CHAPTER - III

GALLIUM VACANCY DIFFUSION MODEL FOR ALLOYED OHMIC CONTACTS TO GaAs

INTRODUCTION

Alloying technique is extensively being used for formation of ohmic contact to GaAs and other compound semiconductors (1-8). However, this method, which even now is the basis of the device fabrication, is still accepted as a technical art because the thermally induced interactions, during alloying of a metal to the semiconductor, are complex and not well understood.

Over the past 15 years many in-situ and post annealed microscopic investigation techniques (9-23) have emerged which have provided a pretty good picture of the metal-semiconductor interface and of the alloyed region. The Au:Ge:Ni-n GaAs system has particularly been studied thoroughly, and this has generated a voluminous literature wherein the electrical and metallurgical investigations are described. However for the major part, the investigations have been for the determination of compositional profiles in complex multi-component film structures undergoing diffusion anneals. This in brief indicates that although a large amount of electrical and physical data have been acquired, nevertheless the detailed alloying mechanism of the system is yet to be established.

The published theoretical studies (24-31) predict that one should be able to obtain contacts of infinitesimal resistance by increasing the doping in the surface layer. But the reported values of the resistance of alloyed AuGeNi-n GaAs contact (2,4,7, 18-20) are not small. The pheno-
menon limiting the minimum value of the contact resistivity and the reason for increase in resistance for annealing beyond optimum temperature are thus required to be investigated to explain the alloying behaviour.

In this chapter an attempt is made to construct a new model that is capable of rationalising the features cited above and provides the necessary foundation for a unified understanding of the previous results. The model is described in the next section and section 3 is devoted to estimate (i) gallium vacancy concentration, following Whipple's theory and (ii) the donor concentration, using thermodynamical results. The experimental data of contact resistance are presented in section 4 and the results are discussed in section 5. Finally, the conclusions are summarised in the last section 6 of the chapter.

3.2 GALLIUM VACANCY DIFFUSION MODEL

Many hypotheses (2,6,7, 33-38) have been conceived to interpret ohmicity of an alloyed metal-semiconductor barrier. A typical measured characteristics of an alloyed AuGeNi-n GaAs (39) is represented by the dashed curve in Fig. 3.1, and this describes the trend generally observed in most of the cases (1,16,18,36,38,40). The solid curves in the figure represent theoretical calculations (41) based on Popovic's theory (31). The low temperature annealing behaviour of this system has been understood quite satisfactorily (2,19,32,33) on the basis of a tunneling mechanism, but the phenomenon limiting the minimum value of the resistance and its tendency to rise at higher alloying temperature are not yet clear. In this section we propose a new model which elucidates these two aspects.

On the basis of findings in the previous chapter and the established results available in the literature, following assumptions are made to construct the model:
FIG. 3.1 OBSERVED RESISTIVITY OF AN ALLOYED AuGeNi-n GaAs SYSTEM (39). SOLID CURVES REPRESENT CALCULATED VALUES OF DONOR CONCENTRATION IN THE SEMICONDUCTOR SURFACE LAYER.
(i) During annealing, gallium atoms from the semiconductor diffuse into grain boundaries of gold, creating gallium vacancies in the crystal surface (20,42,43).

(ii) In the low temperature annealing range, arsenic loss is insignificant (13,14,20,23,42,44), and the dominating centers are donors that are formed by substitution of germanium on gallium sublattice sites (7,8,14,16,45,46).

The notations we are going to use in the proceeding discussion are the same as defined by Hurle (45). Defects are represented by symbols, atoms being represented by their normal chemical symbol, vacancies by V. Subscripts indicate the lattice site, characterized by the atom normally occupying that site. Thus \( V_A \) is a vacancy at an A site. Interstitial sites are indicated by a subscript \( i \), \( A_i \) being A at an interstitial site. For example \( V_{Ga} \), \( Ga_i \) and \( Ga_{As} \) represent vacancy on gallium lattice site, gallium at an interstitial site and gallium at the arsenic site (i.e. antisite defect) respectively. The superscripts + and - denote positive and negative structure elements respectively. Electrons are indicated by e and holes by h.

The detailed behaviour of heat treated n-GaAs is known to be complex (45,47,48). The reactions for the formation and ionisation of Frenkel defects are given by (45, 47).

\[
\begin{align*}
As_{As} + V_i & \iff V_{As} + As_i \quad (3.1) \\
Ga_{Ga} + V_i & \iff V_{Ga} + Ga_i \quad (3.2) \\
V_{As} & \iff V_{As}^+ + e^- \quad (3.3) \\
V_{Ga} & \iff V_{Ga}^- + h^+ \quad (3.4)
\end{align*}
\]

When an AuGeNi-coated n-GaAs is heated, the semiconductor dissociates (13, 49-51) and for temperatures below Au:Ge eutectic point we have

\[
\begin{align*}
[V_{Ga}] & = [Ga_i] \quad (3.5) \\
[V_{As}] & = [As_i] \quad (3.6)
\end{align*}
\]
Arsenic evolution has been assumed to be insignificant, and also gallium exchange with gold centers does not initiate in this temperature range.

For the alloying above the eutectic temperature, gallium and germanium atoms become more mobile. Gallium diffuses into boundaries of gold grains forming an AuGa layer (4,14,19,20,52) at the interface, and germanium incorporates into lattice sites forming donors (7,8,14,16,46,53-55) and acceptors (45, 53).

\[
\begin{align*}
V_{Ga} + Ge &\rightarrow Ge_{Ga}^+ + e^- \quad (3.7) \\
V_{As} + Ge &\rightarrow Ge_{As}^- + h^+ \quad (3.8)
\end{align*}
\]

According to Hurle's (45) postulates, some of the donors recombine with gallium vacancies and germanium substituted arsenic states to form vacancy acceptors \([Ge_{Ga} V_{Ga}^-]\) and neutral pairs \([Ge_{Ga} Ge_{As}^-]\), respectively, via reactions

\[
\begin{align*}
V_{Ga}^- + Ge_{Ga}^+ &\rightarrow Ge_{Ga} V_{Ga}^- + h^+ \quad (3.9) \\
\text{and } Ge_{As}^- + Ge_{Ga}^+ &\rightarrow Ge_{Ga} Ge_{As} \quad (3.10)
\end{align*}
\]

Therefore, the net donor concentration in the crystal is given by

\[
N_D - N_A = [Ge_{Ga}^+] - [Ge_{Ga} V_{Ga}^-] - [Ge_{As}^-] \quad (3.11)
\]

Since the arsenic loss is not substantial up to the optimum alloying temperature, the density of \(Ge_{As}^-\) is not large, and therefore the net effect is donor-type doping in the semiconductor. As has been observed in case of GaAs-Au system in section 2.3, with increase in the annealing temperature dissolution of gallium into gold increases. This increases the gallium vacancy concentration in the semiconductor surface, which in turn increases the donors at the interface, following reaction (3.7).

When the annealing reaches a critical value, at which the AuGa layer gets saturated with gallium, further out-migration of Ga from the
gallium arsenide is prevented by this layer, even if the temperature is increased. This influence of gallium in a gold film has been seen in the ESCA results discussed in the section 2.7 and is supported by the published report (56, 57). Therefore, the formation of a gallium saturated AuGa layer at the interface, obviously causes an increase in the density of interstitial gallium, as there is no sink for them. Under this condition, we may therefore surmise that the interstitials annihilate the acceptor complex to restore the donor state:

$$\text{Ge}_\text{Ga} V_{\text{Ga}}^- + \text{Ga}_i^+ \rightarrow \text{Ge}_\text{Ga}^++e^-$$  \hspace{1cm} (3.12)

Beyond the optimum point, significant arsenic loss (13,23,49,58,59) creates considerable number of arsenic vacancies to form acceptors according to eqn. (3.8), which thus compensate the donors.

The donor formation reactions (3.7) and (3.12) suggest a rise in donor concentration with alloying temperature, since the generation of gallium vacancies $V_{\text{Ga}}$ and interstitials $\text{Ga}_i$ increase with temperature. Although some of the donors are lost by formation of neutral pairs $\text{Ge}_\text{Ga}^+\text{Ge}_\text{As}^-$, nevertheless, increase in its concentration is expected to continue until arsenic loss is significant. We suggest that at an optimum temperature at which the arsenic evolution is so large that the acceptor formation rate begins to exceed that of the donors, the donor doping attains a maximum level, which is proportional to the amount of gallium vacancies created in the semiconductor at that temperature. For annealing above the optimum temperature, due to excessive arsenic loss, the arsenic vacancy generation exceeds the gallium vacancy concentration and thus diminishes donor doping due to subsequent formation of acceptors and neutrals according to eqns. (3.8), (3.10) and (3.11). The model thus explains the behaviour of donor formation depicted in Fig. 3.1, on the basis of vacancy dependent phenomena in the alloyed AuGeNi-n GaAs system.
3.3 THEORY

To interpret the experimental data on contact resistivity by the proposed model, the quantitative estimation of gallium vacancy concentration and donor density is necessary. In this section we employ Whipple's theory of grain boundary diffusion (20, 60) and the thermodynamical results of Hurle (45) to compute these quantities.

3.3.1 GALLIUM VACANCY CONCENTRATION

A number of studies have analysed interdiffusion in thin metal films (61-66) using Whipple's theory of grain boundary diffusion. Poate et al. (62) have demonstrated a novel procedure to estimate solute concentration in grain boundaries in such a case. This has recently stimulated great interest in the detailed understanding of degradation mechanisms in silicon devices (61, 67). For the first time in the present study, we employ the Whipple theory to study gallium diffusion in gold grain boundaries using the diffusivity data obtained in the Chapter II. We adopt the procedure of Ref. (62) to estimate the quantity of gallium which has diffused into gold grains.

The Whipple expression for grain boundary diffusion is given by (41,60, 68,69).

\[ D_B \delta = \left( \frac{\partial \ln C}{\partial [X^{6/5}]} \right)^{-5/3} \left( \frac{4 D_L}{t} \right)^{1/2} (0.78)^{5/3} \]  (3.13)

Where \( D_B \) and \( D_L \) are grain boundary and lattice diffusivities, respectively, \( \delta \) is grain boundary width, \( C \) is the concentration at a depth \( X \) from the M-S interface, \( t \) is the time of anneal. Having obtained \( D_B \) from Fig. 2.7, \( C \) and \( X \) with the aid of Fig. 2.6 and assuming grain boundary width \( \delta = 5 \mu \) (61, 62), the lattice diffusivity \( D_L \) of gallium in gold is computed from Whipple's expression (3.13).

To estimate the amount of gallium diffused in gold grains, the grain boundary diffusion parameter (62) \( X_B = D_L (t/4a^2) \), for the optimum alloying temperature of 470°C and time = 60 sec. (39) is calculated. The concentra-
tion of gallium in gold for both cubic and columnar grains is determined from Fig. 3.2a (which is a reproduction of Fig. 10 of ref. 62) and results for different grain dimensions 2a are illustrated in Fig. 3.2b. For a 1000-Å gold particle size (61,62,70) the normalized gallium concentrations of 0.003 in cubic and 0.002 in columnar grains are obtained from the Fig. 3.2b.

Considering the gallium arsenide surface layer, which contains $2.21 \times 10^{22}$ atoms/cm$^{-3}$ (71), as a constant source of gallium for grain boundary diffusion (43) and assuming error function distribution, the above solute concentration corresponds to the doping of the order of $6 \times 10^{19}$ cm$^{-3}$ and $4 \times 10^{19}$ cm$^{-3}$ in cubic and columnar grains respectively. Therefore, the average gallium vacancy concentration, corresponding to the gallium amount that has diffused in gold grains of the overlying contacting layer, is of the order of $5 \times 10^{19}$ cm$^{-3}$.

3.3.2 DONOR CONCENTRATION

The model described in section 3.2 indicates that a part of the gallium vacancies generated in the crystal is occupied by germanium to give donors, and the rest are consumed in the formation of the donor-gallium vacancy complex $\text{Ge}^+ \text{Ga}^- \text{V}^-$ and neutral pairs $\text{Ge}^+ \text{Ga}^- \text{Ge}^- \text{As}^-$. According to Hurle (45), about 80% of the germanium is present in the form of neutral pairs. This suggests that out of $5 \times 10^{19}$ cm$^{-3}$ gallium vacancies, as deduced above, approximately $4 \times 10^{19}$ cm$^{-3}$ are lost in the formation of neutral pairs and the remaining $1 \times 10^{19}$ cm$^{-3}$ are used in generating donors $\text{Ge}^+ \text{Ga}^- \text{Ge}^- \text{As}^-$. With the aid of eqn. 3.11 and Hurle's results of compensation ratios, that are

$$\frac{[\text{Ge}^+ \text{Ga}^- \text{V}^-]}{[\text{Ge}^+ \text{Ga}^- \text{V}^+ \text{Ga}^-]} = 3 \quad \text{(3.14)}$$

and

$$\frac{[\text{Ge}^+ \text{Ga}^- \text{V}^-]}{[\text{Ge}^- \text{As}^-]} = 5.9$$
FIG. 3.2(a) The averaged solute concentration in a grain $f(X_B)$ as a function of the grain-boundary-assisted lattice diffusion parameter $X_B$ (Ref. 62).

FIG. 3.2(b) The averaged solute concentration in gold grain $c_{Au}$ versus grain size.
one can easily derive \( N_D = 6.6 \times 10^{18} \text{ cm}^{-3} \) in the present case. Therefore, for a gallium vacancy concentration of \( 5 \times 10^{19} \text{ cm}^{-3} \), the upper limit of donor formation is about \( 6.6 \times 10^{18} \text{ cm}^{-3} \).

### 3.4 SPECIFIC CONTACT RESISTIVITY

To obtain dependence of specific contact resistivity \( \rho_c \) on substrate doping \( N_D \), we used Popovic's expression (1.30) which has been described in section 1.4.2 of the chapter I. The calculated results are plotted in Fig. 3.3. Table 3-1 lists the numerical values of constants used in the calculations.

The measured minimum values of \( \rho_c \) of alloyed AuGeNi-n GaAs system, as reported by a number of studies, are also depicted in the figure. It is seen that the theoretical line corresponding to surface carrier concentration \( N_D = 5 \times 10^{18} \text{ cm}^{-3} \) and barrier height \( \phi_D = 0.4 \text{ eV} \) gives the best fit to the measured values. The scatter of measured data in the figure is probably due to different fabrication methods and measurement techniques used in these studies.

To correlate the contact resistivity with the surface concentration, for a measured value of resistivity, \( N_D \) is computed using Popovic's expression for \( \phi_D = 0.4, 0.6 \) and \( 0.8 \text{ eV} \) (41). This is represented by solid curves in the Fig. 3.1, which indicate that corresponding to \( \phi_D = 0.4 \text{ eV} \), at optimum alloying temperature of \( 470^\circ \text{C} \), the surface concentration \( N_D = 5 \times 10^{18} \text{ cm}^{-3} \). These results are very consistent with the published experimental values of \( N_D \) and \( \phi_D \), which are summarised in Table 3-II.

### 3.5 RESULTS & DISCUSSIONS

The experimental alloying characteristics of AuGeNi-n GaAs system have been depicted by the dashed curve in Fig. 3.1. The interface doping behaviour, represented by the solid curves in the figure, has been discussed
FIG. 3.3 OBSERVED CONTACT RESISTIVITY Vs BULK DOPING OF ALLOYED AuGeNi-n GaAs SYSTEM. LINES REPRESENT THEORETICAL CALCULATIONS USING POPOVIC'S THEORY (41). NUMBERS IN THE INSET IDENTIFY THE REFERENCE NUMBER OF THE CITED POINT.
### TABLE - 3-I

**NUMERICAL VALUES OF CONSTANTS FOR n-GaAs (T-300K)**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_c )</td>
<td>( 4.7 \times 10^{11} \text{ cm}^{-3} )</td>
<td>71</td>
</tr>
<tr>
<td>( m_t )</td>
<td>0.068 ( m_o )</td>
<td>30</td>
</tr>
<tr>
<td>( A^* )</td>
<td>8.0 ( \text{amp/cm}^2 \text{°K} )</td>
<td>30</td>
</tr>
<tr>
<td>( E_d )</td>
<td>11.0</td>
<td>27</td>
</tr>
<tr>
<td>( E_s )</td>
<td>12.5</td>
<td>27</td>
</tr>
</tbody>
</table>

### TABLE - 3-II

**ALLOYED CONTACTS TO n-GaAs**

<table>
<thead>
<tr>
<th>Metallization System</th>
<th>Alloying Temperature (°C)</th>
<th>Barrier Height (( \Phi_B )) (eV)</th>
<th>Carrier Concentration (cm(^{-3} ))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au:Ge:Ni</td>
<td>400</td>
<td>0.4</td>
<td>( 3 \times 10^{18} )</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.4-0.5</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Au:Ge</td>
<td>200</td>
<td>0.35</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.27</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.60</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>0.45</td>
<td>( 2 \times 10^{18} )</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.40-0.27</td>
<td>( 8 \times 10^{18} )</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.40</td>
<td>-</td>
<td>34</td>
</tr>
</tbody>
</table>
in the sec. 3.2. Following the concept of increase in barrier conductance with doping in semiconductor of a M-S junction, the interface doping variation, evidently, explains the observed mirror image behaviour of the annealing characteristics. At the optimum point, the minimum in contact resistivity corresponds to a maximum value of the donor concentration. Since the upper limit of donor doping is restricted by the limited amount of available gallium vacancies, extremely low value of barrier resistance could not be achieved.

Thus the model is capable of answering many features of alloying characteristics of the AuGeNi-nGaAs system, on the basis of vacancy governed processes in gallium arsenide. It predicts that the maximum gallium vacancy concentration is about $5 \times 10^{19}$ cm$^{-3}$ and this corresponds to theoretical doping limit of the order of $6.6 \times 10^{18}$ cm$^{-3}$ as arrived in the sec. 3.2.2. This is in excellent agreement with the experimental value of $5 \times 10^{18}$ cm$^{-3}$ obtained in sec. 3.4. The conjecture (7, 72) that the maximum doping is limited by germanium deficiency is questionable, since Aina and Katz (73) have recently measured a considerable amount of inactive germanium at the interface.

In brief, the model suggests that, in practice, the maximum carrier concentration achievable by alloying of AuGeNi to n-GaAs is of the order of $5 \times 10^{18}$ cm$^{-3}$ with a resultant barrier height of about 0.4 eV. The reduction in barrier height from the intrinsic value of 0.8 eV (4, 7, 16, 33, 35, 73) to 0.4 eV after alloying is due to the doping increase at the interface and can be understood by established theories of barrier lowering effect (14, 27, 35, 71, 74-76).

3.6 CONCLUSIONS

The proposed ohmic model enunciates that the donor doping in an alloyed AuGeNi-n GaAs system is a vacancy dependent phenomenon. Whilst
gallium vacancies generate the donors Ge$_{Ga}^{+}$, arsenic sites add to the formation of acceptors Ge$_{As}^{-}$ and neutral pairs Ge$_{Ga}^{+}$Ge$_{As}^{-}$. It is illustrated in the study that notwithstanding that a major part of the germanium-occupied vacancy states form neutral pairs, the net concentration of donors is about 10% of the available gallium vacancies in the semiconductor, when the system is annealed at an optimum temperature. It is assumed that most of the donors which were consumed in the formation of the acceptor complex Ge$_{Ga}^{+}$V$_{Ga}^{-}$ are recovered by their annihilation with gallium interstitials via reaction (3.12). Thus we conclude that the donor formation is proportional to the gallium vacancy concentration in the crystal.

The Whipple theory used for quantitative analysis of the model predicts a gallium vacancy concentration of $5 \times 10^{19}$ cm$^{-3}$ for optimum alloying of AuGeNi to n-GaAs. However, this is more than an order of magnitude higher than Brice’s value of $1.3 \times 10^{18}$ cm$^{-3}$ (77). This discrepancy may perhaps be accounted by the following explanation.

(i) The great affinity of gallium for gold (20) is likely to enhance the vacancy generation process in a gold coated gallium arsenide system. In Brice’s study of high temperature affects in GaAs, such a sink does not exist for gallium consumption.

(ii) It is seen from Fig. 3.2b that the gallium content in gold grains falls rapidly with grain size. A careful examination of histograms of De Bonte et al. (70) indicates that the range above 1000 Å represents the model class of gold grain size. More recent work (4) has also mentioned grains of one micron size. It is possible, therefore, that the preferred low value of 1000 Å for the present estimation has led to an excess value of gallium vacancy concentration.

In view of above explanations, however, a value larger than that of Brice is expected, nevertheless, the error in the estimation, due to some
uncertainty in the grain dimension cannot be ruled out. Following Hurle's (45) results, Brice's gallium vacancy value gives a donor concentration of $1.7 \times 10^{17} \text{ cm}^{-3}$. This differs widely from the experimental value of $5 \times 10^{18} \text{ cm}^{-3}$ obtained here and does not approximate to any one of the published values, tabulated in the Table 3-IL. This reveals that the Brice's estimation of gallium vacancy concentration is too low for gold coated gallium arsenide and suggests that the one predicted by our analysis is the most appropriate.

The above discussion strongly supports the proposed model and the relevance of application of grain boundary diffusion theory to alloyed AuGe Ni-n GaAs system. This implies that we are not likely to achieve a much higher value of donor doping for alloyed contacts compared with that obtained in practice and that the ultra-low resistance contacts require fabrication of heavily doped surface layer by some exotic process such as implantation or MBE and then alloying with an AuGeNi film. This has recently been reported where extremely low values of contact resistance (34, 78, 79) are obtained.
REFERENCES

64. J.E.E. Baglin and J.M. Poate, in Ref. 20, pp. 305.