantly assist radiation-induced carrier removal. Under hole injection—obtained using SBD's—$E\alpha3$ transforms to $E\alpha3^*$ in the temperature range 80 to 160 K, while under zero as well as reverse bias $E\alpha3^*$ transforms back to $E\alpha3$ by hole emission in the temperature range 160–190 K. This metastable behavior of $E\alpha3$ may either result in unstable, or if properly taken advantage of, tunable device characteristics. The energy levels of $E\alpha3^*$ could not be detected by DLTS measurements, since its large lattice relaxation moves it to a position where the energy transition to the conduction band is too large for DLTS to detect it, because the DLTS peak temperature is around 250 K, which is much higher than the $E\alpha3^* \rightarrow E\alpha3$ transformation temperature interval of 160–190 K. This is illustrated in the C-C diagram (Fig. 5).

It has been shown by Goodman, Auret, and Myburg[20] that is possible to remove the $E\alpha3$ defect permanently by means of thermal annealing at a temperature of 513 K in a high-purity argon atmosphere for 2 h.

The physical natural of these defects can presently at best be speculated about, but the existing evidence suggests that the presence of $E\alpha3$ depends on the dopant used and on the GaAs free-carrier concentration and that is requires a larger energy of formation than primary electron-irradiation-induced defects.

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