PROPERTIES OF SEMI-INSULATING GALLIUM ARSENIDE GROWN BY THE BRIDGMAN METHOD

by J. P. FARGES

Abstract

Properties of GaAs grown by the horizontal Bridgman method are related to growth conditions. Crystal assessment has been mainly performed using high temperature Hall effect measurements, spectroscopic methods (DLTS, OTS) and I.R. optical absorption for chromium concentration measurements. A four level model of compensation and the Shockley diagram have been used to understand electrical properties of semi-insulating materials. Poor results obtained by ion implantation in chromium doped substrates have been related to Si contamination, but chromium plus gallium oxide co-doping has overcome this difficulty. Thermal conversion phenomena follow a diffusion like law \( D = 1.03 \times 10^4 \exp(-3.38) \text{ eV kT}^{-1} \text{ cm}^2 \text{s}^{-1} \), which could be related to Cr out-diffusion.

1. Introduction

Semi-insulating GaAs is mainly used as substrate material for FET- and IC-devices using epitaxial growth or ion implantation techniques. Performance of such devices are greatly influenced by the quality of the substrate material\(^1,2\)), so the knowledge of the influence of metallurgical growth parameters on the substrate properties to obtain a good quality substrate is of prime interest. Bulk GaAs is usually obtained by the melt-growth technique, such as boat-growth method, horizontal Bridgman (HB) or horizontal gradient freeze (HGF) and liquid encapsulated Czochralski (LEC).

In this paper, after a brief survey of the HB growth method (most of samples studied herein were grown using this method), and the compensation model for semi-insulating chromium doped gallium arsenide, we present experimental procedures and main results obtained.

1.1. Growth of bulk GaAs

Stoichiometric GaAs is obtained by the melt-growth technique, such as HB or LEC. The main problem comes from the volatility of arsenic, which makes GaAs easily dissociable. At the melting point (1238 °C) the arsenic pressure...
is close to 1 atmosphere (fig. 1). Two steps are necessary to obtain a GaAs single crystal using the HB method (fig. 2):
— synthesis of the GaAs;
— growth of the single crystal by moving the solid liquid interface.

This can be achieved by moving the furnace (HB method) or by changing the temperature gradient of the furnace (GF method). Most of the crystals studied were grown at RTC Caen using this last method.

The temperature profile of the furnace includes two zones:
— the low temperature zone where arsenic is kept in sufficient quantity to provide the desired pressure at a temperature of about 600 °C;
— the high temperature zone where the gallium melt and a seed of GaAs generally (111) oriented are kept close to 1250 °C.

Without intentional doping, bulk melt growth GaAs is usually $n$-type, with a room-temperature resistivity in the $10^{-1}$ Ω cm range and a mobility of about 5000 cm$^2$/Vs. These properties are related to background impurities, particularly silicon which comes from a reaction with the silica boat$^{3,4}$. Thus, to obtain semi-insulating material, doping is necessary.

Previous works have dealt with oxygen doping$^{5,6}$, and crystals with room
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![Diagram of Bridgman growth method]

Temperature resistivity in the $10^7 \Omega \text{ cm}$ range have been obtained. Experiments by Cronin and Haisty\textsuperscript{7)} with chromium doping have given reproducible results, with a room-temperature resistivity in the $10^8 \Omega \text{ cm}$ range.

1.2. Compensation models

Early work on semi-insulating chromium doped GaAs assumed that high resistivity of the material was related to the compensation of Si shallow donors by Cr deep acceptors. At the moment a more sophisticated physical model is used, which includes four levels in the bandgap as follows (fig. 3):

- the deep acceptor level related to the chromium dope, with concentration $N_{DA}$,
- the deep donor level, related to oxygen\textsuperscript{8)}, or an electron trap labelled EL2\textsuperscript{9)} with concentration $N_{DD}$,
- a shallow acceptor level, related to different impurities such as zinc, carbon, manganese, copper or arsenic vacancies, with concentration $N_{SA}$,
- a shallow donor level, usually related to silicon and sometimes to sulphur, with concentration $N_{SD}$.
Position of the Fermi level $E_F$ in the bandgap can be calculated from the condition of charge neutrality

$$n + N_{DA^-} + N_{SA^-} = p + N_{DD^+} + N_{SD^+}$$

with the usual notations, $n$ and $p$ free electron and hole concentrations respectively, $N_{DA^-}$ and $N_{SA^-}$ ionized acceptor concentrations, $N_{DD^+}$ and $N_{SD^+}$ ionized donor concentrations.

$n$ and $p$ are given by

$$n = N_C \exp \left( -\frac{E_C - E_F}{kT} \right)$$
$$p = N_V \exp \left( -\frac{E_F - E_V}{kT} \right)$$

and

$$N_C = 2 \left( \frac{2m_e kT}{\hbar^2} \right)^{\frac{1}{2}}, \quad N_V = 2 \left( \frac{2m_h kT}{\hbar^2} \right)^{\frac{1}{2}},$$

where $E_C$ and $E_V$ are the energies of the conduction and valence band edges; $E_F$ is the Fermi energy; $N_C$ and $N_V$ are the effective densities of states in conduction and valence band; $m_e$ and $m_h$ are effective mass of electrons and holes; $k$ is Boltzmann’s constant; $T$ is the absolute temperature, and $\hbar$ is Planck’s constant.

$N_{A^-}$ and $N_{D^+}$ are given by

$$N_{A^-} = N_A \left[ 1 + g_a \left( -\frac{E_A - E_F}{kT} \right) \right]^{-1}$$
$$N_{D^+} = N_D \left[ 1 + g_a \left( \frac{E_F - E_D}{kT} \right) \right]^{-1}$$
where \(g_a\) and \(g_d\) are the degeneracy factors of acceptor and donor levels, and \(E_A\) and \(E_D\) the energies of acceptor and donor levels.

Equation (1) can be solved in an easy way using a graphic method proposed by Shockley\(^\text{10}\). The concentration of free electrons \(n\), free holes \(p\), ionized acceptors \(N_{DA^-}\), \(N_{SA^-}\) and ionized donors \(N_{DD^+}\), \(N_{SD^+}\) are plotted on a logarithmic scale as functions of the position of the Fermi level in the band gap. Position of the Fermi level is at point \(F\), the intersection of the curves \((n + N_{DA^-} + N_{SA^-})\) and \((p + N_{DD^+} + N_{SD^+})\).

The Shockley diagram is an attractive tool which shows easily the influence of background impurities and Cr-levels on the Fermi level position. For example, increasing the chromium deep acceptor concentration \(N_{DA}\) moves the intersection point from \(F\) to \(F'\), thus giving a \(p\) type material (fig. 4).

**Fig. 4. Shockley diagram for solving the condition of charge neutrality**

\[n + N_{DA^-} + N_{SA^-} = p + N_{DD^+} + N_{SD^+}.\]
2. Experimental

2.1. Experimental procedures

Measurements were mainly performed on ingots grown by the GF method at the RTC Caen using exclusively 6 N elemental gallium and arsenic and on some samples purchased from different suppliers.

<table>
<thead>
<tr>
<th>supplier and abbreviation used</th>
<th>growth method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sumimoto (SU)</td>
<td>three temperatures HB</td>
</tr>
<tr>
<td>laser diode laboratories (LD)</td>
<td>HB</td>
</tr>
<tr>
<td>metal research limited (MR)</td>
<td>LEC</td>
</tr>
<tr>
<td>naval research laboratories (NRL)</td>
<td>LEC</td>
</tr>
<tr>
<td>mining and chemical products (MCP)</td>
<td>HB and LEC</td>
</tr>
</tbody>
</table>

In bulk melt-grown GaAs, the major sources of impurities are well known:
— background impurities from the Ga and As elements;
— contamination coming from the cleaning and handling procedures for the silica boat, ampoule and Ga and As elements;
— silicon contamination from a reaction between the silica boat and the Ga melt.

This last point is obviously the major contamination source. Therefore, several undoped crystals have been grown using combinations of different coated silica boats. Usually, crystals were grown in \( \langle 111 \rangle \) direction, then \( \langle 100 \rangle \) wavers were cut with \( 6^\circ \) off in the \( \langle 110 \rangle \) direction.

Studies on semi-insulating GaAs have been carried out using chromium and chromium plus gallium oxide \( (\text{Ga}_2\text{O}_3) \) doping. Moreover, special doping experiments such as \( \text{Cr}–\text{Al} \), \( \text{Si}–\text{Ga}_2\text{O}_3 \), \( \text{Cr}–\text{Si}–\text{Ga}_2\text{O}_3 \) have been performed.

2.2. Crystal assessment

Assessment of bulk GaAs is made using the following methods on slices cut on the seed and tail side of crystals.
(a) Etch pit density using the Abrahams and Buiochhi \( ^{11} \) etch.
(b) Residual impurities and doping concentration;
— Chromium concentration by optical absorption in the near infra-red range \( (1.35 \, \mu\text{m}) \) \( ^{12} \). This method gives reliable results in the \( 10^{16} \) to \( 10^{17} \) \text{cm}^{-3} \) range (fig. 5) which is the usual doping concentration for most of the crystals measured.
— Oxygen concentration by tritium activation \( ^{13} \). Application of this radioactive method to carbon and silicon analysis is still under study.
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Fig. 5. Plots of the absorption coefficient related to the presence of chromium versus the Cr concentration measured by neutron activation analysis (after Martin et al.\textsuperscript{12}).

(c) Electrical properties assessment using results obtained by spectroscopy methods, i.e. deep level transient spectroscopy (DLTS)\textsuperscript{14,15} and optical transient spectroscopy (OTS)\textsuperscript{16} which give information on the two main deep levels (chromium acceptor and deep donor).

High temperature Hall effect measurements give information on the Fermi level position and on carrier mobility. Hall equipment allows a 350 to 700 K temperature variation and plots directly the resistivity $\rho$, the Hall mobility $\mu_H$, the free carrier concentration $n$ or $p$ against the reciprocal temperature $T^{-1}$. Plot of the product $nT^{-1}$ against $T^{-1}$, corrected for the variation of the density of states in the valence and conduction bands leads to the activation energy.

Clovers leaf shaped samples as mentioned by Van der Pauw\textsuperscript{17} were used, and contacts made by eutectic indium gallium droplets disposed on each leaf before installation in the sample holder (fig. 6).

(d) Sensitivity of the GaAs to thermal conversion is assessed by a thermal treatment for the simulation of the realization of the device's active layer:
— 750 °C anneal under hydrogen flow during one hour, for the epitaxial growth;
— 875 °C anneal under argon flow during 15 minutes after capping under silicon nitride Si₃N₄ for the ion implantation.

(e) Substrates for ion implantation are selected by an implantation test of $3.5 \times 10^{12}$ Se at cm⁻² at 280 keV, followed by the above mentioned heat treatment. After ion implantation, the doping profile is determined from C/V measurements on double mercury diodes.
3. Results and discussion

3.1. Undoped GaAs

Several undoped crystals have been grown in silica boats with different coating combinations:
- sand blasted silica boat,
- sand blasted silica boat with silica cloth,
- sand blasted silicon boat coated with pyrolytic carbon,
- sand blasted silica boat coated with silica cloth and pyrolytic carbon.

Results are summarized in table 1. We notice that the choice of the silica boat coating influences the properties of the obtained crystals.

Pyrolytic carbon coating lowers the etch pit density (EPD), but affects electrical properties. A good compromise between electrical and crystalline properties is given by the use of a sand blasted silica boat coated with silica cloth, and subsequently all the crystals studied here-after were grown using this combination.

![Fig. 7. High temperature Hall effect for undoped GaAs. Plot of resistivity $\rho$, Hall mobility $\mu_H$ and $n$ versus reciprocal temperature $T^{-1}$.](image-url)
<table>
<thead>
<tr>
<th>Boat type and type coating</th>
<th>((N_D - N_A) \text{ cm}^{-3}) at 300 °K</th>
<th>(N_D - N_A) cm(^{-3}) at 77 °K</th>
<th>(\mu_H \text{ cm}^2/\text{Vs}) at 300 °K</th>
<th>(\mu_H \text{ cm}^2/\text{Vs}) at 77 °K</th>
<th>EPD cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. sand blasted silica boat</td>
<td>5 (\cdot) 10(^{15}) to 2 (\cdot) 10(^{16})</td>
<td>3 (\cdot) 10(^{15}) to 10(^{16})</td>
<td>4500 to 5500</td>
<td>8000 to 15000</td>
<td>5 (\cdot) 10(^{4})</td>
</tr>
<tr>
<td>2. sand blasted silica boat + cloth coating</td>
<td>10(^{16}) to 5 (\cdot) 10(^{16})</td>
<td>7 (\cdot) 10(^{15}) to 5 (\cdot) 10(^{16})</td>
<td>4000 to 4900</td>
<td>7000 to 11000</td>
<td>10(^{4}) to 2 (\cdot) 10(^{5})</td>
</tr>
<tr>
<td>3. sand blasted silica boat + pyrolitic carbon coating</td>
<td>3 (\cdot) 10(^{17}) to 9 (\cdot) 10(^{17})</td>
<td>3 (\cdot) 10(^{17}) to 9 (\cdot) 10(^{17})</td>
<td>2000 to 3000</td>
<td>2000 to 3000</td>
<td>8 (\cdot) 10(^{3})</td>
</tr>
<tr>
<td>4. sand blasted silica boat + cloth coating + pyrolitic carbon coating</td>
<td>4 (\cdot) 10(^{17}) to 10(^{18})</td>
<td>3,5 (\cdot) 10(^{17}) to 9 (\cdot) 10(^{17})</td>
<td>2000 to 3000</td>
<td>2000 to 3000</td>
<td>5 (\cdot) 10(^{3})</td>
</tr>
</tbody>
</table>
3.1.1. Semi-insulating undoped GaAs

Sometimes, undoped crystals are high resistivity or semi-insulating. In such a case, melt grown HB ingots are usually n-type at the seed side, becoming high resistivity or semi-insulating at the tail side (fig. 7). Table II summarizes results or measurements performed on undoped semi-insulating crystals.

Taking into account the measured concentration of EL2 deep donor \( N_{DD} = 2 \times 10^{16} \) at cm\(^{-3} \), Si shallow donors \( N_D \leq 10^{16} \) at cm\(^{-3} \), we have plotted Shockley's diagram for undoped semi-insulating materials.

To obtain semi-insulating material without intentional doping, the following condition must be achieved,

\[
N_{DD} > N_{SA} > N_{SD}.
\]

To satisfy this condition, and explain the variation of resistivity from seed to tail of ingots, we can assume that the shallow acceptor concentration \( N_{SA} \) increases from seed to tail, which implies that the segregation coefficient of the impurity is smaller than unity, \( k < 1 \) (fig. 8).

Therefore, the experimental observations are satisfied;

| TABLE II |
| Semi-insulating undoped crystals |

<table>
<thead>
<tr>
<th>(\varrho) ((\Omega \text{ cm}))</th>
<th>Hall measurements at 400 K</th>
<th>activation energy deduced from the slope of the curve ( nT^{-1} = f(10^3/T) ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varrho) ((\Omega \text{ cm}))</td>
<td>(\mu_H) ((\text{cm}^2/\text{Vs}))</td>
<td>(n) (cm(^{-3}))</td>
</tr>
<tr>
<td>329 tail</td>
<td>9.5 (\times) 10(^3)</td>
<td>4200</td>
</tr>
<tr>
<td>373 seed</td>
<td>3.4 (\times) 10(^4)</td>
<td>3700</td>
</tr>
<tr>
<td>392 tail</td>
<td>1.15 (\times) 10(^4)</td>
<td>4500</td>
</tr>
<tr>
<td>407 seed</td>
<td>9.8 (\times) 10(^1)</td>
<td>4200</td>
</tr>
<tr>
<td>407 seed</td>
<td>9.3 (\times) 10(^3)</td>
<td>5000</td>
</tr>
<tr>
<td>415 seed</td>
<td>1.2 (\times) 10(^{-1})</td>
<td>3300</td>
</tr>
<tr>
<td>415 tail</td>
<td>5 (\times) 10(^2)</td>
<td>1700</td>
</tr>
<tr>
<td>416 seed</td>
<td>10(^2)</td>
<td>2450</td>
</tr>
<tr>
<td>416 seed</td>
<td>9.5 (\times) 10(^1)</td>
<td>4300</td>
</tr>
<tr>
<td>417 seed</td>
<td>3.2 (\times) 10(^{-1})</td>
<td>4800</td>
</tr>
<tr>
<td>417 seed</td>
<td>6.2 (\times) 10(^4)</td>
<td>4100</td>
</tr>
</tbody>
</table>
Fig. 8. Shockley diagram for undoped GaAs with $N_{DD} = 2 \cdot 10^{16}$ cm$^{-3}$, $N_{SD} \leq 10^{16}$ cm$^{-3}$, and $N_{SA}$ increases from seed to tail of ingot.

- at the seed side, $n$-type material, $N_{DD} > N_{SD} > N_{SA}$,
- at the tail side, semi-insulating material, $N_{DD} > N_{SA} > N_{SD}$.

This hypothesis can well explain results summarized in table II for ingots 329, 392, 407, 417. However, in other cases, we can assume that ingot 373 exhibits a higher seed side shallow acceptor concentration $N_{SA}$, close to $2 \times 10^{16}$ at cm$^{-3}$ and that ingots 415 and 416 have a very slight variation of $N_{SA}$ between seed side and tail side.

3.2. Chromium doped GaAs

Dealing with experiments on undoped crystals, chromium doped ingots were also grown in sand blasted silica boat with silica cloth. However, we have checked that ingots grown in a silica boat with pyrolitic carbon coating were
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n-type with carrier concentration higher than $10^{16}$ cm$^{-3}$, even for high level chromium doping (ratio Cr/GaAs in the melt $\geq 10^{-3}$).

Semi-insulating material is reproducibly obtained as soon as the ratio Cr/GaAs weight in the melt is higher than $1.2 \times 10^{-4}$ ($6.6 \times 10^{15}$ at cm$^{-3}$). Usually the ratio Cr/GaAs in the melt is ranging from 2 to $3 \times 10^{-4}$ (1.1 to $1.65 \times 10^{16}$ at cm$^{-3}$), while commercially available semi-insulating substrates are ranging from $5 \times 10^{16}$ to $2 \times 10^{17}$ at cm$^{-3}$.

Figure 9 shows the variation of the 400 K resistivity with the ratio Cr/GaAs in the melt. We notice that the resistivity is higher at the tail side than at the seed side of the ingot, moreover the resistivity is higher at the wafer bottom. Furthermore, we notice a strong variation of the chromium concentration between top and bottom of the same wafer and between seed side and tail side of the ingot (fig. 10).

![Graph showing variation of 400 K resistivity with Cr/GaAs weight in the melt. Full line is expected variation after Martin et al.2 assuming EL2 deep donor concentration equal $10^{16}$ cm$^{-3}$ and shallow donor and acceptor concentration $N_D - N_A$ equal $10^{16}$ cm$^{-3}$.

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Etch pit density too shows a strong variation between top and bottom of the same wafer. We can define three zones A, B and C where the mean values of EPD (cm⁻²) are respectively $5 \times 10^3 - 10^4$, $10^4 - 5 \times 10^4$ and $> 5 \times 10^4$.

These resistivity and EPD variations are related to the segregation coefficient of chromium in GaAs, ($6.4 \times 10^{-4}$ after Haisty and Cronin [18]), $8.9 \times 10^{-4}$ after Martin et al. [12]), see fig. 11) and the growth conditions, pulling along ⟨111⟩ direction with an inclined solid-liquid interface and slicing along (100)
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planes at $54^\circ$ with respect to the $\langle 111 \rangle$ growth plane (fig. 12). For semi-insulating materials (ratio $\text{Cr}/\text{GaAs}$ in the melt $> 1.2 \times 10^{-4}$), the activation energy deduced from the slope of the curve $nT^{-1}$ versus $T^{-1}$ is pinned at a value of approximately 750 meV with respect to BC. The Shockley diagram described above (see fig. 4) shows easily the slight dependence of the Fermi level with the chromium concentration $N_{DA}$. The Hall mobility $\mu_H$ is decreasing, as the chromium concentration of ingot increases (fig. 13). Seed side mobility is usually higher than bottom side mobility.

Main results of the ion implantation test performed on semi-insulating chromium doped GaAs are summarized in table III. Pinch-off voltages $V_{po}$ are laying between 3.8 to 5.3 V, with scattering as high as 0.8 V on the same wafer. Mobility is in the 4.000 cm$^2$/Vs range. The N-profile does not fit the theoretical LSS distribution (Lindhard et al.\textsuperscript{19}) and exhibits an heterogeneous profile tail, varying from wafer to wafer, and from top to bottom of the same wafer (fig. 14). Therefore, chromium-doped ingots are not qualified for ion implantation devices, but they are well suited for epitaxial growth.

### TABLE III

Results of implantation tests performed on chromium doped GaAs

<table>
<thead>
<tr>
<th>Ingot</th>
<th>RT 400</th>
<th>RT 366</th>
<th>RT 515</th>
<th>RT 448</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio Cr/GaAs weight in the melt</td>
<td>$2.5 \cdot 10^{-4}$</td>
<td>$2.5 \cdot 10^{-4}$</td>
<td>$3 \cdot 10^{-4}$</td>
<td>$5 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Pinch-off voltage and scattering (volts)</td>
<td>$3.8 \pm 0.4$</td>
<td>$4.4 \pm 0.7$</td>
<td>$4.0 \pm 0.5$</td>
<td>$5.3 \pm 0.8$</td>
</tr>
<tr>
<td>Observations concerning the doping profile</td>
<td>Profile tail</td>
<td>idem</td>
<td>idem</td>
<td>idem</td>
</tr>
</tbody>
</table>
Fig. 13. Variation of the 400 K Hall mobility with doping ratio Cr/GaAs weight in the melt. Expected variation after Martin et al. assuming:

<table>
<thead>
<tr>
<th>curve</th>
<th>EL2 deep donor concentration (cm$^{-2}$)</th>
<th>Shallow donor and acceptor concentration $N_D - N_A$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dashed line</td>
<td>10$^{16}$</td>
<td>3 \times 10^{16}</td>
</tr>
<tr>
<td>full line</td>
<td>10$^{16}$</td>
<td>3 \times 10^{16}</td>
</tr>
<tr>
<td>dotted line</td>
<td>5 \times 10^{16}</td>
<td>3 \times 10^{14}</td>
</tr>
</tbody>
</table>

3.3. Chromium plus gallium oxide $Ga_2O_3$ doped GaAs co-doping experiments

Several chromium plus gallium oxide $Ga_2O_3$ doped ingots have been grown. The chromium concentration was kept close to the optimum concentration previously defined ($1.1 \times 10^{16} < Cr < 1.65 \times 10^{16}$ at cm$^{-3}$). Results are summarized in table IV.

In the past, several authors$^{6,6,9}$ have assumed that oxygen produces semi-insulating material, but recent work$^{20}$ has demonstrated that the deep donor
<table>
<thead>
<tr>
<th>ingot</th>
<th>Cr/GaAs</th>
<th>Ga$_2$O$_3$/GaAs</th>
<th>Hall measurements at 400 K</th>
<th>implantation test</th>
<th>oxygen analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(weight in the melt)</td>
<td>Q (Ω cm)</td>
<td>$\mu_H$ (cm$^2$/Vs)</td>
<td>n (cm$^{-3}$)</td>
<td>$E_A$ (meV)</td>
</tr>
<tr>
<td>RT 701</td>
<td>10$^{-4}$</td>
<td>2 $\cdot$ 10$^{-4}$</td>
<td>1,1 $\cdot$ 10$^6$</td>
<td>2800</td>
<td>1,85 $\cdot$ 10$^{11}$</td>
</tr>
<tr>
<td>RT 512</td>
<td>2 $\cdot$ 10$^{-4}$</td>
<td>1 $\cdot$ 10$^{-5}$</td>
<td>8 $\cdot$ 10$^4$</td>
<td>3900</td>
<td>2 $\cdot$ 10$^{10}$</td>
</tr>
<tr>
<td>RT 526</td>
<td>2,1 $\cdot$ 10$^{-4}$</td>
<td>3,2 $\cdot$ 10$^{-5}$</td>
<td>1,1 $\cdot$ 10$^5$</td>
<td>3200</td>
<td>6,3 $\cdot$ 10$^4$</td>
</tr>
<tr>
<td>RT 533</td>
<td>3,2 $\cdot$ 10$^{-5}$</td>
<td>1 $\cdot$ 10$^{-4}$</td>
<td>3 $\cdot$ 10$^6$</td>
<td>3200</td>
<td>6,3 $\cdot$ 10$^4$</td>
</tr>
<tr>
<td>RT 604</td>
<td>1 $\cdot$ 10$^{-4}$</td>
<td>2,5 $\cdot$ 10$^{-4}$</td>
<td>1,6 $\cdot$ 10$^6$</td>
<td>2600</td>
<td>1,1 $\cdot$ 10$^{10}$</td>
</tr>
<tr>
<td>RT 522</td>
<td>2,5 $\cdot$ 10$^{-4}$</td>
<td>2 $\cdot$ 10$^{-5}$</td>
<td>2,2 $\cdot$ 10$^6$</td>
<td>3300</td>
<td>9 $\cdot$ 10$^9$</td>
</tr>
<tr>
<td>RT 527</td>
<td>2,5 $\cdot$ 10$^{-5}$</td>
<td>2,5 $\cdot$ 10$^{-4}$</td>
<td>2,6 $\cdot$ 10$^6$</td>
<td>2900</td>
<td>8 $\cdot$ 10$^9$</td>
</tr>
<tr>
<td>RT 343 T</td>
<td>3 $\cdot$ 10$^{-4}$</td>
<td>2 $\cdot$ 10$^{-5}$</td>
<td>4,4 $\cdot$ 10$^6$</td>
<td>3600</td>
<td>5,5 $\cdot$ 10$^9$</td>
</tr>
<tr>
<td>RT 555</td>
<td>10$^{-4}$</td>
<td>3,4 $\cdot$ 10$^6$</td>
<td>3400</td>
<td>5,3 $\cdot$ 10$^9$</td>
<td>770</td>
</tr>
<tr>
<td>RT 571</td>
<td>10$^{-4}$</td>
<td>4,1 $\cdot$ 10$^6$</td>
<td>3400</td>
<td>5 $\cdot$ 10$^9$</td>
<td>757</td>
</tr>
<tr>
<td>RT 616</td>
<td>10$^{-4}$</td>
<td>4,6 $\cdot$ 10$^6$</td>
<td>3000</td>
<td>6 $\cdot$ 10$^9$</td>
<td>766</td>
</tr>
<tr>
<td>RT 369 T</td>
<td>2 $\cdot$ 10$^{-4}$</td>
<td>4,6 $\cdot$ 10$^6$</td>
<td>3000</td>
<td>5 $\cdot$ 10$^9$</td>
<td>762</td>
</tr>
<tr>
<td>RT 437</td>
<td>2 $\cdot$ 10$^{-4}$</td>
<td>4,4 $\cdot$ 10$^6$</td>
<td>3000</td>
<td>5 $\cdot$ 10$^9$</td>
<td>762</td>
</tr>
</tbody>
</table>

**TABLE IV**

Results of Hall measurements, ion implantation and oxygen analysis performed on semi-insulating chromium doped and chromium plus Ga$_2$O$_3$ doped crystals.
level EL2 was not related to oxygen. Chromium plus Ga$_2$O$_3$ co-doping improves the electrical properties of the material (see table V). For the same chromium concentration (ratio Cr/GaAs in the melt = $3 \times 10^{-4}$), addition of Ga$_2$O$_3$ increases the resistivity and the Fermi level energy, and decreases the EPD. This could be achieved by a decrease of the Si shallow donor during the growth, as reported by Jacob et al.$^{21}$). Ion implantation tests are also improved by chromium plus Ga$_2$O$_3$ co-doping (table IV).

Scattering on the pinch-off voltage $V_{po}$ is lowered and the N-profile fits very well the theoretical LSS profile (see fig. 14). According to table V, best results are obtained for a ratio Ga$_2$O$_3$/GaAs in the melt = $10^{-4}$. Higher ratio affects the crystallinity.

Special co-doping experiments have been performed to verify that the impurity responsible for the results obtained with chromium-doped ingots was silicon, e.g. doping with:
- chromium plus aluminium,
- chromium plus silicon,
TABLE V

Comparison between chromium doped and chromium plus Ga$_2$O$_3$ doped crystals

<table>
<thead>
<tr>
<th>No.</th>
<th>Cr/ GaAs weight in the melt</th>
<th>Ga$_2$O$_3$/ GaAs weight in the melt</th>
<th>$\rho$ ((\Omega) cm)</th>
<th>$\mu_H$ (cm$^2$/Vs)</th>
<th>$E$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>246 seed</td>
<td>$3 \cdot 10^{-4}$</td>
<td></td>
<td>$2 \cdot 10^6$</td>
<td>2600</td>
<td>720</td>
</tr>
<tr>
<td>485</td>
<td></td>
<td></td>
<td>$7.2 \cdot 10^{-4}$</td>
<td>3300</td>
<td>738</td>
</tr>
<tr>
<td>490</td>
<td></td>
<td></td>
<td>$4.6 \cdot 10^6$</td>
<td>3600</td>
<td>776</td>
</tr>
<tr>
<td>515</td>
<td></td>
<td></td>
<td>$2.1 \cdot 10^6$</td>
<td>3700</td>
<td>762</td>
</tr>
</tbody>
</table>

$\bar{\rho} = (2.36 \pm 1.36) \times 10^6$ $\bar{\mu} = 3200 \pm 500$ $\bar{E} = 749 \pm 25$

| 555 | $3 \cdot 10^{-4}$ | $10^{-4}$ | $4.4 \cdot 10^6$ | 3600 | 782 |
| 571 | $10^{-4}$ | | $3.4 \cdot 10^6$ | 3400 | 770 |
| 616 | $10^{-4}$ | | $4 \cdot 10^6$ | 3400 | 757 |
| 369 | $2 \cdot 10^{-4}$ | | $4.6 \cdot 10^6$ | 3000 | 766 |
| 437 | $2 \cdot 10^{-4}$ | | $4.4 \cdot 10^6$ | 3000 | 762 |

$\bar{\rho} = (4.16 \pm 0.48) \times 10^6$ $\bar{\mu} = 3280 \pm 268$ $\bar{E} = 767 \pm 10$

— silicon plus gallium oxide Ga$_2$O$_3$,
— chromium plus silicon and gallium oxide Ga$_2$O$_3$.

Results are summarized in Table VI. In the case of Cr–Al and Cr–Si co-doping experiments, we increased the ratio Cr/GaAs to obtain semi-insulating material (respectively Cr/GaAs = 1.5 and $1.0 \times 10^{-3}$ instead of $2.5 \times 10^{-4}$ for a standard Cr doped semi-insulating).

Ion implantation tests showed poor results, very low activation efficiency, but decrease of the scattering of the pinch-off voltage for Cr–Al co-doping, and a profile tail for Cr–Si co-doping (fig. 14).

This last point agrees fairly well with the assumption on the poor results obtained with ion implanted Cr substrates related to Si contamination$^{21}$).

3.4. Thermal stability

Systematic heat treatment experiments previously defined (see 2.2(d)) have permitted to point out major topics of the thermal conversion phenomena:
## TABLE VI

Results of special doping experiments: Cr–Al, Cr–Si, Si–Ga$_2$O$_3$ and Cr–Si–Ga$_2$O$_3$

<table>
<thead>
<tr>
<th>ingot</th>
<th>Cr/GaAs</th>
<th>Si/GaAs</th>
<th>Ga$_2$O$_3$/GaAs</th>
<th>Al/GaAs</th>
<th>Hall measurements at 400 K</th>
<th>analysis by activation at cm$^{-3}$</th>
<th>ionic implantation test pinchoff voltage $V_p$ (V)</th>
<th>observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>449 seed</td>
<td>6,25·10$^{-4}$</td>
<td>2,5·10$^{-5}$</td>
<td>5,5·10$^{-2}$</td>
<td>3600</td>
<td>3,5·10$^{18}$</td>
<td>771</td>
<td>2,9 ± 0,1</td>
<td>gaussian profile</td>
</tr>
<tr>
<td>492 seed</td>
<td>1,5·10$^{-3}$</td>
<td>9·10$^{-5}$</td>
<td>900</td>
<td>1,2·10$^{16}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>589 seed</td>
<td>5,8·10$^{-4}$</td>
<td>1,8·10$^{-1}$</td>
<td>3100</td>
<td>19$^{10}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>427 seed</td>
<td>6·10$^{-4}$</td>
<td>2,9·10$^{-2}$</td>
<td>3800</td>
<td>5,7·10$^{18}$</td>
<td></td>
<td>752</td>
<td>C 6.1·10$^{16}$</td>
<td>profile tail</td>
</tr>
<tr>
<td>473</td>
<td>1,25·10$^{-5}$</td>
<td>5·10$^{-4}$</td>
<td>3300</td>
<td>4,5·10$^{9}$</td>
<td></td>
<td></td>
<td>Si 1,7 to 2·10$^{16}$</td>
<td></td>
</tr>
<tr>
<td>487 tail</td>
<td>1,5·10$^{-5}$</td>
<td>4,6·10$^{3}$</td>
<td>4200</td>
<td>3,4·10$^{11}$</td>
<td></td>
<td>683</td>
<td></td>
<td></td>
</tr>
<tr>
<td>404</td>
<td>3·10$^{-4}$</td>
<td>7·10$^{-6}$</td>
<td>3,2·10$^{6}$</td>
<td>3600</td>
<td>6·10$^{9}$</td>
<td>766</td>
<td>Si 5 to 7·10$^{16}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O 2·10$^{16}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C 1,5·10$^{16}$</td>
<td></td>
</tr>
</tbody>
</table>
Properties of semi-insulating gallium arsenide grown by the Bridgman method

Fig. 15. High temperature Hall effect for a converted material. Plot of resistivity \( \rho \), Hall mobility \( \mu_H \) and concentration versus reciprocal temperature \( T^{-1} \).

(a) the converted layer is usually \( p \)-type, sometimes \( n \)-type, with a carrier concentration ranging in the \( 10^{16} \) cm\(^{-3} \). Figure 15 shows Hall effect measurements versus temperature performed on as-grown ingots and after annealing,

(b) photoluminescence spectra at 4 K on converted layers exhibit supplementary lines at 1.409 eV\(^{22} \) with four phonon replicas as compared to as grown material (fig. 16),

(c) conversion phenomena are strongly related to annealing conditions (temperature, time, carrier gas).

— The conversion phenomena increase when annealing under hydrogen carrier gas, decrease under argon, and disappear when chlorine\(^* \) is introduced into the furnace.

\(^* \) Introduction of chlorine into the furnace simulates the in-situ etching of the epitaxial reactor before growth of the active layer.
The conversion phenomena follow roughly a diffusion-like law. Using an etching technique, we have found that the thickness of the converted layer is given by the relation

\[ e = \sqrt{D \tau} \quad \text{with} \quad D = D_0 \exp \left( -\frac{E}{kT} \right). \]

Fig. 17 shows the diffusion coefficient variation versus reciprocal temperature \( T^{-1} \).

(d) \( Si_3N_4 \) capping decreases but does not suppress the conversion phenomena when they appear.

Assumptions on the origin of the conversion phenomena are still a subject of controversy, as it can be related to arsenic or gallium vacancies (Chiang and Pearson\(^{23}\)), or an arsenic vacancy-impurity complex, such as Si-VA\(_s\) (Itoh et al.\(^{24}\)) or C-VA\(_s\) (Lum et al.\(^{25}\)). On the other hand, PL spectra on converted material are very close to those obtained on Mn doped MBE layers (Ilegems et al.\(^{26}\)). Moreover, recent work on the Cr out-diffusion in implanted layers gives a diffusion coefficient \( D = 6.3 \times 10^5 \exp(-3.4) \) eV kT\(^{-1}\) cm\(^2\)s\(^{-1}\) after Kasahara et al.\(^{27}\). Our results are just laying between this value and the diffusion coefficient mentioned by Wolfstirn\(^{28}\) say \( D_{Cr} = 4.3 \times 10^3 \exp(-3.4) \) eV kT\(^{-1}\) cm\(^2\)s\(^{-1}\). This may suggest that Cr out-diffusion could be involved in the
Properties of semi-insulating gallium arsenide grown by the Bridgman method

Fig. 17. Variation of diffusion coefficient deduced from etching experiments on converted substrate (assuming that conversion phenomena follow a diffusion-like law).

thermal conversion phenomena. However, impurity contamination (related to manganese) may also arise during crystal growth or annealing experiments.

4. Conclusions

Major aim of the work was to improve the quality of semi-insulating HB grown GaAs substrates for ion implantation and epitaxial growth. A four levels compensation model and the Shockley diagram were used to understand electrical properties of semi-insulating Cr-doped or undoped materials. We have assumed that high purity starting materials would permit the reduction of the Cr concentration necessary to obtain semi-insulating material.

Studies on undoped ingots have shown that material properties are related to the nature of the boat. The choice of silica cloth coated silica boat is a good
compromise between crystalline and electrical properties.

Chromium doped semi-insulating ingots exhibit a scattering of electrical and crystalline properties — 400 K resistivity and Hall mobility, EPD — between seed to tail of ingots and top to bottom of same wafer, which are related to the chromium segregation coefficient and growth conditions.

Evidence of Si contamination in the case of poor results obtained by ion implantation in Cr-doped substrates has been pointed out. Chromium plus gallium oxide co-doping overcomes this difficulty.

Annealing experiments on a semi-insulating chromium-doped substrate have shown that the thermal conversion phenomena follows a diffusion-like law \[ D = 1.03 \times 10^4 \exp(-3.38 \text{ eV} kT^{-1}) \text{ cm}^2 \text{s}^{-1} \] which is close to the Cr-diffusion coefficient reported by other authors. However, impurity contamination (related to manganese) could arise during crystal growth or annealing experiments.

Acknowledgements

The author is indebted to Mr. J. P. Hallais for his encouragement and support throughout this work. He would also acknowledge Messrs Poiblau and Kleinahns from RTC Caen for supplying ingots, Mrs. A. Mircea-Roussel for photoluminescence studies, and Mr. G. M. Martin for chromium concentration measurements by infrared absorption, DLTS and OTS electrical assessment.

This work was partly supported by D.G.R.S.T. (contracts number 74-17-429 and 75-70-665) and D.R.E.T. (contract number 78-34-378).

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REFERENCES


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