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10-1-1986

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Repository Citation

Look, D. C., Yu, P. W., Theis, W. M., Ford, W., Mathur, G., Sizelove, J. R., Lee, D. H., & Li, S. S. (1986). Semiconducting/Semi-insulating Reversibility in Bulk GaAs. *Applied Physics Letters*, 49 (17), 1083-1085. <https://corescholar.libraries.wright.edu/physics/32>

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Semiconducting/semi-insulating reversibility in bulk GaAs

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(Received 21 July 1986; accepted for publication 2 September 1986)

Bulk, liquid-encapsulated Czochralski GaAs may be reversibly changed from semiconducting ($\rho \sim 1 \Omega \text{ cm}$) to semi-insulating ($\rho \sim 10^7 \Omega \text{ cm}$) by slow or fast cooling, respectively, following a 5 h, 950 °C soak in an evacuated quartz ampoule. This effect has been studied by temperature-dependent Hall-effect, photoluminescence, infrared absorption, mass spectroscopy, and deep level transient spectroscopy measurements. Except for boron, the samples are very pure, with carbon and silicon concentrations less than $3 \times 10^{14} \text{ cm}^{-3}$. Donor and acceptor concentrations, on the other hand, are in the mid 10^{15} cm^{-3} range, which means that the compensation is primarily determined by native defects, not impurities. A tentative model includes a donor at $E_C - 0.13 \text{ eV}$, attributed to $V_{\text{As}} - \text{As}_{\text{Ga}}$, and an acceptor at $E_V + 0.07 \text{ eV}$, attributed to $V_{\text{Ga}} - \text{Ga}_{\text{As}}$.

Bulk, undoped, semi-insulating (SI) GaAs is generally considered to be of high resistivity because of a balance between a shallow donor, Si (or S), a shallow acceptor, C, and a deep donor, EL2, with relative magnitudes as follows: $[C] > [Si]$ and $[EL2] > [C] - [Si]$. However, it is possible with present low-pressure liquid-encapsulated Czochralski (LPLEC) and high-pressure liquid-encapsulated Czochralski (HPLEC) technology to grow crystals with $[C]$ and $[Si] < 5 \times 10^{14} \text{ cm}^{-3}$. With such materials, the compensation is almost entirely due to native defects. We will show that it is possible to make LPLEC crystals *uniformly* conducting or semi-insulating by variations of a simple heat treatment which changes the relative concentrations of donor and acceptor defects. As reported earlier,¹ the process leads to improved uniformity of direct-implant metal-semiconductor field-effect transistors.

The crystals were grown under near-stoichiometric conditions, in PbN crucibles, with 2 atm of N_2 gas. The ingots were 2½–3 in. in diameter, and 2–5 in. long. As grown, the boules were, in general, not semi-insulating and not uniform from seed to tail. However, after a 5 h, 950 °C soak in an evacuated quartz ampoule, and subsequent quench by rapidly removing the ampoule from the furnace, the ingots were both uniform and semi-insulating. These phenomena are illustrated in Table I for three representative boules. It is also seen that the mobilities can increase dramatically due to the better homogeneity.

Table II illustrates the reversibility of the conducting and semi-insulating states for ingot No. 3. Here “950 °C-Q” means the sample was quenched, as described above, whereas “950 °C-A” means the sample was “annealed” after the 950 °C soak, i.e., the furnace was simply turned off. It is clear from Table II that the electrical properties can be cycled back and forth between the two states. A similar phenom-

non was observed by Woodall and Woods,² although over a much reduced resistance range.

The impurity concentrations were checked by local vibrational mode (LVM) absorption spectroscopy, secondary-ion mass spectroscopy (SIMS), and spark source mass spectroscopy (SSMS). For sample 950 °C-A, the results were $[B] \approx 8 \times 10^{16} \text{ cm}^{-3}$, $[C] \approx 3 \times 10^{14} \text{ cm}^{-3}$, $[Si] \leq 2 \times 10^{14} \text{ cm}^{-3}$ with all other *individual* impurity concentrations $\leq 1 \times 10^{15} \text{ cm}^{-3}$ and with *total* impurity donor and acceptor concentrations each $\leq 2 \times 10^{15} \text{ cm}^{-3}$. (Note that no B_{As} was detected by LVM absorption and B_{Ga} is not electrically active.) The EL2 concentration was measured by deep level transient spectroscopy (DLTS) and absorption, and was nearly identical at $1.0 \times 10^{16} \text{ cm}^{-3}$ in both the quenched and annealed crystals. In the as-grown sample, $[EL2]$ was found to be about $6 \times 10^{15} \text{ cm}^{-3}$, by a DLTS measurement. These data are summarized in Table III.

The Hall electron concentrations ($n_H \equiv 1/eR$) of as-grown, annealed, and quenched samples are shown in Fig. 1. The as-grown sample is controlled mainly by a shallow donor ($E_{DS} \approx 3.0 \text{ meV}$) at room temperature and below, with a

TABLE I. Electrical properties before and after 950 °C soak and quench.

Ingot	Position	$\rho (10^7 \Omega \text{ cm})$		$\mu (10^3 \text{ cm}^2/\text{V s})$	
		Before	After	Before	After
1	Seed	3.1×10^{-1}	4.5	1.3	5.0
	Tail	3.7	4.4	4.1	4.9
2	Seed	4.1×10^{-2}	3.9	0.8	5.4
	Tail	4.5	6.7	5.8	4.8
3	Seed	2.5×10^{-7}	9.4×10^{-1}	5.2	5.2
	Tail	6.6×10^{-6}	1.8	2.9	6.4

TABLE II. Electrical properties of ingot No. 3, seed end, after anneal and quench cycles.

Treatment	$\rho(\Omega \text{ cm})$	$\mu(10^3 \text{ cm}^2/\text{V s})$	$n(\text{cm}^{-3})$
1. as-grown	2.5	5.2	4.7×10^{14}
2. 950 °C-Q	9.4×10^6	5.2	1.3×10^8
3. 950 °C-A	7.8	4.6	1.7×10^{14}
4. 950 °C-Q	9.6×10^6	5.1	1.3×10^8
5. 950 °C-A	3.3	7.1	2.7×10^{14}
6. 950 °C-Q	2.7×10^7	6.7	3.4×10^7

small amount of a deeper donor ($E_C - 0.13 \text{ eV}$) becoming noticeable at higher temperatures. (It will be assumed here that the 0.13 eV center is a donor, although we as yet have no proof of that fact.) A fit of n_H vs T down to liquid-helium temperatures³ gives the data shown in Table III. The annealed sample (950 °C-A), on the other hand, has a greatly increased concentration of the 0.13 eV center, but also an increased acceptor concentration. Finally, the quenched sample (950 °C-Q) shows the EL2 activation energy, but accurate quantitative information cannot be obtained from the Hall-effect data since the room-temperature EL2 energy is not precisely known.³ A significant observation from all of these data is that both the as-grown and annealed states show very close compensation. Another observation is that the donor and acceptor concentrations are significantly higher than the electrically active impurity concentrations, at least for sample 950 °C-A. Thus, the electrical properties of this sample are primarily controlled by defects.

Results from DLTS measurements show the following traps with concentrations greater than $1 \times 10^{15} \text{ cm}^{-3}$: as grown, $E_C - 0.15$, and EL2; annealed, $E_C - 0.33$, $E_C - 0.74$, and EL2. Samples quenched from lower temperatures, 750 and 850 °C, were still conductive enough for DLTS measurements, but showed much smaller total trap concentrations. The high trap concentrations of the annealed samples are probably due to the formation of complexes during a slow cooldown.⁴

Photoluminescence (PL) results are displayed in Fig. 2. Here it is seen that the only outstanding difference between the quenched and annealed samples is a spectrum at 1.45 eV in the quenched sample. Note that this center could well be an acceptor at $E_V + 0.07 \text{ eV}$. Further PL studies will be carried out to determine the exact nature of this center. Note that the shallow acceptor spectra show more structure than

FIG. 1. Hall carrier concentration ($n_H = 1/eR$) vs inverse temperature for as-grown and heat-treated samples. The symbol "A" designates slow cooling, and "Q" fast cooling, following a 5 h, 950 °C anneal. The solid lines are theoretical fits.

usual for SI samples, attesting to the good quality of these crystals.

To explain these phenomena we must invoke native defects since there are not sufficient quantities of impurities to account for the donors and acceptors. We assume the sample is in thermal equilibrium after the 5 h, 950 °C soak, in agreement with the study of Woodall and Woods.² Various other workers⁵⁻⁷ have investigated the thermodynamics of such heat treatments and concluded that about 10^{16} – 10^{18} vacancies, mostly arsenic vacancies, would be frozen in after a quench from 950 °C. However, they also observed significant room-temperature annealing, which reduced the vacancy concentration by a factor 10–100. Thus, after many hours at room temperature, we would expect a quenched vacancy concentration of 10^{14} – 10^{17} cm^{-3} , certainly consis-

TABLE III. Concentrations of defects and impurities in ingot No. 3 (in units of 10^{15} cm^{-3}).

Treatment	N_{DS}	N_{AS}	$N_{0.13}$	$N_{AS} - N_{DS}$	[EL2]	$[C_{As}]^d$	$[Si_{Ga}]^d$
1. as-grown	3.6	3.2 ^a	0.2	-0.4	6 ^e		
5. 950 °C-A			5.9	5.3	10 ^{c,e}	0.3	≤ 0.2
6. 950 °C-Q				1 to 4 ^b	10 ^c	0.3	≤ 0.2

^a Denoting all acceptors below $E_C - 0.13 \text{ eV}$.

^b Spread due to uncertainty in room-temperature EL2 energy.

^c Determined by 1.1 μm electronic absorption.

^d Determined by LVM phonon absorption.

^e Determined by DLTS.

FIG. 2. Photoluminescence spectra at 4.2 K for samples 950 °C-Q and 950 °C-A.

tent with our observed donor and acceptor changes of 10^{15} – 10^{16} cm $^{-3}$. The simplest assignments for the donors and acceptors would be V_{As} and V_{Ga} , respectively, although there is some doubt that the V_{Ga} are stable at room temperature.⁸ In any case, we have found that the defects in our samples are stable above 300 °C, therefore ruling out any isolated vacancies, which are known to move freely above this temperature.⁸

However, in light of recent work by Baraff and Schluter,^{9,10} the model must be more complicated than this, because the V_{As} can transform to the complex V_{Ga} – Ga_{As} by a simple nearest-neighbor hop, and the V_{Ga} can transform to V_{As} – As_{Ga} . In fact, the concentrations of each member of a conjugate pair (e.g., V_{As} and V_{Ga} – Ga_{As}) should be about equal if the Fermi level (E_F) is near midgap,¹⁰ certainly true at 950 °C. In the case of a slow cool (anneal), the vacancies would not survive, as is well known from electron-irradiation studies,⁸ but would either annihilate with interstitials or form complexes. One such complex would probably be V_{As} – As_{Ga} since the presence of As_{Ga} is well correlated with the presence of EL2.¹¹ The binding energy of V_{As} – As_{Ga} is high when E_F is near the conduction band, but that of V_{Ga} – Ga_{As} is not.¹⁰ Thus, as E_F approaches the conduction band during the slow cool, the V_{Ga} – Ga_{As} may not survive.

To correlate our experimentally observed centers with the defects discussed above, we will assume that the Hall-effect level at E_C –0.13 is due to a donor defect, although the statistical fit alone cannot distinguish between a donor and an acceptor. Furthermore, we will assume that the PL line at 1.45 eV denotes an acceptor at E_V +0.07 eV. Then the E_C –0.13 eV center is likely V_{As} – As_{Ga} and the E_V +0.07 eV is probably V_{Ga} – Ga_{As} . Indeed, V_{As} – As_{Ga} is predicted to have a (0/+) transition at roughly E_C –0.05 eV,⁹ and V_{Ga} – Ga_{As} is predicted to have a (–/

0) transition at E_V +0.3 eV.¹⁰ The observed experimental energies are not outside of theoretical uncertainties. In both of these cases, the vacancy is a much stronger perturbation on the lattice than the antisite and, indeed, the vacancies themselves have energy levels near those of the complexes.¹² As previously speculated, a variety of levels observed within 0.1–0.2 eV of the band edges are probably defect- and impurity-vacancy complexes.^{13,14}

In this model then, a rapid cooldown (quench) freezes in significant amounts (10^{15} – 10^{16} cm $^{-3}$) of V_{As} – As_{Ga} and V_{Ga} – Ga_{As} . The latter complexes (plus other acceptors below midgap) dominate the former complexes (plus other donors above midgap) so that the deep donor EL2 can render the sample semi-insulating ($[A] > [D]$ and $[EL2] > [A] - [D]$). A slow cooldown (anneal), on the other hand, permits the rather unstable V_{Ga} – Ga_{As} to break up as E_F rises, so that $[D] > [A]$ and the sample is conductive. Other electron traps, as observed by DLTS, may influence this picture, but are of lower concentrations than the E_C –0.13 eV center. Hole traps have not yet been investigated.

In summary, we have described thermal processes which can make bulk LPLEC GaAs homogeneous, and either conducting or semi-insulating. The materials have been studied by several electrical, optical, and analytical techniques and shown to be dominated by native defects. A model is proposed which includes a donor at E_C –0.13 eV, probably V_{As} – As_{Ga} , and an acceptor at E_V +0.07 eV, probably V_{Ga} – Ga_{As} . Theoretical studies are consistent with these assignments. After a slow cooldown from 950 °C the donors dominate, and after a fast cooldown, the acceptors.

Much of this work was performed at the Avionics Laboratory, Wright–Patterson AFB, under contract F33615-84-C-1423. We wish to thank T. Cooper, J. Hoelscher, G. Smith, E. Pimental, J. Galt, and J. Harker for technical assistance. We also wish to thank G. A. Baraff for helpful discussions.

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