On Compensation and Conductivity Models for Molecular-Beam-Epitaxial GaAs Grown at Low-Temperature

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On compensation and conductivity models for molecular-beam-epitaxial
GaAs grown at low temperature

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Molecular-beam-epitaxial GaAs grown at 200 °C has an extremely high (> 10¹⁹ cm⁻³)
concentration of AsGa defects and, after an anneal at 550–600 °C, a high concentration of As
precipitates. The relative roles of the AsGa defects and As precipitates in compensation
and conductivity is controversial. Here criteria are developed to distinguish between two
existing models.

I. INTRODUCTION

Molecular-beam-epitaxial (MBE) GaAs is normally
grown at temperatures of 580–600 °C and, at these temper-
atures, it is relatively routine to attain shallow donor N_D
and acceptor N_A concentrations in the 10¹⁴ cm⁻³ range,
and even smaller deep donor (N_DD) and acceptor (N_AA)
concentrations. Recently, however, Smith et al.¹ showed
that MBE GaAs grown at 200 °C had many different prop-
eties, and that when used as a buffer layer could remark-
ably improve some critical characteristics of GaAs metal-
semiconductor field-effect-transistor (MESFET) devices;
since then many groups have studied the application of this
material to a variety of other devices.²⁻⁶ The outstanding
characteristic of low-temperature-grown MBE (LTMBE)
GaAs is a large excess of As (1%–2%), which leads to a
depth donor (AsGa) related concentration N_DD > 10¹⁹
cm⁻³ and, after a 600 °C anneal, large (~60 Å), dense
(~10¹⁷ cm⁻³) precipitates of As.⁷⁻¹³ The point of this
paper is to discuss some controversial aspects of how these
two entities affect the compensation and conductivity of
LTMBE GaAs.¹⁰⁻¹²

II. THE POINT DEFECT (“STANDARD”) MODEL

Look et al.¹⁰ have proposed a model in which the com-
penstation is accomplished in exactly the same way as that
in semi-insulating (SI) GaAs, but in which the conductivity
involves an additional component, i.e., carrier hopping
between the EL2 like centers. Others have proposed simi-
lar models, although less extensive and differing in some
details.¹⁴⁻¹⁵ The compensation of SI GaAs is well explained
by a simple charge-balance equation:¹⁶

\[ n + (N_A + N_AA - N_D) \]

\[ = \frac{N_{DD}}{1 + \left(\frac{g_1}{g_0}\right)\left(\frac{n}{N_C}\right)e^{E_{DD}/kT}} \]

\[ = \frac{N_{DD}}{1 + \left(\frac{g_1}{g_0}\right)\left(\frac{n}{N_C}\right)e^{-\alpha c_{DD}/kT}}, \tag{1} \]

where \( N_C = 2(2\pi m^* k)^{3/2} T^{3/2}/\hbar^3 \), the effective conduction-band density of states. Also, \( E_{DD} = E_{DDo} - \alpha T \) with \( E_{DDo} = 0.748 \text{ eV}, \alpha = 3.3 \times 10^{-4} \text{ K}^{-1} \), and \( g_1/g_0 = 2 \) for

the deep donor EL2 (\( N_{DD} = [\text{EL2}] \)). Because \( E_{DDo} \) is so
large, the “low-temperature” form of Eq. (1) holds up to
about 600 K:

\[ n = \frac{\left(\frac{N_{DD}}{N_{DDo}}\right) - 1}{C_1^T^{3/2}e^{-E_{DD}/kT}}, \tag{2} \]

where \( N_{DD}^* = N_A + N_AA - N_D \) and \( C_1 = 1.85 \times 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2} \). Typical values of \( N_{DD} \) and \( N_A \) for SI
GaAs grown by the liquid-encapsulated Czochralski (LEC) method are \( 1 \times 10^{16} \) and \( 1 \times 10^{15} \text{ cm}^{-3} \), respectively,
giving \( n \sim 1.5 \times 10^{17} \text{ cm}^{-3} \). Usually \( N_{DD}^* \sim [\text{C}], \) and
since \( n, [\text{C}], \) and \([\text{EL2}] \) can all easily be measured by in-
dependent techniques (n by Hall effect, [C] and [EL2] by
absorption spectroscopy), the validity of Eq. (2) for un-
doped, SI GaAs is well documented and is fully accepted
by workers in the field.¹⁶⁻¹⁹ [Minor questions, such as
whether native-defect acceptors are comparable to carbon
in importance, do not detract from the overall applicability
of Eq. (2).] For LTMBE GaAs, the model of Ref. 10 again
assumes the validity of Eq. (2), but with a much higher
value of \( N_{DD} \), namely, \( 3 \times 10^{18} \text{ cm}^{-3} \) for material grown at
200 °C and not annealed. This number is confirmed by
1.1-µm absorption measurements, the same technique used
for [EL2] determination.⁵ After annealing at 550 °C, the
number decreases to about \( 3 \times 10^{16} \text{ cm}^{-3} \).

The conductivity \( \sigma \) and Hall coefficient \( R \) in LTMBE
GaAs are intimately connected with the compensation
mechanism, because the conduction-band contribution to \( \sigma \)
is just \( \sigma_1 = en\mu_1 \), where the mobility \( \mu_1 \) is mainly due to
scattering from neutral deep donors, and the Hall coeffi-
cient contribution is \( R_1 = 1/en. \) However, as mentioned
earlier, there is another contribution to the conductivity,
because the close spacing between the \( 3 \times 10^{18} \text{ cm}^{-3} \) deep
donors promotes carrier hopping. As discussed in Ref. 10,
the hopping conductivity at room temperature and above is
given by

\[ \sigma_2 = C_2 e^{-\frac{\gamma}{a\alpha c_{DDo}} - \epsilon_i/T}, \tag{3} \]

where \( C_2 \) and \( \gamma \) are constants, \( a \) is the extent of the deep-
donor (AsGa) wave function, and \( \epsilon_i \) is the difference be-
tween the isolated donor energy and the Fermi energy.
However, hopping conductivity leads to a vanishing Hall
coefficient, so that \( R_2 = 0. \) Then the combined conductivity
and Hall coefficient equations are¹⁶

\[ \sigma = \sigma_1 + \sigma_2, \tag{4} \]
By changing only the parameter $N_{DD}$, this model fits both the $\sigma$ vs $T_m$ and $R$ vs $T_m$ ($T_m$ is measurement $T$, not annealing $T$) data very well for $T_m = 300-400$ K (the only range measured), as a function of sample annealing temperature, $T_a = 250-550$°C. Note that the value of $R$ at $T_m = 300$ K covers nearly eight orders of magnitude over this range of $T_a$.

Thus, there can be little doubt concerning the basic validity of the conductivity/compensation model given in Ref. 10. However, that is not to say that all of the fitted parameters are firmly established, or are in agreement with the results of other experiments. In particular, consider $N_{A}^{\text{net}}$. The data of Ref. 10 are well fitted, over the entire range $T_a = 200-550$°C, by the value $N_{A}^{\text{net}} = 10^{15}$ cm$^{-3}$. This value makes some sense because it is about the expected concentration of C, and C is also observed in photoluminescence data. Furthermore, passivation experiments with 1000-Å, 200°C cap layers are consistent only with $0 < N_{A}^{\text{net}} < 1 \times 10^{16}$ cm$^{-3}$ or else $N_{A}^{\text{net}} < 0$.20 However, such a low $N_{A}^{\text{net}}$ is in apparent disagreement with EPR experiments carried out in similar unannealed samples7,8 which give $[\text{As}^3_+]/N_{A}^{\text{net}} = 5 \times 10^{18}$ cm$^{-3}$. (In annealed samples, $[\text{As}^3_+]$ is below the EPR sensitivity limit, about $1 \times 10^{18}$ cm$^{-3}$ in thin layers, and thus could possibly be in agreement with the Hall value of $N_{A}^{\text{net}}$.) Although this discrepancy is serious and is not resolved yet, we offer one possible solution here. Because of sensitivity problems, the EPR experiments have been performed in relatively thick samples, $d \geq 2$ μm. On the other hand, it is also known that the 200°C samples become polycrystalline, and form large pyramidal defects for $d \geq 2$ μm.21,22 It is possible that such massive defects, or also perhaps grain boundaries, surfaces, and interfaces, are decorated with rather shallow acceptor impurities or defects, such as $V_\text{Ga}$, which would then attract electrons from the $\text{As}^0_\text{Ga}$, forming $\text{As}^+_\text{Ga}$. This picture is, of course, entirely equivalent to the "depletion" process, operative with metal Schottky barriers or with surface states on conductive layers [see the discussion following Eq. (8), below]. If about 15% of the $\text{As}_\text{Ga}$ volume were thus affected, then the EPR experiment could be explained by the $\text{As}^+_\text{Ga}$ near the large defects or grain boundaries, while the conductivity would take place in the other 85% of the sample, which would presumably have a small $N_{A}^{\text{net}}$ and thus contain mostly $\text{As}^0_\text{Ga}$. An obvious experiment that would shed light on this issue would be to carefully measure both the Hall and EPR concentrations on the same samples as a function of sample thickness to see if the heavily defected regions produce more $\text{As}^+_\text{Ga}$.

### III. THE AS-PRECIPITATE MODEL

We now consider another point of contention, i.e., the role of the As precipitates in compensation and conductivity. Warren et al.12 have offered the interesting suggestion that the high resistivity of the samples grown at 200°C and annealed at 600°C is due to overlapping of the depletion regions formed between the metallic As clusters and the "conductive" bulk. They have even suggested that the SI nature of common LEC GaAs substrates could be explained by the same mechanism. This latter assertion can be strongly refuted, as explained below, but the former merits careful consideration. We will consider, in order, the effect of the precipitates on SI GaAs, undoped LTMBE GaAs, and doped LTMBE GaAs.

The problem with applying the As-precipitate model to standard SI GaAs substrate material, grown by the LEC method, is twofold: (i) There simply aren't enough precipitates to deplete a significant fractional volume; and (ii) the standard compensation model [Eqs. (1) and (2)] works very well and can be verified by independent experiments. In regard to the first point, Martin et al.23 have summarized the annealing data of several groups and found that, for common annealing temperatures between 800 and 950°C, As precipitates range in size $2r_0$ from 1000 Å to 2000 Å, and concentration $N_p \leq 10^{17}$ cm$^{-3}$. By using the maximum $r_0$ (1000 Å), maximum potential difference $\Delta V$ (0.7 V), maximum $N_p$ ($10^9$ cm$^{-3}$), and minimum $N_{DD}$, $N_D$, or $N_A$ ($1 \times 10^{15}$ cm$^{-3}$), Eqs. (6)–(8) in the following section give a depleted fraction $f < 0.001$. Thus, the As-precipitate model cannot explain the semi-insulating nature of the most common type of SI GaAs. In regard to the second point, above, the standard compensation model can be independently checked for validity. For example, $N_{DD}$ (i.e., $[\text{EL}2]$) is well calibrated with the 1.1-μm electronic absorption, $N_{\text{As}}^{\text{net}}$ (mostly C) with 582-cm$^{-1}$ local-vibrational mode (LVM) absorption or with secondary-ion mass spectroscopy SIMS, and $n$ with Hall-effect measurements. Such measurements have been carried out in our own laboratory and in those of others, and have confirmed the validity of Eq. (2).18,19 In simpler terms, if $N_{\text{As}}^{\text{net}} > 0$, and $[\text{EL}2]$ (i.e., $N_{DD}$) $> N_{\text{As}}^{\text{net}}$, then the Fermi level $E_F$ will be near midgap, whether or not there are As precipitates. Since the Schottky barrier energy due to As is also about one-half the gap energy, there will be little or no potential difference between the metal and bulk, and thus almost no depletion in the region of the precipitates. Therefore, the model presented by Warren et al. cannot apply to standard SI GaAs.

We will next apply the As cluster model to LTMBE GaAs layers. Warren et al.12 have found that a layer grown at 200°C and annealed for 10 min. at 600°C contains As precipitates of concentration $N_p$ about $10^{17}$ cm$^{-3}$, and average radius $r_0$ of about 30 Å. We will use these same numbers for purposes of illustration, in spite of the fact that different growth conditions will likely lead to different concentrations and sizes. The idea proposed by Warren et al. is that a metallic As cluster will form a Schottky barrier and pin $E_F$ at about $E_C - 0.8$ eV in $n$-type material, and $E_V + 0.6$ eV in $p$-type material. A charge $Q$ will deposit on the metallic sphere in order to balance this barrier. Gauss' law for a sphere of radius $r_0$ gives

$$Q = 4 \pi r_0^2 \Delta V,$$

where $\Delta V$ is the difference in potential between the metal surface and the semiconductor bulk. For an undoped LTMBE layer, this charge will have to come from the
EL2-like deep donors (there are very few shallow donors), and leave a positively charged sphere of radius \( r_d \) concentric with each metallic sphere. The radius \( r_d \) can be found from the condition of charge balance around each sphere:

\[
(4\pi/3)(r_d^3 - r_0^3)eN_{DD} = Q.
\]

The fraction of sample volume filled by these depleted spheres of radius \( r_d \) is then

\[
f \approx (4\pi/3)r_d^2N_p
\]

From the data of Ref. 10, for an anneal temperature of 550 °C, the fitted parameters are \( N_{DD} = 3 \times 10^{18} \text{ cm}^{-3} \) and \( N_A = 7 \times 10^{14} \text{ cm}^{-3} \) so that from Eq. (2), \( n \approx 7.4 \times 10^{13} \text{ cm}^{-3} \), or \( E_F \approx E_C - 0.45 \text{ eV} \). (For Si GaAs, \( E_F \approx E_C - 0.6-0.7 \text{ eV} \), because \( N_{DD} \) is much lower.) Therefore, \( \Delta V = 0.35 \text{ V} \), giving \( Q = 9e \) [from Eq. (6)], \( r_s \approx 90 \text{ Å} \) [from Eq. (7)], and \( f \approx 0.3 \) [from Eq. (8)]. Thus, about 30% of the sample volume would be filled with these insulating spheres. However, it should be remembered that the annealed material would be highly resistive to begin with (\( \sigma = ne\mu \approx 10^{-5} - 10^{-6} \Omega^{-1} \text{ cm}^{-1} \)), without any precipitates, so that the effect of the precipitates in undoped LTMBE material, with \( N_A > 0 \) and \( N_{DD} > N_A^{\text{net}} \), is minimal. If \( N_p \) were higher, so that the depleted spheres did overlap and pinned \( E_F \) between \( E_C - 0.8 \text{ eV} \) and \( E_V + 0.6 \text{ eV} \), then the sample would be \( p \) type, contrary to experiment. Furthermore, it can easily be shown that the maximum \( \sigma \) in this case would be about \( 4 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1} \), two orders of magnitude lower than observed. (Note that hopping conduction is negligible for samples that have experienced an annealing temperature \( T_a > 500 \text{ °C} \).

It is also of interest to look at the effect of the As precipitates on transport properties. Because the depleted spheres have very low carrier concentration (since \( E_F \) is near midgap), and because they have an electric field that opposes carrier penetration, they can be modeled as spheres with vanishing conductivity imbedded in a host having conductivity \( \sigma \) and mobility \( \mu \). In this limit, Voronkov et al.\textsuperscript{24,25} find that

\[
\sigma_{\text{meas}} = \sigma(1 - f), \quad (9)
\]
\[
\mu_{\text{meas}} = \mu \left[ (1 - f^2)/(1 - f) \right]. \quad (10)
\]

For \( f \approx 0.3 \), \( \nu_{\text{meas}} \approx 0.55\nu \) and \( \mu_{\text{meas}} \approx 0.6\mu \). However, a problem immediately arises here. Suppose we measure \( \mu \) at 400 K to minimize hopping conduction with respect to band conduction; then the maximum possible \( \mu_{\text{meas}} = 0.6(5600) \approx 3400 \text{ cm}^2/\text{V s} \), since the lattice-limited mobility at 400 K is about 5600 cm\(^2\)/V s.\textsuperscript{16} However, Look et al.\textsuperscript{10} found that \( \mu \) (400 K) \( \approx 3800 \text{ cm}^2/\text{V s} \), and this includes strong scattering from the neutral \( N_{DD} \). It follows therefore that \( f < 0.3 \).

A final observation on mobility concerns the fact that, if the As precipitates are responsible for the high resistivity of annealed material, then the mobility should go through a strong minimum as the depleted spheres just begin to overlap, requiring percolated conductivity between the remaining conductive pockets. Warren et al.\textsuperscript{12} noted this fact also. This mobility decrease is in addition to the one described by Eq. (10). However, a strong decrease in mobility as a function of annealing temperature is not found in the samples of Ref. 10. In fact, the exact opposite occurs.

**IV. CONCLUSIONS**

The following criteria can then be used to determine if As precipitates are affecting the compensation or conductivity of undoped LTMBE GaAs.

(i) If \( N_{DD}^{\text{net}} > 0 \) and \( N_{DD} > N_A^{\text{net}} \), then the sample will already be highly resistive, with \( \sigma \approx 10^{-5} \text{ cm}^{-1} \), and the sample will be semiconducting.

(ii) If As precipitates are overlapping and pinning \( E_p \) between \( E_V + 0.6 \text{ eV} \) and \( E_C - 0.8 \text{ eV} \), then \( \sigma \) should be lower than \( 10^{-1} \text{ cm}^{-1} \), and the sample will be weakly \( p \) type.

(iii) As a function of annealing temperature \( \sigma \) will decrease monotonically due to the loss of hopping conduction, the decrease of \( N_{ULB} \), and the increase of volume occupied by the As precipitates. However, \( \mu \) should drop sharply as the depleted spheres begin to overlap, because then percolated conductivity will be necessary, but \( \mu \) should rise again when the whole sample is uniformly semi-insulating. Thus, \( \mu \) should go through a strong minimum as a function of \( T_a \).

By comparing these criteria with the data of Ref. 10, it is clear that As precipitates are not greatly influencing the compensation or conductivity. Other sets of data will have to be examined individually to determine if the precipitates are important.

Finally, we want to examine the effect of As precipitates on doped LTMBE layers. It is known that the doping of MBE GaAs grown at low temperature is very difficult. We have attempted to dope 200 °C-grown material with \( 2 \times 10^{17} \text{ cm}^{-3} \) Si, but the conductivity is about the same as that of undoped material, dominated by hopping in the deep-donor band.\textsuperscript{26} Since the Si is definitely present in these samples, as shown by SIMS, it is either not activated (i.e., not present in the form of Si\textsubscript{GaAs}), or it is fully compensated by acceptors (\( N_A^{\text{net}} > 0 \)), or it is compensated by As precipitates. However, it is doubtful that As precipitates exist at all in unannealed material, because they are not seen by TEM.\textsuperscript{11} We next note that a 600 °C anneal, which will produce the precipitates, does not produce a conductive sample.\textsuperscript{26} To explain this, it is theoretically possible that the anneal activates the Si, and that the precipitates then compensate the Si; however, no annealing experiments that we have carried out give any indication that the Si activates. A final point is that there is evidence (from EPR) that acceptors in the mid-10\(^{18}\) cm\(^{-3}\) concentration range can exist in 200 °C unannealed material, which would give \( N_{DD}^{\text{net}} > 0 \) even in the presence of \( 2 \times 10^{17} \text{ cm}^{-3} \) Si. However, it is also argued by the same researchers that these acceptors anneal out at 600 °C (Ref. 7); therefore, they could not compensate the Si in annealed material. From these considerations, we believe that our doping experiments are explained by the nonactivation of Si, rather than by compensation due to As precipitates or...
by other acceptors. However, other doping experiments that do not produce conductivity may be consistent with one of these other cases.

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