Evidence for EL6 ($E_c - 0.35$ eV) acting as a dominant recombination center in n-type horizontal Bridgman GaAs

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Horizontal Bridgman grown n-type GaAs is shown to contain two important electron traps EL6 (0.35 eV) and EL2 (0.80 eV) in the 10^{15} cm^{-3} concentration range. A heat treatment at 800 °C for 1 h results in the reduction of EL6 to about 10^{13} cm^{-3} to a depth of at least 10 μm and an increase in EL2 by an amount about equal to the reduction of EL6. Measurement of the minority-carrier (hole) diffusion lengths in this depth range by an electron beam induced current (EBIC) technique shows an inverse correlation with the concentration of the EL6 trap. The results may be explained if EL6 is assumed to be V_{Ga}-V_{As}, EL2 to be As_{Ga}-V_{As}, and the interaction between the two traps to involve As_i.

INTRODUCTION

Non-phonon-assisted recombination processes set an upper limit to the excess minority-carrier lifetime in a direct band-gap material such as GaAs. However, because of the high recombination center content in GaAs (especially bulk GaAs) the upper limiting lifetimes are hardly ever approached.[1] The recombination centers may be associated with native point defect complexes, the presence of trace heavy metals (particularly the transition metals) or exceptionally the presence of high densities of gross defects such as dislocations.

Studies by Partin *et al.*[1–6] suggest that the A level at $E_v + 0.40$ eV is the minority-carrier (hole) lifetime controller in liquid phase epitaxial (LPE) GaAs. In vapor phase epitaxial (VPE) growth the process is normally arsenic rich and Miller *et al.*[7] suggest that gallium vacancy complexes or arsenic interstitial complexes are playing a role in determining carrier lifetime. The EL2 level has been proposed as the dominant lifetime controller for certain specimens, but the evidence for this is not strong. Mitonneau *et al.*[8] conclude that a hole trap HL10 at $E_v + 0.83$ eV is an important recombination level. In a study of capture cross sections for VPE GaAs Partin *et al.*[2–6] concluded that an electron trap at $E_c - 0.39$ eV (after correction to 300 K for the capture cross-section activation energy of 0.09 eV) was the important hole recombination level. It was also found that Ni is a lifetime killer in VPE GaAs layers through its effect on the $E_c - 0.39$ eV level. Recently a study of minority-carrier hole diffusion lengths in as-grown and Ni- or Cu-diffused bulk n-GaAs by Liang *et al.*[9] suggests that EL5 at $E_c - 0.40$ eV (measured at about 200 K) is the dominant recombination center.

For the horizontal Bridgman (HB) GaAs material of the present study a level EL6 at $E_c - 0.35$ eV is found to be the important recombination center. This is inferred from correlation of electron beam induced current (EBIC) measurements with changes in the deep level transient spectroscopy (DLTS) spectra after a proximity anneal at 800 °C.

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EXPERIMENT

For our study the n-type HB-GaAs material had carrier concentration, electron mobility, and etch pit density of 3×10^{16} cm^{-3}, 4060 cm^2/V s, and 9000 cm^{-2}, respectively. The thermal annealing experiment was carried out with two specimens face to face in a cleaned and etched evacuated quartz ampoule (type GE 214) at a temperature of 800 °C with some GaAs chips added to the ampoule. After one hour the ampoule was withdrawn from the furnace and quenched in cold water. For probing the variation in the concentration of deep levels to about 10 μm below the surface, angle etching ($\theta \sim 0.04°$) was performed on the annealed and control samples by slowly immersing the specimen in an etching solution ($5H_2SO_4$:$1H_2O_2$:$1H_2O$). A non-etched region was retained by black-wax masking and the height differences between the original and etched levels determined with a step profiler. A set of semitransparent Al (150 Å) Schottky-barrier diodes was formed on the etched slope and on the unetched region by electron beam evaporation through a metal mask. DLTS studies of the electron traps as a function of depth were then made with an MRI electronics system operating at 1 MHz. This was followed by EBIC measurements made in the electron bombardment mode[10] on each diode. In this way the relationship between DLTS spectra and diffusion lengths at various depths was determined. The DLTS measurements were made with a voltage swing from -2 to 0 V and a rate window of 116.3 s^{-1}. A filling pulse duration of 5 ms was used for the control sample to discriminate a trap EC4 on the shoulder of the large peak of trap EC5 (see Fig. 1) and a pulse duration of 0.1 ms was used for the annealed specimens. The average trap concentrations in the top layer of each sample were calculated taking into account the non-ionized region effect in the depletion layer (the so-called λ effect) and using the λ correction given by Zohta and Watanabe[11] in their Eq. (8). The net carrier concentration values, $N_D - N_A$, were obtained by C-V measurements.

In the EBIC measurements the semitransparent diode Schottky barriers were penetrated by an electron beam whose energy was varied from 5 to 39 keV. This EBIC technique allows measurement of short diffusion lengths and is insensitive to surface recombination effects.[10] The electron

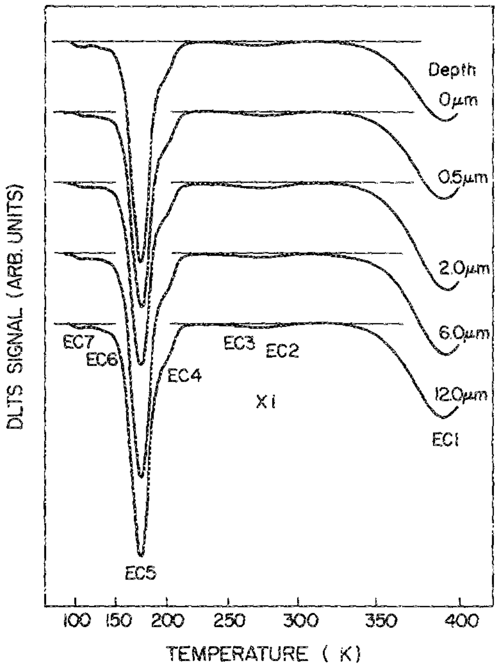

FIG. 1. DLTS spectra of electron traps in as-received horizontal Bridgman grown n-GaAs ($n = 3\times 10^{16}$ cm^{-3}) at different depths exposed by angle etching. DLTS conditions: bias -2 V, filling pulse amplitude 2 V, filling pulse duration 5 ms, $t_1 = 2$ ms, $t_2 = 11.5t_1$ for a rate window 116.3 s^{-1}.

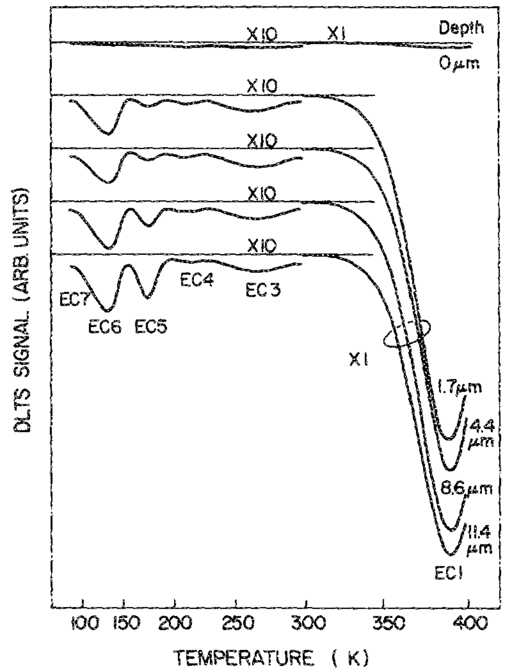

FIG. 2. DLTS spectra of electron traps for sample next to specimen of Fig. 1 after annealing at 800 °C for 1 h. DLTS filling pulse duration was 0.1 ms, conditions otherwise as in Fig. 1. Note the dramatic decrease of EC5 and associated increase of EC1.

beam induced current I_i depends on the diffusion length L_p and on the maximum penetration range R of the primary electrons, which is a function of electron beam energy E_0. Experimentally the EBIC collection efficiency defined by $e = I_i/qG$ (where q is the electron charge and G the total generation rate per unit time) can be determined by $e = E_i I_i / E_0 I_0 [1 - \eta(E_0)]$, where E_i is the average energy required to generate one electron-hole pair (about 4.68 eV for GaAs),[10] I_0 is the beam current measured by using a Faraday cup and is typically in the range 0.2–1.4$\times 10^{-9}$ A, and $\eta(E_0)$ is the fraction of the backscattered primary electrons. The collection efficiency is calculated from $e = (I_d + I_b)/qG$, where I_d and I_b respectively represent the collected current due to carriers generated in the depletion and in the bulk regions. Therefore, the e value can be determined from the maximum penetration range R, depletion region width w, the thickness of the metal layer, d, and the minority-carrier diffusion length L_p. Since d and L_p dominate the current collection efficiency at low and high beam energies, respectively, fitting the theory and experiment at high energy can be used to determine the L_p value.

RESULTS

The variation in DLTS spectra at different depths from the surface for control and annealed samples is shown in Figs. 1 and 2. From Fig. 1 seven electron traps (labeled EC1–7 in this work) exist in the as-grown HB GaAs. EC1 and EC5 are the main electron traps and these are the EL2 and El6 defects commonly referred to in the literature.[12] Almost identical DLTS spectra are observed in Fig. 1 for the control specimen at different depths indicating that the traps have uniform distribution in the bulk in the range studied, 0–12 μm. From Fig. 2 drastic changes in DLTS spectra are seen to have occurred after the 800 °C anneal. The concentration of trap EC5 (EL6) decreases by more than 100 times and the concentration of trap EC1 (EL2) increases by about two and one-half times. Near the surface a gradual decrease in concentration of EC5 and EC6 can be observed and at the top surface (within a depletion depth of about 0.2 μm) almost all the traps except EC1 disappear, i.e., fall below a concentration of 10^{13} cm^{-3}. The trap energies, capture cross-section values, and changes in density with depth before and after anneal are listed in Table I.

The EBIC collection efficiency versus beam energy curves for the control and annealed samples are shown in Fig. 3. Application of the theory for this EBIC technique results in a value of 0.19 μm for the hole diffusion length of the control specimen.

The larger current collections for the diodes on the annealed sample show that the anneal has produced a considerable increase in L_p even at a depth of 11.4 μm. L_p increases as the surface is approached and is estimated to become at least 1.4 μm. Exact calculation is not trivial because of the dependence of L_p on depth and the fact that at energies between 25 and 40 keV the penetration depth of the electron beam is several microns.

DISCUSSION

The large increase in L_p means the concentration of the dominant recombination center (lifetime killer) should decrease by two orders of magnitude. This matches the decrease in concentration of trap EC5 (EL6) in Fig. 2. Note that EC1 (EL2) is not a candidate for the dominant recombination action since it increases rather than decreases with the heat treatment. Since we have n-type material the expression for hole lifetime may be simplified to

TABLE I. Properties of electron traps in HB grown n-type GaAs.

Defect	Commonly referenced defect labels[a]	Energy[b] $E_C - E_t$ (eV)	Capture cross section $\sigma_{n\infty}$ (cm^2)	Concentration[c] N_T (cm^{-3}) Before anneal at all depths[d]	After anneal (800 °C, 1 h) At top surface[e]	At different depths[f]	DLTS peak temperature[g] (K)
EC1	EL2	0.80	6.6×10^{-14}	$\sim 4.7\times 10^{15}$	5.1×10^{14}	$\sim 1.2\times 10^{16}$	392
EC2	EL3	0.60	6.4×10^{-13}	$\sim 1.9\times 10^{14}$	$<1.0\times 10^{13}$	$<3.4\times 10^{13}$	275
EC3	Ni-related	0.48	1.35×10^{-14}	Unknown	$<1.6\times 10^{13}$	$\sim 4.6\times 10^{13}$	261
EC4	EL5	0.37	2.0×10^{-14}	Unknown	$<8.1\times 10^{12}$	$\sim 1.8\times 10^{13}$	210
EC5	EL6	0.35	1.0×10^{-13}	$\sim 6.2\times 10^{15}$	$<3.6\times 10^{12}$	$(2.2–9.6)\times 10^{13}$	179
EC6	EL9 or EL14	0.215	2.3×10^{-15}	Unknown	$<3.2\times 10^{12}$	$(5.9–12)\times 10^{13}$	137
EC7	EL10 or EB8	0.18	1.3×10^{-14}	$\sim 9.2\times 10^{13}$	$<2.4\times 10^{12}$	Unknown	109

[a] Reference 12.
[b] Trap energy is not corrected for the activation energy of capture cross section.
[c] Average concentration in top layer of sample after λ effect correction.
[d] Concentrations at various depths from 0 to 12 μm were nearly the same.
[e] Diode at top surface of annealed sample.
[f] Concentrations at various depths from 1.7 to 11.4 μm tended to be unchanged except for EC5 and EC6.
[g] Rate window 116.3 s^{-1} with $t_1 = 2$ ms and $t_1/t_2 = 11.5$.

$$\tau_p = L_p^2/D_p = (v_p \sigma_p N_T)^{-1}. \qquad (1)$$

Hence if L_p is taken as the measured value 0.19 μm and the EC5 concentration is 6.2×10^{15} cm^{-3} for the control specimen (Table I), the hole capture cross section is calculated from L_p^2/D_p to be about 2.5×10^{-13} cm^2 where D_p is taken to be 9 cm^2/s. This value may then be used to estimate the expected diffusion length for an annealed specimen. At a depth of 10 μm the concentration of EC5 is about 7.2×10^{13} cm^{-3} and from Eq. (1) the hole diffusion length expected is 1.8 μm. However, the observed value estimated from the EBIC measurements of Fig. 3 is about 0.7 μm. The discrepancy may be due to the annealing process having reduced

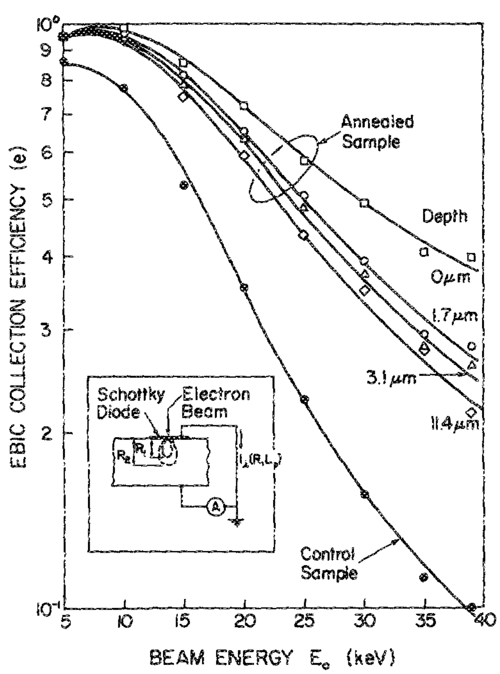

FIG. 3. EBIC collection efficiency as a function of electron beam energy E_0 for Al (150 Å) GaAs Schottky-barrier diodes on different depths from the original surface of annealed and control specimens. The annealed specimens have increased hole diffusion lengths.

EC5 (EL6) to a level that causes the remaining recombination center EC1 (EL2) to become important. For simplicity assume EC1 to be entirely determining the L_p value of 0.7 μm then from L_p^2/D_p for $N_T = 1.2\times 10^{16}$ cm^{-3} the value obtained for σ_p is about 1×10^{-14} cm^2. The hole capture cross section (σ_p, 300 K) of the EL2 level has been shown by Prinz and Rechkunov[13] to vary in the range 10^{-18} cm^2–10^{-13} cm^2 as the electric field is increased from a low value to 10^4 V cm^{-1} as discussed in the review by Martin and Makram-Ebeid.[14]

The trap EL6 (EC5) [$\Delta E = 0.33 \pm 0.02$ eV, $\sigma_n = (1–1.5)\times 10^{-13}$ cm^2] often has been reported in n-type bulk HB GaAs with a concentration of 10^{14}–10^{16} cm^{-3} as one of two important electron traps (the other one being EL2).[15–17] It has been reported to be reduced in concentration after furnace (800 °C) or infrared rapid thermal (900 °C) annealing.[17,18] But some studies[9,15,19,20] on n-type liquid encapsulated Czochralski (LEC) GaAs have shown EL5 (EC4) [$\Delta E = 0.40 \pm 0.02$ eV, $\sigma_n = (1-2)\times 10^{-13}$ cm^2, $N_T = 10^{14}$–10^{16} cm^{-3}] to be an important trap that also can be annealed out by heat treatment (850 °C).[16] A deep level optical spectroscopy (DLOS) study[16] of the main electron traps in bulk GaAs showed the largest Franck–Condon shift value of ~0.6 eV for trap EL6. The traps EL5 and EL6 are also seen in VPE grown GaAs layers. Because HB, LEC, and VPE GaAs are grown in As-rich conditions, these two traps can be reasonably associated with a point defect or defect impurity complexes containing Ga vacancies. The possible candidate for these complexes might be As_{Ga}-V_{Ga}, Si_{Ga}-V_{Ga}, Te_{As}-V_{Ga} and even V_{Ga}-V_{As}. These tentative assignments are compatible with the conclusion based on positron lifetime measurements on Zn-doped, Si-doped, and undoped GaAs.[21] The conclusions were that (i) for impurity concentrations larger than 4.5×10^{17} cm^{-3} only monovacancy complexes such as Zn_{Ga}-V_{As}, Si_{Ga}-V_{Ga}, or As_{As}-V_{Ga} were observed, corresponding to a positron lifetime of 265 ps, (ii) for impurity concentrations less than 1×10^{17} cm^{-3} divacancies, probably V_{Ga}-V_{As}, dominate corresponding to a positron lifetime of 295 ps. Therefore for lightly n-type doped GaAs we tentatively assign the defect complex V_{Ga}-V_{As} to the trap EL6. During long-time anneal we suggest the defect complex V_{Ga}-V_{As} tends to destruct by the formation of stable complexes with other defects or impurities. For example, the antisite defect complex As_{Ga}-V_{Ga} assigned[22] to trap EL2 might be created by reaction of V_{Ga}-V_{As} with interstitial arsenic As_i expected to be present under arsenic-rich growth conditions. This could explain the annealing out of EL6 occurring with the enhancement of EL2 by a factor of about 2.5 seen between Figs. 1 and 2. In addition a copper related complex Cu_{Ga}-V_{As} might be created by reaction of the complex V_{Ga}-V_{As} with Cu_i (the development of a small amount of copper contamination from the sample surface or quartz tube during heat treatment has been seen by photoluminescence studies).[23] Another possibility is reaction of V_{Ga}-V_{As} with As_i, resulting in V_{Ga}-As_{As} (i.e., V_{Ga}). These actions might explain the decrease in concentration of the EC5 (EL6) trap (considered to be V_{Ga}-V_{As}) as the surface is approached as due to the formation of Cu_{Ga}-V_{As} or V_{Ga}.

Figure 2 shows that EL2(EC1) becomes low in concentration very close to the surface after the anneal and this is in agreement with other studies of 800–850 °C heat treatments.[17–19,24,25] This is generally attributed to the loss of arsenic leading to the destruction of the As_{Ga}-V_{As} complex. However, the results of Fig. 2 show that the effect is very surface localized and does not extend as deep as 1.7 μm under the condition of our heat treatment.

In summary, we provide direct experimental evidence for EL6 acting as a dominant recombination center in n-type HB GaAs.

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