Observations on residual donors in GaP LPE

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OPTOELECTRONIC MATERIALS I.

OBSERVATIONS ON RESIDUAL DONORS IN GaP LPE

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Résumé. — Les concentrations d'électrons et de donneurs, et les mobilités des porteurs des couches de GaP non dopées, préparées par l'épitaxie de phase liquide sont étudiées en fonction du traitement thermique précédant la croissance. Les donneurs principaux ou la présence de plus d'un donneur sont identifiés par les énergies d'ionisation des donneurs. On observe une incorporation de soufre après de courts traitement thermiques, tandis qu'après de longs traitements thermiques, on observe une incorporation de silicium.

Abstract. — Electron and donor concentrations and mobilities of non doped liquid phase epitaxial GaP layers were studied when varying the annealing process prior to growth. Main donors or the presence of more than one donor were identified by donor ionization energies. After short annealings the incorporation of sulphur, after long annealings the incorporation of silicon were observed.

1. **Introduction.** — Identifying the nature and sources of residual impurities in intentionally non-doped $A^{III}B^{V}$ semiconductor epitaxial layers is one of the most important information needed to grow high purity or controllably doped device quality crystals. Silicon contamination has been already observed in GaP LPE layers and the presence of Si in undoped GaAs and GaP LPE layers has been attributed to the temperature dependent reaction between the carrier gas H_2 and the quartz reactor tube [1, 2].

Sulphur contamination has been found in commonly available graphite materials by mass-spectroscopic and in 6 N purity Ga by microchemical analysis in our laboratory. The elimination of sulphur and other unwanted impurities from the layers requires the annealing of the melt used for LPE at high temperatures. This is the case in the GaAs technology, when the heat treatment of the boats and melts is generally used in order to grow layers of low impurity concentrations. However, the processes involved in the annealing are not known in details. Annealing temperatures and times are often chosen empirically.

In this paper we present the results of a systematic study of residual donors in GaP LPE layers grown after various melt annealings. Layers are characterized by the mobilities and concentrations of charge carriers and by the chemical nature of dominant donors. The dominant donors were identified by the thermal activation energies deduced from Hall effect data, properly corrected for the concentration dependence of the donor ground state ionization energy. The dependence of donor concentration has been experimentally established on well characterized samples containing S, Te or Si as dominant donors. Sample characterization and impurity identification have been aided by low temperature photoluminescence measurements.

Our specific objective was to interpret donor concentrations and donor ionization energies as a result of impurity generation and transport processes originating from the solid graphite, the melt and the gas phase.

2. **Growth procedure and sample preparation.** — Growth of epitaxial material was carried out in a horizontal sliding boat [3] under flowing H_2. Undoped monocrystalline GaP ($n_{300} = 1.3 \times 10^{17}$ cm^{-3}, $\mu_{77K} = 600$ cm^2/Vs, $E_D = 84$ meV indicating Te as the main residual donor in the source material, $N_D = 2.0 \times 10^{17}$ cm^{-3}, $N_A = 2.8 \times 10^{16}$ cm^{-3}) was dissolved in Ga of 6 N purity, obtained from Ajka Aluminium Works, Hungarian Aluminium Co. Gallium was prebaked under high vacuum at abt. 650-700 °C for six hours. Morganite graphite slider boats were used. Mass spectrometric analysis showed traces of sulphur in this graphite material.

The boats were cleaned in acids, washed in deionized water and baked out under high vacuum at abt. 1 300 °C for a few hours. During growth an overpressure of 0.5 atm was maintained in the leak-proof growing system. Typical values of oxygen content, checked by an Engelhard oxygen meter, at the inlet and the outlet point of the growing system were 0.6 and 2.0 ppm respectively.

Two melts were used for the epitaxial process; one of them was saturated with GaP at the initial temperature of the epitaxy, the other one was undersaturated. First the undersaturated melt was contacted with the substrate. Growth took place from the saturated melt on the renewed (111) B face of the semi-insulating or p-type substrate. The melts were baked out and contacted with the substrate at the

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same temperature. Layers of 10-20 μm thicknesses were grown at a cooling rate of 3 °C/min. In-Ni contacts were soldered to the cleaved samples for the Van der Pauw measurements.

3. **Electrical measurements and evaluation methods.** — All the Hall effect measurements were carried out using the Van der Pauw method in the temperature range from 77 to 400 K. The estimated total error of the measured electrical parameters (Hall constant conductivity, mobility) was less than 10 per cent. The electron concentration *versus* temperature curves were analysed using an effective reduced density of states value of $N_c' = 1.15 \times 10^{16}\ T^{3/2}\ cm^{-3}$.

This value is thought to be a reasonable approximation in the light of the recently established structure of conduction band minima in GaP [4-7]. Using a non-linear least-square method the donor ground state ionization energies E_D, donor and acceptor concentrations (N_D and N_A) were deduced with typical errors of ± 2 → 3 meV, ± 10 → 20 per cent and ± 20 → 50 per cent respectively, making it possible to distinguish donors having ionization energy differences of the order of 10 meV. Allowance was also made for the different degeneracies of the ground states of the P-site (S or Te) and Ga-site (Si) donors.

S, Te and Si containing, well characterized samples were used to produce calibration curves for the identification of unknown samples (Fig. 1).

Donor ionization energies of S, Te and Si donors showed a linear dependence on the cubic root of the acceptor concentration, i.e. of the ionized donor concentration, due to concentration broadening. From the data presented in figure 1 we have

$$E_{D_S} = (105 \pm 2) - (3.8 \pm 0.7) \times 10^{-5}\ N_A^{1/3}$$
$$E_{D_{Te}} = (94.5 \pm 2) - (3.8 \pm 0.4) \times 10^{-5}\ N_A^{1/3}$$
$$E_{D_{Si}} = (83.5 \pm 2) - (4.6 \pm 0.2) \times 10^{-5}\ N_A^{1/3}\ .$$

Where the energies are in meV and the acceptor concentrations in cm^{-3}. These relations agree well with those, reported by Vink *et al.* [8]. The donor ionization energies extrapolated for infinite dilution are consistent with the recently revised optical values [4, 5, 6 also 7] and with the recent values obtained from the analysis of infrared absorption spectra [5].

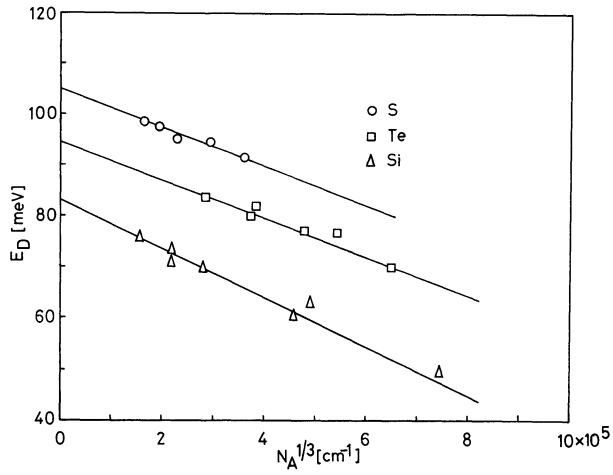

FIG. 1. — Plots of donor ionization energies *vs* cubic root of acceptor concentration of calibrating samples containing S, Te and Si.

4. **Results and discussion.** — Results of the consecutive growth runs at 990 °C and 900 °C are listed in tables I and II. The electron concentration (n_{300}), mobility (μ_{77}), concentrations of ionized donors and acceptors (N_A, N_D) and the donor ionization energy E_D data are obtained from the Hall effect measurements.

If the outdiffusion of volatile impurities controls the impurity content of the melt, the concentration of impurities will depend on the annealing time t as $\exp\left(\frac{-\pi^2 Dt}{4d^2}\right)$, where D is the diffusion constant of the impurity in the melt and d is the thickness of the melt.

The outdiffusion of volatile impurities originally present in the gallium and source material causes a concentration decrease in one order of magnitude after a bake out time of 3 hours.

TABLE I

Annealing times and electrical data for growths at 990 °C

Run No	Annealing time × 10^3 (s)	Annealing time *cumulative* × 10^3 (s)	n_{300} × 10^{17} (cm^{-3})	μ_{77} (cm^2/V s)	E_D (meV)	N_D × 10^{17} (cm^{-3})	N_A × 10^{16} (cm^{-3})
NK 0321	4.2	4.2	5.5	702	92	6.0	5.0
NK 0607	1.8	7.8	3.0	990	102	4.9	1.1
NK 0608	4.8	12.6	7.0	760	95	1.6	4.5
NK 0619	12.0	36.6	3.7	756	95	0.59	0.93
NK 0628	37.8	74.4	3.5	1 350	85	0.70	2.0
NK 0703	73.8	148.2	4.9	1 400	74	0.88	2.2

TABLE II

Annealing times and electrical data for growth at 900 °C

Run No	Annealing time $\times 10^3$ (s)	Annealing time *cumulative* $\times 10^3$ (s)	n_{300} $\times 10^{17}$ (cm^{-3})	μ_{77} ($cm^2/V\,s$)	E_D (meV)	N_D $\times 10^{17}$ (cm^{-3})	N_A $\times 10^{16}$ (cm^{-3})
NK 0705	1.5	149.7	4.1	1 260	85	3.6	4.0
NK 0707	4.5	154.2	2.9	1 400	83	5.0	3.0
NK 0710	11.7	165.9	0.22	1 900	92	0.38	1.0
NK 0711	36.9	202.8	0.41	1 600	90	0.75	2.2
NK 0712	72.9	275.7	0.76	1 300	87	1.3	3.0

Another part of the impurities present in the melt comes from the boat during annealing, and the depletion of the graphite reservoir controls their concentration in the melt by a factor of $\frac{1}{A\sqrt{\pi D t_{cum}}}$. The annealing time is cumulative (t_{cum}) in this relation. A is the contact surface between the melt and the graphite.

Assuming that A is a constant and

$$D = 10^{-5}\ \mathrm{cm^2\ s^{-1}},$$

an estimation was made for the depletion of the reservoir. According to this estimation the concentration of the volatile impurities will decrease with one order of magnitude after a bake out time of 20 hours.

A similar time constant of 3 hours might be expected for the saturation of the melt with Si, if the process is controlled by the diffusion of Si in the melt. On the basis of all these considerations n_{300}, μ_{77} and $N_A + N_D$ data of experiment at 990 °C are plotted against cumulative times of annealing in figure 2. To characterize the chemical nature of the dominant donor impurity the parameter $\frac{E_D - E_{Ds}}{E_{Dsi} - E_{Ds}}$ was constructed with the help of the E_D *vs* $N_A^{1/3}$ curves (Fig. 1). Figure 2 represents the decrease of the impurity concentration of epitaxial GaP layers according to the depletion of the impurity content of the graphite boat and the melt. Parallel to the decrease of the impurity concentration a change from sulphur to silicon as the dominant donor impurity takes place. A slight increase in ionized impurity concentration is detectable after very long baking times. In this case the main donor impurity is silicon.

Following the experiments at 990 °C another series of growths was performed using the same boat already depleted in sulphur. The annealing temperature in these experiments was 900 °C and a comparatively rapid decrease of the impurity level originally present in the melt, the growth of high purity, high mobility layers and the incorporation of silicon as the dominant donor only at very long baking times of at all was expected.

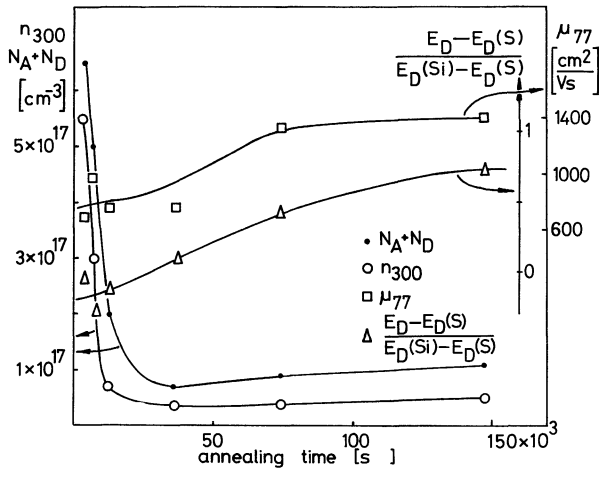

FIG. 2. — Electron concentration, $N_A + N_D$, mobility and $\frac{E_D - E_{Ds}}{E_{Dsi} - E_{Ds}}$, characterizing the chemical nature of the main donor in GaP LPE layers grown at 990 °C as function of cumulative annealing times.

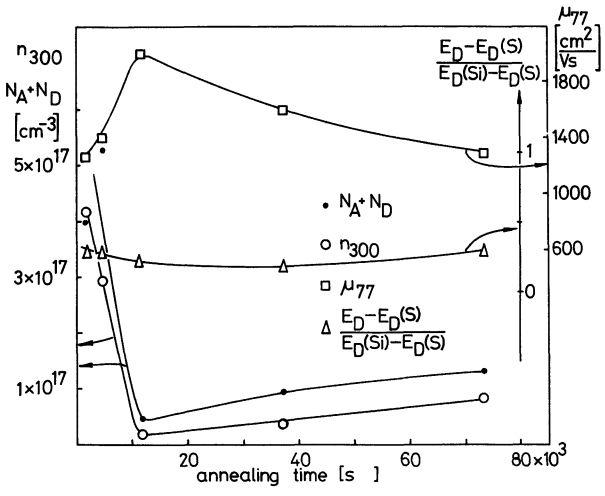

FIG. 3. — Electron concentration, $N_D + N_A$, mobility and $\frac{E_D - E_{Ds}}{E_{Dsi} - E_{Ds}}$, in GaP LPE layers grown at 900 °C as function of annealing times. The growths were performed in the boat used at the 990 °C experiments.

The results of the growth runs at 900 °C (Fig. 3) appear to fall short of expectations. The values of E_D in all of the 900 °C experiments correspond to tellurium, but photoluminescence spectra at 4 K do not show any evidence of tellurium. We suppose that not one but more (at least two) donors (S + Si) are incorporated into the layers.

The parameter $\frac{E_D - E_{Ds}}{E_{Dsi} - E_{Ds}}$ remains constant when varying annealing times, however, the electron concentration and the sum of ionized donors and acceptors show a minimum and the mobility shows a maximum.

In comparison to the experiments carried out at 990 °C the initial value of parameter $\frac{E_D - E_{Ds}}{E_{Dsi} - E_{Ds}}$ is higher. This presence of silicon in epilayers grown after short annealings at this series of experiments. After such short annealings at the first series of experiments Si was not detectable in the layers. The saturation of porous graphite boat with silicon containing melt at the 990 °C experiments may be considered as the source of silicon at the later growths.

5. **Conclusion.** — The connection of sulphur contamination in undoped GaP LPE layers with sulphur traces of the graphite boat has been demonstrated experimentally. A decrease of the sulphur level in epilayers has been shown when annealing the boat in contact with gallium. Parallel to the decrease of sulphur level an increase in $N_D + N_A$ and a decrease in E_D connected with the incorporation of silicon has been observed. Silicon generation at high temperature may result in memory effects using ordinary graphite boats without covering.

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