Ion Implantation of Double-Barrier Resonant-Tunnelling Diodes

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A Thesis submitted to the Faculty of Science of the University of Surrey for the degree of Doctor of Philosophy

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Dedicated to S.T.
SUMMARY

Many doses of ions have been implanted through near-surface AlGaAs/GaAs double-barrier diodes. The first objective of this work was the creation of a resistive layer beneath the diodes in selected areas of the wafer. It is shown that if the damage within the double-barrier diodes could be annealed without removing the resistive layer, the three-dimensional integration of the diodes with a second level of devices beneath the resistive layer could be attained. Implantation-and-annealing to create either a damaged or a chemically-compensated resistive layer has been attempted, where, during both types of process, the damage within the double-barrier diodes was much less than that below them. After implantation of $5.0 \times 10^{13}$ 2.0MeV B$^+$ ions cm$^{-2}$, and anneals at 600°C, near-surface Al$_{0.4}$Ga$_{0.6}$As/GaAs double-barrier diodes still had good quality negative differential-resistance. It is shown that if (the smaller and less damaging) 1.2MeV Be$^+$ ions were implanted instead of the 2.0MeV B$^+$ ions, an n$^+$-doped layer beneath the diodes can, in principle, be chemically compensated without destroying the diodes irreparably. This work was the first to successfully carry out the anneal-induced recovery of an ion-implanted electronic device having quantum-length-scale layers.

The second objective of this work was the elucidation of the electronic and structural characteristics of the same implanted-and-annealed double-barrier diodes. Before annealing, electron conduction through the ion-implanted diodes was limited primarily by field-enhanced emission of electrons from defect states within the lightly-doped spacer layers. The current of ballistic electrons through the as-grown double-barrier structures was suppressed by implantation-and-annealing; this was probably caused by scattering of these electrons by the remaining defect states. The suppression of the ballistic-electron current within implanted-and-
annealed double-barrier diodes is proposed to be the primary cause of their larger-than-as-grown 5K and 77K peak-to-valley current ratios.

Multi-stage annealing of defects within the double-barrier diodes has been investigated by electrical measurements. The anneal-induced creation of defect clusters within the device mesas was confirmed by both DC and AC measurements, where these clusters were surrounded by percolation paths of as-grown material. Single-electron switching and resonant tunnelling through donor states have been observed within the percolation paths at 4.2K; these observations indicate that the typical diameter of the paths was probably less than five microns, and possibly less than one micron.
Publications

The articles which describe the results and conclusions of the principal work are listed below, together with those describing other work carried out.


A very brief description of the first ten months of the author's PhD research.


The preliminary results and analysis of the work described in Chapter 3.


The concluding results of the work described in Chapter 3.


A description of the work carried out primarily by Vicky Wilkinson, where she investigated the manufacturability of tunnel diodes. During the first half of 1996 the author carried out the final stages of the project, suspending his PhD research for four months to do so.

K. Billen, L. Eaves, M. Henini, T.J. Foster, M.J. Kelly, R.M. Gwilliam and S. Hutchinson. - "Multi-stage annealing of defects in ion-implanted double-barrier diodes" (in preparation for publication)

Almost a verbatim reproduction of Chapter 6.

K. Billen, M.J. Kelly, M. Henini, R.M. Gwilliam and S. Hutchinson. - "The electronic transport through ion-implanted double-barrier diodes" (in preparation for publication)

The principal results of the work described in Chapter 5.
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Although I am grateful to everyone from whom I received assistance during my research, here I shall restrain myself to thanking only those whose contributions were requisite for the completion of this thesis. I thank

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Mohamed Henini (Nottingham) for growing and supplying me with high-quality double-barrier diode samples; and
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I also thank Bob Glosser and Stuart Hutchinson for reading and constructively criticising this thesis.

On a more personal note, I thank: most of my friends for their support, the most notable are Kostas Palakidis, Gareth Jones, Sylvie Bone (the most elegant, gracious and facetious person I have met), Dimitra Darambara and Nirmal Garawal; my family back in Wales for not forgetting about me in my almost complete absence; Peggy Walker for all the tea, coffee, home-made cakes, cheer, chat, etc.; Byron Morgan for his assistance when amenable, i.e. when not behaving with his customary ‘dangerous Welshness’; Charles and Melissa Maynard for their consistent encouragement and friendship during my time at both Aberystwyth and Guildford; Qantas and Continental for flying me around the world during April, May and June 1995, and therefore contributing towards my enjoyment of some of the best months of my life; and Dave Smith, Tim Davies, Mark Broom and Barry Mageean at 12 Stanley Road in Aberystwyth for their ‘comments on earlier drafts, and general intellectual input’.
"The real voyage of discovery consists not in seeking new landscapes, but in having new eyes."

Marcel Proust
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This thesis describes the implantation of long-range ions through near-surface AlGaAs/GaAs double-barrier structures. Ion implantation has been used before both in the research laboratories and in the production line to horizontally-isolate advanced multilayer devices (high electron mobility transistors, planar-doped barrier diodes, and heterojunction bipolar transistors), but one of the two principal objectives of the author's work involved the development of a process where ions were implanted through a double-barrier structure to create a buried resistive layer. If the implantation-created damage within the double-barrier structure could be annealed without removing the buried resistive layer, the vertical isolation of electronic devices in a semiconductor wafer having two levels of devices could be attained; thus expediting the three-dimensional integration of the devices (where the second level of devices would be beneath the resistive layer).

The subsequent elucidation of the electronic and structural characteristics of implanted-and-annealed double-barrier diodes was the other principal objective of the work: routine variable-temperature DC measurements, AC measurements, theoretical modelling of conduction-band edges, x-ray diffraction, and electrically-active impurity profiling were carried out.

The thesis is divided into four distinct parts: part 1 introduces the relevant details of the devices and implantation processes used, part 2 describes the experimental procedure used and the results obtained during the process-development work described above, and part 3 describes the investigations of the electronic and structural characteristics of implanted-and-annealed double-barrier diodes. Part 4 concludes the thesis. As mentioned above, many experimental techniques and apparatus were used throughout the work; hence the absence of the usual introductory chapter describing all the experimental procedures used. Each experimental procedure is described when mentioned first in Parts 2 and 3.

Chapter 1 introduces and summarises the relevant physics of the devices investigated in chapters 3 to 6. The theory of quantum-mechanical tunnelling through a single-barrier tunnel diode is introduced. Although the physics of the single-barrier tunnel diode is unusual and interesting, it is still primarily a 'research-only' device. The only application likely to be a future commercial reality, i.e. the use of a single-barrier structure to detect microwave signals, is described. With reference to that application, the basics of microwave detection and mixing are
reviewed. Secondly, the electronic transport through a double-barrier diode is described. Since those first observations of resonant tunnelling were made by Chang, Esaki and Tsu, almost every aspect of the double-barrier diode has been investigated, and a countless number of applications have been proposed. This section focuses attention on arguably the most useful application for the double-barrier diode, namely the generation of microwave signals.

Ion implantation has been incorporated into the fabrication of commercial electronic devices since the early 1960s. It can be used to create both n and p-type layers in selected volumes of a semiconductor, to synthesise a compound of the original semiconductor and the implanted atoms, or to create high-resistivity layers between adjacent electronic devices (the technique known as implant isolation). Chapter 2 introduces the transport of implanted ions through solids, and the two complementary implant-isolation processes which have been developed (both of which were attempted during the work described in parts 2 and 3). Chapter 2 is not purely introductory: the first ten months of the author’s research at Surrey are described very briefly therein. The three ion accelerators used during the work described in the subsequent chapters are described briefly at the end of the chapter.

Chapter 3 is the first of four chapters describing the use of ion implantation during the processing of double-barrier resonant-tunnelling diodes. It begins with an introduction to what was the first of the two principal objectives of this research, namely the development of an implantation process with which the horizontal and vertical integration of multilayer tunnel-diodes in a two-level wafer could be attained. The results of the preliminary investigations carried out to discover whether a near-surface double-barrier structure (consisting of quantum-length scale layers) could withstand an implantation-and-anneal process are described. To create a damaged resistive layer at a depth of about two microns, several doses of 300keV protons were implanted through the double-barrier structures; these were then subjected to an appropriate rapid thermal-annealing process.

The second set of attempts at creating an electrically-isolating layer two microns below a near-surface double-barrier structure are described in Chapter 4. Implantations of either C⁺ ions or Mg²⁺ ions to create a chemically-compensated resistive layer were carried out. AC measurements of the net carrier density as a function of depth in Mg²⁺-implanted bulk GaAs specimens were also carried out. The anneals which attained the most useful activation of implanted atoms in this bulk GaAs were used to repair the double-barrier diodes, the DC characteristics of which were investigated subsequently. The post-anneal DC performance of asymmetric
spacer-layer tunnel diodes, which are suitable devices for integration with double-barrier diodes (see Chapters 1 and 3) were investigated also.

Understanding the physics of the electronic transport through an implanted-and-annealed double-barrier diode would facilitate the designing of a diode which performs optimally after one of the implantation-and-anneal processes described in Chapters 3 and 4. Detailed investigations of the electronic transport through implanted-and-annealed near-surface double-barrier diodes are described in Chapter 5. This work involved variable-temperature DC measurements carried out before annealing, and between each annealing stage. In addition to the expected results, a few surprising results were obtained, the explanations of which are described. Also described is the theoretical modelling of conduction-band edges which was carried out in conjunction with the experimental work.

Chapter 6 describes the investigations of the annealing characteristics of GaAs where resonant tunnelling was used as a probe of the large-scale structural changes within the device mesas. Again, DC measurements at various temperatures were conducted between each annealing stage. To corroborate some of the more unusual results obtained during these routine DC measurements, some of the implanted-and-annealed material was subjected to AC measurements at 77K, very-low bias DC measurements at 4.2K, and fixed-bias DC measurements at 4.2K where the current was measured as a function of time.

The thesis is concluded by Chapter 7, which contains several feasible suggestions for how the author's research could be continued.
GLOSSARY OF ABBREVIATIONS AND SYMBOLS

1D, 2D, 3D,... one-dimensional, two-dimensional, three-dimensional,...

$a_0$ the Bohr radius

$A$ cross-sectional area

ASPAT asymmetric spacer-layer tunnel

$\alpha$ curvature coefficient

$B_w$ amplitude of backward-travelling wave

$\beta$ voltage sensitivity

$c_n$ electron-trapping rate of a defect state

$C$ capacitance

$C_F$ the Faraday constant

$C(V)$ capacitance(voltage)

d capacitative thickness

DBD double-barrier diode

$\Delta R_p$ projected straggle of implanted ions

$e$ charge of an electron

$e_n$ electron-emission rate of a defect state

$eC(V)$ electrochemical capacitance(voltage)

$E$ kinetic energy of an electron

$E_{0_{\text{acc}}}$ lowest-energy quasi-2D state within an accumulation layer

$E_{0_{\text{con}}}$ energy of a state confined between two potential barriers

$E_d$ displacement energy of a lattice atom

$E_F$ Fermi level

$E_{F_{\text{acc}}}$ quasi-Fermi level within an accumulation layer

$E_i$ energy of the quasi-2D state $i$ within an accumulation layer

$E_l$ total energy loss of a ballistic particle in a solid

$E_t$ activation energy of a defect state

$\varepsilon$ relative permittivity

$\varepsilon_0$ permittivity of free space

$f$ frequency

$f_c$ maximum frequency of oscillation

$F$ fraction of as-grown material in a mesa

$F_w$ amplitude of a forward-travelling wave

$\phi$ height of a potential barrier

$\phi_{\text{min}}$ minimum ion dose necessary to amorphise a crystal
minimum ion-dose necessary for chemical compensation

g

crystal density

G

conductance

γ

degeneracy

ℏ

the Planck constant divided by 2π

η

efficiency of DC-to-RF power conversion

I_e

etching current during electrolysis

I_p

peak current of the main resonance

I_{pd}

peak-current density of the main resonance

I_v

valley current beyond the main resonance

I_{va}

valley-current density beyond the main resonance

I(V)

current(voltage)

IMPATT

impact-avalanche transit time

k

momentum of an electron outside a potential barrier

k_B

the Boltzmann constant

K

momentum of an electron inside a potential barrier

L

distance between two potential barriers

LCR

inductance-capacitance-resistance

LO

local oscillator

LOP

longitudinal optical phonon

m

modulation factor

m*

effective mass of an electron

M

mass number of an atom or an ion

M_w

molecular weight of a crystal

MBE

molecular beam epitaxy

MOCVD

metal-organic chemical vapour deposition

n

free-electron density

n_t

density of occupied defect states

N

atomic density

N*

net carrier density

N_d

number of displaced atoms

N_D

donor density

N_t

density of defect states

NDR

negative differential-resistance

P_{max}

maximum RF-power output

PDB

planar-doped barrier
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>PVCR</td>
<td>peak-to-valley current ratio</td>
</tr>
<tr>
<td>QWITT</td>
<td>quantum-well injection transit-time</td>
</tr>
<tr>
<td>r</td>
<td>reflection amplitude</td>
</tr>
<tr>
<td>$r_d$</td>
<td>average closest-distance an ion approaches a nucleus</td>
</tr>
<tr>
<td>R</td>
<td>resistance</td>
</tr>
<tr>
<td>$R_n$</td>
<td>average range normal to the surface of a crystal</td>
</tr>
<tr>
<td>$R_N$</td>
<td>magnitude of negative differential-resistance</td>
</tr>
<tr>
<td>$R_p$</td>
<td>projected range of implanted ions</td>
</tr>
<tr>
<td>$R_s$</td>
<td>series resistance</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>$S(E)$</td>
<td>nuclear cross section</td>
</tr>
<tr>
<td>SBD</td>
<td>single-barrier diode</td>
</tr>
<tr>
<td>$\sigma_n$</td>
<td>electron-trapping cross-section of a defect state</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>$t_t$</td>
<td>transmission amplitude</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$T(E)$</td>
<td>transmission probability</td>
</tr>
<tr>
<td>$v_n$</td>
<td>drift velocity of an electron</td>
</tr>
<tr>
<td>$V_p$</td>
<td>main-resonance voltage</td>
</tr>
<tr>
<td>$V_r$</td>
<td>repulsive potential between two particles</td>
</tr>
<tr>
<td>W</td>
<td>thickness of a potential barrier</td>
</tr>
<tr>
<td>$W_s$</td>
<td>thickness of a specimen</td>
</tr>
<tr>
<td>X</td>
<td>depth below the surface of a crystal</td>
</tr>
<tr>
<td>$X_s$</td>
<td>etch depth during electrolysis</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
<tr>
<td>$\psi$</td>
<td>1D electron envelope function</td>
</tr>
<tr>
<td>z</td>
<td>valence</td>
</tr>
<tr>
<td>Z</td>
<td>atomic number of an atom or an ion</td>
</tr>
</tbody>
</table>
PART 1

Introduction
Chapter 1

THE PHYSICS AND APPLICATIONS OF SINGLE- AND DOUBLE-BARRIER TUNNEL DIODES

1.1 - Introduction

The inventions of advanced multilayer electronic devices such as the high electron-mobility transistor\textsuperscript{1}, the heterojunction bipolar-transistor\textsuperscript{2}, the heterojunction Gunn diode\textsuperscript{3}, etc. resulted primarily from the development of both molecular beam epitaxy\textsuperscript{4} (MBE) and metal-organic chemical vapour deposition\textsuperscript{4} (MOCVD) as methods of growing semiconductor crystals layer by layer. The ultimate abilities of both MBE and MOCVD are such that the dopants can be confined almost to a single atomic layer, and/or crystal layers almost as thin as a single atomic layer can be grown. The physics and applications of the two III-V semiconductor multilayer structures investigated during this work, both of which incorporate layers thinner than 6nm, will now be described.

1.2 - The single-barrier tunnel diode

The Esaki tunnel diode\textsuperscript{5,6} and the Josephson junction\textsuperscript{5} were the first devices which utilised quantum-mechanical tunnelling phenomena for useful applications. Because of the inadequate growth-technologies used to manufacture semiconductor materials before the inventions of MBE and MOCVD, it was not until the mid-1970s before the first useful single-barrier tunnel diode (SBD) could be fabricated. Since the mid-1970s the SBD has been investigated thoroughly by many research groups\textsuperscript{7-9}, and one potentially useful commercial application for the single-barrier structure has been demonstrated\textsuperscript{8}.
1.21 - Modelling the DC characteristics

To model the qualitative DC characteristics of an SBD, the quantum mechanics of an electron which has kinetic energy \( E \) incident on a potential barrier of thickness \( W \) and height \( \phi \), where \( \phi > E \), must be considered. At each interface of the potential barrier with the material on either side of it, the solutions of the Schrödinger equation must be matched. The momentum of the electron is given by

\[
\begin{align*}
  k &= \left[ 2m^*E/\hbar^2 \right]^{0.5} \quad \text{outside the barrier, and} \\
  K &= \left[ 2m^*(\phi - E)/\hbar^2 \right]^{0.5}
\end{align*}
\]

inside the barrier. \( m^* \) and \( \hbar \) are their usual quantities. Within the layers depicted in figure 1.1 the electron wavefunctions are given by

\[
\begin{align*}
  \exp(ikz) + r \exp(-ikz) & \quad \text{in layer 1, where } r \text{ is the reflection amplitude;} \\
  F_w \exp(Kz) + B_w \exp(-Kz) & \quad \text{in layer 2;} \\
  t_\text{t} \exp(ikz) & \quad \text{in layer 3.}
\end{align*}
\]

\( F_w \) and \( B_w \) are the amplitudes of the forward- and backward-travelling waves respectively, \( z \) is the direction of motion of the incident wave, and \( t_\text{t} \) is the amplitude of the transmitted wave. By applying equations (1-3) to (1-5) the transmission probability can be determined if the incident wave is normalised, and is given by

\[
T(E) = |t_\text{t}|^2 = \left| \frac{\exp(-ikW)[1 - \chi^2]}{\exp(KW) - \chi^2 \exp(-KW)} \right|^2 \quad \text{where}
\]

\[
\chi = \frac{K + ik}{K - ik}
\]

If \( E < \phi \) then \( |\chi| = 1 \); therefore, \( T(E) \) will be small. If \( E > \phi \) then the equation

\[
K'^2 = 2m^*(E - \phi)/\hbar^2
\]

gives the momentum of the electron within layer 2, and the transmission probability is now given by
Figure 1.1  A schematic of the conduction-band edge across a single barrier.
Chapter 1  THE PHYSICS AND APPLICATIONS OF SINGLE- AND DOUBLE-BARRIER TUNNEL DIODES

\[ T(E) = \frac{\exp(-iK'W)[1 - \theta^2]/[\exp(iK'W) - \theta^2 \exp(-iK'W)]}{2} \]

where

\[ \theta = \frac{(K' + k)}{(K' - k)}. \]

If \( E > \phi \) then \( T(E) \) will therefore be almost equal to unity. Figure 1.2a depicts the transmission probability of an electron as a function of \( E \) when incident on a typical potential barrier. The current of electrons transmitted through the potential barrier as a function of voltage (the 'I(V)' characteristics of the SBD) is modelled as follows: the products of the occupancy of all the original states, the normal incident group velocity of the original states, and the energy- and bias-dependent transmission coefficient of the electrons at the barrier are integrated with respect to \( E \).

1.22 - Detection of microwaves

The 'I(V)' characteristics of the SBD are non-linear but antisymmetric. If the doping profile in the layers above the potential barrier is very different to that below then the 'I(V)' characteristics will also be asymmetric (i.e. AC rectifying) because different proportions of the bias voltage will be applied above and below the barrier. Efficient 'I(V)' rectification is fundamental for the detection of microwaves\(^9\) (see figure 1.2b). If a signal \( V_{\text{sig}} \cos(2\pi ft) \) is incident on a diode which has such 'I(V)' characteristics (where \( f \) is frequency and \( t \) is time) then by carrying out the Taylor expansion

\[ I = I_0 + (dI/dV) \big|_{V_0} (V - V_0) + (0.5)(d^2I/dV^2) \big|_{V_0} (V - V_0)^2 \]

about the DC bias point \((V_0, I_0)\), the induced current passing through the diode will include a DC term \( \beta V^2/2 \) (where \( \beta \) is defined as \( d^2I/dV^2 \)). \( \beta \) is directly proportional to the 'curvature coefficient' at \((V_0, I_0)\), which is given by (as stated by Syme\(^10\))

\[ \alpha = \frac{(d^2I/dV^2)}{(dI/dV)}. \]

The DC term resulting from the Taylor expansion could be detected easily if \( \beta \) was relatively large and/or the bias voltage across the diode was zero.

1.23 - The asymmetric spacer-layer tunnel diode

The asymmetric spacer-layer tunnel (ASPAT) diode\(^8,10\) is an SBD which has an asymmetric doping profile above and below the potential-barrier layer, and
Figure 1.2  a) $T(E)$ of an electron incident on a single barrier; and b) the rectifying $I(V)$ characteristics necessary for the detection of microwave signals (the two parts of the figure are not correlated).
therefore can be used to detect microwaves. The layer structure of a typical ASPAT diode is depicted in figure 1.3, onto which the conduction-band edge is superimposed. The 3nm-thick AlAs layer creates the thin potential barrier through which tunnelling of electrons occurs. The only asymmetry within the structure is the very different thickness of undoped GaAs above the AlAs to that below it. The 5nm undoped GaAs layer above the AlAs is not necessary for good AC rectification in theory, but is grown in practise to minimise the (detrimental) diffusion of Si into the AlAs from the n-doped material during its growth; thus minimising electron tunnelling through Si-associated states within the band-gap of the AlAs when biased (such tunnelling would ‘short out’ the AlAs potential barrier).

Above and below the AlAs, a 50nm n-doped layer is usually grown between the undoped layers and the n⁺ contacts. The n-doped layers are grown to change the bending of the conduction-band edge such that a low but broad potential barrier is created below the n⁺ contacts, and a thin ‘accumulation layer’ (~5nm thick) contiguous to the emitter barrier is created when the structure is biased. When biased, the electrons in the n⁺ contacts are emitted thermionically over the broad and low potential barrier; these electrons can either tunnel through the AlAs ballistically (which most do not do) or, before tunnelling, they can thermalise into the accumulation layer (which most do). The bending of the conduction-band edge within the accumulation layer is abrupt enough to cause quasi two-dimensional (quasi-2D) quantisation of the electron states therein. Figure 1.2b depicts the experimental $I(V)$ characteristics of a typical ASPAT diode. The high rate at which the forward-bias current increases with bias voltage is a result of the quasi-2D quantisation of the original electron states: the majority of the states are not spread out in a quasi-3D continuum of energy, but are at a very similar discrete energy; thus resulting in a sharp increase of the current with bias because most of the incident electrons have a very similar transmission probability at a specific bias.

When compared to the planar-doped barrier (PDB) diode and other microwave-detector diodes, the ASPAT diode is a low-noise device which has good sensitivity, very good dynamic range, and excellent temperature stability. Also, the AlAs potential barrier within the ASPAT diode structure is easier to fabricate than the p-type δ-doped layer within the PDB-diode structure. The doping profile necessary to attain the highest performance ASPAT diode involves a compromise: it should always include 1) very high doping in the n⁺ contacts to provide enough tunnelling electrons; and 2) an emitter spacer-layer having i) a low enough
Figure 1.3  A schematic of the layer structure and conduction-band edge of a typical ASPAT diode (in forward bias).
resistance to transfer a high current of electrons from the n+ contacts to the AlAs, but ii) a low enough Fermi level ($E_F$) to ensure that the bending of the conduction-band edge contiguous to the AlAs was abrupt enough to create an accumulation layer populated by many thermalised electrons (in quasi-2D states).

1.24 - Mixing microwaves

When using radio-frequency (RF) systems for communication, the transmission of information involves the modulation of the carrier signal (the RF) with the audio/video signal to be communicated (a much lower frequency). The received signal must be demodulated to extract the audio/video frequencies. For both the modulation and demodulation of RF signals, a mixer device with non-linear $I(V)$ characteristics is necessary. Assuming the received signal is given by

$$V = A(1 + m\cos 2\pi pt)\cos 2\pi ft$$

(1-13)

(where $A$ is a constant, $f$ is the carrier frequency, $p$ is the modulation frequency, and $m$ is the modulation factor), the output signal of a diode with rectifying $I(V)$ characteristics would be

$$I = I_{DC} + \beta A^2 m\cos 2\pi pt + \text{higher frequency terms}$$

(1-14)

where $I_{DC}$ is the resulting DC term. The higher-frequency terms can be filtered out by a low-pass filter. The magnitude of the audio/video signal may, however, be very low compared to the $1/f$ noise; therefore, the carrier signal is mixed with a signal from a local oscillator (LO). By designing the LO frequency to be slightly different to the carrier frequency, the difference frequency will be very much lower and could be amplified more easily; thus resulting in a large increase of the signal-to-noise ratio of the detection system. Mixing systems are, unfortunately, relatively expensive but by integrating a microwave-detector diode with an LO on the same circuit, obviously the cost and complexity of such systems is much less; this has been attained using transistor structures integrated horizontally. A circuit in which a dedicated high-performance microwave-detector diode is integrated both horizontally and vertically with a dedicated high-performance microwave-generator diode (to form a high-performance microwave-mixer integrated circuit) cannot be fabricated when using present-day crystal growth and processing technology.
1.25 - Summary
The physics of quantum-mechanical tunnelling through a single-barrier structure has been described. A microwave-detector diode which makes use of tunnelling through a single barrier was compared to other microwave-detector devices, and its excellent all-round performance at RF was mentioned. The advantage of integrating a microwave-detector diode with an LO, thus forming a microwave-mixer device, was described.

1.3 - The double-barrier resonant-tunnelling diode
A device which could be used as the LO mentioned above is the double-barrier resonant-tunnelling diode (DBD). Resonant tunnelling of electrons through a double-barrier structure was described theoretically in the early 1960s, and was first observed experimentally in 1974 by Chang et al. The double-barrier structure consists of a pair of thin potential barriers, between which is a thin layer (usually an undoped layer of the substrate crystal) containing at least one confined energy-state (as depicted in figure 1.4).

1.31 - Modelling the qualitative DC characteristics
To calculate the transmission coefficient of an electron incident on this structure, the same theory as that used for the single-barrier structure is applied. An electron is incident on the first potential barrier, and, depending on $E$, it will be either reflected or transmitted. Consider the exponential growth and decay of the electron wavefunctions between the potential barriers (length $L$ apart, and each having thickness $W$), and the travelling wavefunctions within the three other layers: a wave is incident on the first potential barrier, some of which is reflected and the remainder is transmitted through the entire double-barrier structure.

Using the same definitions of $k$, $K$, and $K'$ as those used in the previous section, the transmission probability of an electron incident on the double-barrier structure is given by

$$T(E) = \frac{8 \exp(-ik(L + 2W))}{|D_1 \exp(-2KW) + D_2 \exp(2KW)|^2}$$

where, for $E<\phi$, 

$$D_1 = 2\cos(kL)(2 + 1/\theta + \theta) -i\sin(kL)(\theta^2 + 2\theta + 2 + 2/\theta + 1/\theta^2)$$

and

$$D_2 = 2\cos(kL)(2 + 1/\theta + \theta) + i\sin(kL)(\theta^2 + 2\theta + 2 + 2/\theta + 1/\theta^2)$$
Figure 1.4  A schematic of the layer structure and conduction band-edge of a typical Al$_x$Ga$_{1-x}$As/GaAs DBD.
\[ D_2 = 2 \cos(kL)(2 - \frac{1}{\theta} - \theta) - i \sin(kL)(\theta^2 - 2\theta + 2 - \frac{2}{\theta} + 1/\theta^2) \] where \( \theta = i k/K \). \hspace{1cm} (1-17)

\[ \theta = i k/K. \] \hspace{1cm} (1-18)

\( D_1 \) and \( D_2 \) can be considered as functions of energy. Note that when \( E < \phi \) the 'exp(2kW)' factor in equation (1-15) is preponderant; therefore, \( T(E) \) will be small. If \( D_2 \) in equation (1-15) is zero then \( T(E) \) would be almost unity: it would seem as though the double barrier did not exist. Within the layer between the potential barriers there are confined energy-states: it is when \( E \) is degenerate with one of the confined states that \( D_2 = 0 \), and a large current of electrons can flow through the double-barrier structure; this is known as 'resonant tunnelling'. If it is assumed that both the thickness and the height of the potential barriers are equal, \( T(E) = 1 \) when the exponential decay of the waves within the potential barriers is prevented by the constructive interference of the forward- and backward-travelling waves between the barriers. In real devices, however, \( T(E) \) is always somewhat less than 1 because the two intentionally-identical potential barriers will have neither an identical thickness nor an identical composition.

### 1.32 - Typical \( I(V) \) characteristics

Figure 1.5 depicts the \( I(V) \) characteristics of a typical Al\(_x\)Ga\(_{1-x}\)As/GaAs DBD, which can be explained as follows (with reference to figure 1.4): assuming there is one confined energy-state between the barriers, resonant tunnelling occurs at the bias at which the confined state is degenerate with the uppermost quasi-2D sub-band within the accumulation layer. If the bias voltage is increased then the confined energy-state will be brought below the energy of the uppermost sub-band; therefore, the current decreases because the two energy states are no longer degenerate. The current decreases with increasing bias until either the confined energy-state is degenerate with a lower-energy quasi-2D sub band (if one exists) or when the second potential barrier becomes small enough to allow the tunnelling electrons to pass over it. The second and third resonances depicted in figure 1.5 are tunnelling through to the confined energy-state from the uppermost sub-band and the lowest sub-band respectively. The electron population of the uppermost sub-band is always smaller than that of the lowest because of its higher energy relative to \( E_f \) within the emitter. The resonant-tunnelling current increases with the electron population of the sub-band from which the tunnelling electrons originated.
Figure 1.5 The $I(V)$ and $[dI/dV](V)$ characteristics of a typical $\text{Al}_x\text{Ga}_{1-x}\text{As/GaAs DBD}$.
Therefore, the first tunnelling current is always smaller than the second. Wu et al.\(^\text{14}\) proved the existence of three sub-bands within the accumulation layer of a specially-designed Al\(_{0.4}\)Ga\(_{0.6}\)As/GaAs DBD.

Resonant tunnelling originating from the quasi-continuous 3D emitter states can also occur, preponderantly so within double-barrier structures which have no spacer layers - no accumulation layer contiguous to the emitter barrier is created in such structures. The peak current of this '3D-2D' resonant tunnelling is, however, much less abrupt than that of the '2D-2D' tunnelling described above because of the quasi-continuousness of the original energy states. The first resonance depicted in figure 1.5 is attributed to 3D-2D resonant tunnelling of electrons originating from the quasi-continuous 3D emitter states.

**Negative differential-resistance**

When, within a certain range of bias, the current flowing through an electronic device decreases with increasing bias (as described above) its differential resistance and differential conductance (\(\text{d}I/\text{d}V\)) are, obviously, both negative. Figure 1.5 depicts the \([\text{d}I/\text{d}V](V)\) characteristics derived from the \(I(V)\) characteristics. Note that negative differential-resistance (NDR) occurs twice: when the DBD is biased beyond both the second-resonance voltage and the main-resonance voltage (\(V_p\)). NDR is essential for conversion of DC power to RF power (more details of this will be described in sub-section 1.3.3).

**The peak-to-valley current ratio**

A very useful gauge-of-quality for DBDs is the peak-to-valley current ratio (PVCR). Figure 1.5 depicts a room-temperature PVCR of ~1.7:1, which is a mediocre PVCR for the Al\(_x\)Ga\(_{1-x}\)As/GaAs material system (4.0:1 is the highest room-temperature PVCR attained when investigating a Al\(_x\)Ga\(_{1-x}\)As/GaAs DBD). A 295K PVCR of 51.6:1 has been observed when investigating diodes made of other materials\(^\text{15}\). To attain a high main-resonance peak current \((I_p)\) the potential barriers within a DBD should be thin, and the doping profile within the emitter should be such that an accumulation layer populated by many electrons is created when the structure is biased (see sub-section 1.2.2). To attain a low valley-current \((I_v)\) the potential barriers should be high. The existence of populated quasi-continuous 3D emitter states and/or more than one populated quasi-2D sub-band within the accumulation layer increases \(I_v\) because there are more states from which a
non-resonant tunnelling current of electrons can originate.

With decreasing temperature the extent of thermionic emission of electrons over the double-barrier structure, and the inelastic scattering of tunnelling electrons caused by absorption of phonons both decrease; therefore, $I_v$ decreases. With decreasing temperature both the number of available collector states, and the abruptness of the distribution of populated electron states within the accumulation layer increase; therefore, the resonance peak becomes sharper and, consequently, $I_p$ increases. With decreasing temperature the combination of the decrease of $I_v$ and the increase of $I_p$ results in a large increase of the PVCR. Figure 1.6 depicts the 77K and 295K $I(V)$ characteristics of a typical DBD.

**LOP-assisted resonant tunnelling**

The paragraph above describes the scattering of resonant-tunnelling electrons by absorption of phonons. Resonant-tunnelling electrons can also be scattered inelastically by the emission of longitudinal optical phonons (LOPs). The small peaks in the 77K valley-current region depicted in figure 1.6 are caused by this so-called LOP-assisted resonant-tunnelling: at the bias voltages at which these small peaks occur, the confined energy-state between the barriers is ~45meV below the quasi-Fermi level ($E_{F_{acc}}$) within the accumulation layer (the energy of an LOP at an AlAs-like interface is 47meV). LOP-assisted resonant-tunnelling is observable most easily when the main resonance is abrupt, and when both the intrinsic $I_v$ and the value of $|E_{F_{acc}} - E_{0_{acc}}|$ are low (where $E_{0_{acc}}$ is the energy of the uppermost populated quasi-2D sub-band within the accumulation layer).

**Experimental $I(V)$ characteristics**

Figure 1.6 depicts an (unintentional) asymmetry between the forward and reverse bias $I(V)$ characteristics of the DBD; this is usual, and is caused by an asymmetry of either the dopant distribution or the double-barrier structure itself.

The 295K $I(V)$ characteristics depicted in Figure 1.6 include discontinuous experimental data in the region of NDR; these are a consequence of there being very small oscillations on the power supply which cause the DBD to oscillate. Connecting a capacitance in parallel with the DBD can eliminate this unwanted effect if the resistance at $V_o$ (see figure 1.5) is larger than ~1kΩ; however, its occurrence during $I(V)$ measurements is not a problem if all one wants to measure is the PVCR.

The forward-bias $I(V)$ characteristics at room temperature have current
Figure 1.6  The forward- and reverse-bias $I(V)$ characteristics of a typical DBD. The numbers in brackets are the PVCRs in forward and reverse bias.
bistability in the region of $I_v$. Space-charge accumulation between the barriers at resonance was once suggested as an explanation for this current bistability, but after much debate\textsuperscript{18} the consensus is that the bistability is another effect caused by the extrinsic oscillations described above. Nevertheless, a current bistability caused by the intrinsic accumulation of space-charge does exist in some biased DBDs\textsuperscript{19,24}.

### 1.33 - Generation of microwaves

With reference to figure 1.5, if a DBD is biased at $V_o$ then the addition of a small RF signal will decrease the current. When used this way the DBD is analogous to a conventional inductance-capacitance-resistance (LCR) circuit: the amplitude of the RF signal applied to the biased diode will increase exponentially until it is equal to $\Delta V$, i.e. the RF signal will be amplified by the diode.

DBDs have the widest bandwidth of any amplification device: the fastest electronic device tested at the time of writing is an InAs/AlSb DBD, investigated by Brown \textit{et al}\textsuperscript{25}, which operates at 712GHz. AlAs/GaAs DBDs have been observed operating at 420GHz\textsuperscript{26}. Potentially, DBDs should be able to operate at more than 1THz. The maximum frequency at which a DBD has NDR is given by

$$f_c = 1/[(2\pi R_N C)(R_N/R_s - 1)^{1/2}]$$

(1-19)

where $R_N$ is the magnitude of the NDR, $R_s$ is the resistance in series with the double-barrier structure, and $C$ is the capacitance of the diode.

When $f < f_c$ the maximum RF-power output and the DC-to-RF conversion efficiency of a DBD can be approximated by

$$P_{\text{max}} = (3/16)\Delta I \Delta V$$

(1-20)

and

$$\eta = P_{\text{max}}/[(I_p - \Delta I/2)(V_p + \Delta V/2)]$$

(1-21)

Typical values of $P_{\text{max}}$ and $\eta$ are $\sim 10^3$W and $\sim 10\%$ respectively. $P_{\text{max}}$ is limited fundamentally by $\Delta V$ ($\sim 0.25$V), which is a function of both the conduction-band offsets and the energy of the confined state between the barriers ($E_{\text{conf}}$).

### 1.34 - The quantum-well injection transit-time diode

For commercial applications it is necessary to increase both the maximum
power-output and the DC-to-RF conversion efficiency of the DBD because compared to other devices, such as the heterojunction Gunn diode and the impact-avalanche transit time (IMPATT) diode, the DBD can generate only small amounts of RF power. If a relatively-thick undoped layer existed between the double-barrier structure and the collector, $\Delta V$ in equations (1-20) and (1.21) would be larger because an increased proportion of the bias voltage would exist across the thick undoped layer. The DC-to-RF conversion efficiency of a double-barrier structure would therefore increase with increasing thickness of the undoped layer. Consequently, the transit time of the electrons through the undoped layer would increase; thus decreasing $f_c$. When configured this way, the double-barrier structure performs as a quantum-well injector of electrons into the undoped layer; hence the name quantum-well injection transit-time (QWITT) diode. QWITT diodes can perform impressively: $\eta \sim 50\%$ and $P_{\text{max}} \sim 20\text{mW}$ per diode have been measured at 2GHz when investigating $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{AlAs}$ devices. $\text{Al}_{x}\text{Ga}_{1-x}\text{As}/\text{GaAs}$ QWITT diodes have the potential to generate $\sim 4\text{mW}$ of power per device. The high-efficiency/moderate power-output of the QWITT diode is the performance necessary for short-range communication systems, and it is in this application that the double-barrier structure is, arguably, most likely to be used commercially.

### 1.35 - Summary

The basic theory of resonant tunnelling through a double-barrier structure has been described both mathematically and conceptually. Resonant tunnelling from both quasi-continuous 3D states and quasi-2D sub-bands within the emitter were described and compared. Some of the phenomena associated with resonant tunnelling were described, e.g. the tunnelling of electrons scattered by LOPs; and the current bistability caused by extrinsic oscillations of the bias voltage. Intrinsic bistability, an unusual phenomenon investigated recently, was mentioned. Also mentioned were the impressive DC and RF performances of some of the advanced and exotic double-barrier structures investigated recently, and the moderate capabilities of $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ double-barrier structures. The generation of microwaves by utilising the NDR of the double-barrier structure between certain bias-voltages was described, together with the design of a such a structure which has the potential to become a commercial microwave-generator device in short-range/high-efficiency communication systems.
1.4 - REFERENCES

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11. Data reproduced with the permission of V.A. Wilkinson
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Chapter 1

The Physics and Applications of Single- and Double-BARRIER Tunnel Diodes

Chapter 2

ION IMPLANTATION FOR THE ELECTRICAL ISOLATION OF III-V SEMICONDUCTOR DEVICES

2.1 - Introduction

The physics and applications of ion implantation for the electrical isolation of III-V semiconductor devices were reviewed recently by Pearton. The majority of this chapter is a summary of the relevant details described in Pearton's review, but the important contributions of others (including those of the author) are also described. The chapter ends with a description of the ion accelerators used by the author.

N.B. Hereafter the phrase 'ion implantation for the electrical isolation' will be shortened to 'implant isolation'.

2.2 - Implant isolation techniques

There are two different implant-isolation techniques which can create highly resistive material in both n and p-type III-V semiconductors: the technique used most often is the implantation of a neutral element, such as H, He, B, or O, which creates defects that trap free electrons within the deep electronic states associated with the defects - the defect states being several hundred meV below the conduction-band edge. The other implant-isolation technique involves the creation of high-resistivity within the material by implantation of an element which, after annealing, moves onto a lattice site to chemically-compensate the original dopants. For a specific application the most effective implant-isolation technique will depend on the highest temperature at which any subsequent processing of the ion-implanted material will occur: most implantation-created damage anneals at a
temperature which is dependent on both the implanted dose and the mass of the ions, e.g. most of the damage created by medium-dose He⁺ and O⁺ implantation anneals at 500°C and 600°C respectively. The movement of an implanted element onto a lattice site to create chemical compensation, however, does not occur until temperatures higher than 650°C have been attained.

Implant isolation is an expedient alternative to chemical etching because it avoids the creation of active surface-states and non-planar surfaces, and, in general, there is less lateral intrusion underneath the mask. These advantages have meant that implant isolation has been incorporated into the fabrication of many electronic devices. Sub-sections 2.21 and 2.22 describe the two different implant-isolation techniques, both of which have been used during the investigations described in Chapters 3 to 6.

2.21 - Ion implantation to create damaged layers

The implantation of ions to create defects in a crystal lattice was the technique used most often during this work. Defects in solid materials are created by elastic collisions of the implanted ions with nuclei or whole atoms: the target atoms absorb some of the kinetic energy of the ions, and if the absorbed energy is greater than the energy necessary to remove the atom from its lattice site then a vacancy is created. Associated with the vacancies are electronic states which can trap free electrons. The displaced nuclei which recoil from the implanted ion may have enough energy to displace other nuclei; this leads to a ‘cascade’ of recoiled atoms. Eventually the cascade ends when the energy absorbed per collision becomes too small for the creation of vacancies.

The energy absorbed by nuclear stopping is proportional to both the total energy transferred during all individual collisions, and the atomic density of the target. If the interaction of the implanted ion with a target nucleus is considered to be a Rutherford collision, i.e. an elastic collision between two hard spheres, then such an interaction causes the ion to be deflected from its initial trajectory. The repulsive potential between the two particles is given by

$$V_r = [Z_1 Z_2 e^2 / 4 \pi \varepsilon_0 r_d] [a/r_d]$$

(2-1)

where $a/r_d$ is the Thomas-Fermi screening function which gives the electron screening of the nuclear repulsion, $r_d$ is the average closest-distance an ion
approaches a nucleus, and \( Z_1 \) and \( Z_2 \) are the atomic numbers of the incident ion and the target nucleus respectively. \( a \) is given by

\[
a = 0.885a_0 \quad \text{where } a_0 \text{ is the Bohr radius (0.53Å).} \quad (2-2)
\]

The nuclear cross-section of the solid as 'experienced' by the ion is given by

\[
S (E) = -\frac{(\text{d}E}{\text{d}X}) \quad \text{eV cm}^2 \quad (2-3)
\]

where \( N \) is the atomic density of the solid, and \( \frac{\text{d}E}{\text{d}X} \) is the energy loss per unit distance caused by nuclear collisions (assumed to be elastic); this is given by

\[
-\frac{\text{d}E}{\text{d}X} = (2.8 \times 10^{-15})(Z_1 Z_2 M_1 M_2 N) \quad \text{eV cm}^{-1} \quad (2-4)
\]

where \( M_1 \) and \( M_2 \) are the mass numbers of the incident ion and the target nucleus respectively.

**Ion mass**

When implanted into a crystalline material, light ions such as protons or \( \text{He}^+ \) ions cause relatively-little damage to the crystal lattice: initially they slow down primarily by electronic-stopping processes, e.g. the ionisation of target atoms, which cause little damage to the lattice, but nuclear stopping becomes the primary energy-loss mechanism when the ions have slowed down at the ends of their trajectories. A heavier ion, however, can damage the lattice along its entire trajectory because it is slowed down precipitously by nuclear stopping.

**The efficiency of damage creation**

The total number of atoms displaced by an implanted ion is given by

\[
N_d \sim \frac{E_t}{2E_d} \quad (2-5)
\]

where \( E_t \) is the total energy loss of a particle during primary and secondary nuclear collisions, and \( E_d \) is the displacement energy of a lattice atom (~20eV in GaAs). \( N_d \)
for a 10keV O$^+$ ion in GaAs is $-105$, for a 200keV O$^+$ ion it is $-860$, and for a 200keV proton it is $-12$. At a specific ion-energy, therefore, O$^+$ ions are more efficient at creating damage than protons. The relative inefficiency of proton implantation necessitates the implantation of larger ion-doses to create a specific amount of damage. At a specific energy, however, protons have a longer range than any other (heavier) ion; this makes proton implantation useful for long range damage creation when the terminal voltage of the ion accelerator is limited to $\sim$200kV, which is the usual maximum of commercial accelerators$^{12}$.

With increasing damage, the creation of an amorphous layer involves a sudden collapse of the crystalline structure. The minimum ion dose needed to create an amorphous layer, assuming that all the target atoms must be removed from their lattice site to do so, is given by

$$\phi_{am} \sim \frac{2E_d N}{(dE/dX)}.$$  \hfill (2-6)

Equation (2-6), however, does not regard the temperature dependence of the damage creation during ion implantation: an increase of dose rate (ion-beam current) may decrease $\phi_{am}$ because the damage can accumulate before it self-anneals; however, when using very large dose rates the sample may heat up to a temperature at which an amorphous layer is never created because of the occurrence of intrinsic annealing$^{17}$ during the implantation process.

**Types of lattice defects**

The simplest implantation-created lattice defect consists of a vacancy and the associated displaced atom (known as an interstitial); this is known as a Frenkel pair. Divacancies, trivacancies, clusters of vacancies, and clusters of interstitials can be also created by ion implantation. More complex defects such as line dislocations caused by the accumulation of point defects are common within ion-implanted material. With increasing ion dose the defects begin to overlap, and an amorphous layer is created eventually. As mentioned above, some intrinsic annealing occurs when implanting ions into GaAs: microcrystalline structures can be created within the amorphous layer when this is so.

**Damage distributions**

Three different implantation-created distributions of damage are depicted in
figure 2.1a; these were calculated using the well-known TRIM Monte Carlo ion implantation simulation software\textsuperscript{18}. Note that during the two long-range implantation processes there exists relatively-little damage near the surface, i.e. most of the damage is at the end of the range of the ions: nuclear energy-loss is small at high ion-energies because fast ions have only a short time to interact with a target nucleus, and it is only when the ions have slowed down at the ends of their trajectories that nuclear stopping and, hence, considerable damage creation occurs. Figure 2.1b depicts the relative sizes of the electronic and nuclear stopping in GaAs during an implantation of 2\text{MeV} B^+ ions: note that the amount of electronic stopping remains larger than the nuclear stopping along most of the ion trajectory; this is typical of most long-range implantation processes.

The theoretical distributions of damage depicted in figure 2.1a are 'worst-case scenarios', i.e. they represent the maximum damage which could result experimentally. The amount of intrinsic annealing of damage during ion implantation increases with the temperature at which the implantation is carried out. The near-surface damage, in particular, can be minimised\textsuperscript{19} by carrying out the implantation process at relatively-high temperatures (~100\textdegree C to 300\textdegree C); this is an important fact which was considered during the work described in subsequent chapters.

Varying the ion-beam current

As mentioned above, varying the ion-beam current can change the amount of damage created by a specific implantation process. Before this research project was commenced, very few measurements had been carried out to investigate the effects of varying the ion-beam current\textsuperscript{20} during implant isolation of electronic devices. To become familiar with some of the experimental procedures to be used during the work described in Chapters 3 to 6, a project which involved implant isolation of a simple multilayer structure in GaAs was carried out during the first ten months of the author's research: the results of this project demonstrated the effects of varying the ion-beam current. The test material was Si \(δ\)-doped GaAs\textsuperscript{21-22} grown by MBE (a \(δ\)-doped semiconductor has all its dopants confined to a very few atomic layers). The insets of figures 2.2 and 2.3 depict the depth of the \(δ\)-doped layer, and the theoretical distribution of vacancies created in GaAs by the two isolation steps used (calculated using TRIM). The first isolation step was a room-temperature implantation of \(1\times10^{14}\) 30\text{keV} protons cm\(^{-2}\) into several samples onto which Hall-bar masks of photoresist had been spin-coated and developed\textsuperscript{23}. To create more damage around each isolated
Figure 2.1  a) The TRIM-calculated theoretical distributions of vacancies in GaAs implanted with 30keV protons, 300keV protons and 750keV He\(^+\) ions; and b) both the electronic stopping and nuclear stopping within GaAs during an implantation of 2MeV B\(^+\) ions.
Hall-bar specimen, a room-temperature implantation of $1 \times 10^{14}$ 45keV protons cm$^{-2}$ was carried out at a later date. The lateral spread of the 45keV protons would have been greater than that of the 30keV protons (the lateral spread of an ion in a solid increases with the depth it reaches); therefore, the second implantation step created more depletion of electrons underneath the mask.

The data obtained during the variable-temperature Hall-effect measurements of all types of specimen are depicted in figures 2.2 and 2.3. Good electrical isolation between adjacent Hall-bar specimens was attained by the first implantation step, but the measured free-electron density ($n$) was 10±2% less than that for an equivalent wet-chemical etched device. The second implantation step, when using a 50nA ion-beam current, decreased $n$ by another 19±2%; this is attributed to the additional vacancies created within the already-implanted material, and to the greater lateral spread at 3000Å of the 45keV protons. The temperature-dependent migration of defects into the masked material, which would decrease $n$ if it occurred, will have been unmeasurable within the large active region (720µm x 80µm) of the Hall bar used, and should have been inconsiderable at the maximum temperature of the samples during their preparation (160°C).

During the second implantation of protons into several specimens a 250nA beam current, which was still too small to have caused intrinsic annealing, was used instead: the result was a greater decrease of $n$, which is consistent with the results obtained during previous investigations of dose-rate dependent damage creation.

The resistivity of implantation-damaged layers

Kato et al investigated the resistivity of implantation-damaged layers in GaAs as a function of ion mass, ion dose, ion energy, anneal temperature and measurement temperature: it was discovered that the post-implantation sheet resistivity of a damaged layer of GaAs is many orders of magnitude higher than the pre-implantation resistivity ($\sim 10^2 \Omega$ square$^{-1}$). The post-implantation resistivity is never higher than $10^6 \Omega$ square$^{-1}$ because at low bias the trapped electrons within the damaged layer can 'hop' from one defect state to another, a process which is activated thermally. Above 180K the current of hopping electrons is proportional to $\exp(T^{1/4})$, where $T$ is the absolute temperature; and below 180K it is proportional to $\exp(T^{1/2})$, which is similar to that of amorphous semiconductors at such temperatures. The sheet resistivity of ion-implanted GaAs can be increased to $\sim 10^7 \Omega$ square$^{-1}$ by annealing some of the mechanisms which cause the hopping of...
Chapter 2  Ion Implantation for the Electrical Isolation of III-V Semiconductor Devices

Figure 2.2  The 2D electron-density and electron mobility of wet-chemical etched δ-doped specimens and implant-isolated δ-doped specimens (the dotted lines are guides to the eye). The inset depicts the measured depth of the δ-doped layer, and the damage distributions created by the two implantation processes.
Figure 2.3  The 2D electron-density and electron mobility of wet-chemical etched δ-doped specimens and implant-isolated δ-doped specimens (the dotted lines are guides to the eye). The inset depicts the measured depth of the δ-doped layer25, and the damage distributions created by the two implantation processes.
electrons between defects. The optimum anneal-temperature used to decrease the hopping conduction of electrons and, hence, attain the highest resistivity increases with both the ion mass and the ion dose. After an implantation of \( \sim 10^{14} \) protons cm\(^2\) into GaAs the optimum anneal-temperature is \( \sim 200^\circ C \), after a dose of \( \sim 10^{15} \) cm\(^2\) it is \( \sim 260^\circ C \), after a dose of \( \sim 10^{13} \) B\(^+\) ions cm\(^2\) it is \( \sim 420^\circ C \), and after a dose of \( \sim 10^{12} \) O\(^+\) ions cm\(^2\) it is \( \sim 580^\circ C \). To maintain adequate resistivity of the implantation-damaged GaAs it is essential, therefore, to know the maximum temperature at which any subsequent processing of the ion-implanted material will occur; however, other factors such as the depth of the layers to be damaged, and the maximum ion-energy attainable from the accelerator, may predetermine the element to be implanted.

**Trapping and emission of electrons by defect states**

At a finite temperature, each defect state continually traps and emits single electrons\(^6,26\). If in an n-type semiconductor there are \( n \) free electrons per unit volume moving with RMS velocity \(<v_n>\), \( n<v_n> \) electrons per unit area per unit time passes over each defect state. If the density of defect states is \( N_t \), and at any moment the number of these populated with electrons is \( n_t \), the number of electrons trapped within the \((N_t-n_t)\) empty states in a subsequent short time \( \Delta t \) is

\[
\Delta n_t = \sigma_n<v_n>n(N_t-n_t)\Delta t
\]

(2-7)

where \( \sigma_n \) is the trapping cross-section of the state. The trapping rate of an empty defect state is therefore given by

\[
c_n = [(\Delta n_t/\Delta t)/(N_t-n_t)]\quad \text{and, hence,}
\]

\[
c_n = \sigma_n<v_n>n.
\]

(2-9)

When \( N_t \) is very small relative to \( n \), few electrons are trapped. When \( N_t \) is large relative to \( n \), all the once-free electrons are trapped within defect states; thus greatly increasing the resistivity. The rate of change of electron population of a defect state is defined as

\[
dn_t/\Delta t = c_n(N_t-n_t) - e_n n_t
\]

(2-10)

where \( e_n \) is the electron-emission rate of the state. In thermal equilibrium the
population of a defect state is therefore given by

\[ \frac{n_i}{N_t} = \frac{c_n}{(c_n + e_n)}. \]  
(2-11)

Alternatively, \( \frac{n_i}{N_t} \) can be described by the Fermi-Dirac distribution function: within a defect state at energy \( E_t \) with degeneracy of \( \gamma_0 \) when empty, and \( \gamma_1 \) when populated by one electron, equation (2-11) is equal to

\[ \frac{n_i}{N_t} = \left\{ 1 + \left( \frac{\gamma_0}{\gamma_1} \right) \exp \left[ \frac{(E_t - E_p)/k_B T}{\gamma_0} \right] \right\} \]  
(2-12)

where \( k_B \) is the Boltzmann constant. By combining equations (2-11) and (2-12), it can be shown that

\[ \frac{e_n}{c_n} = \left( \frac{\gamma_0}{\gamma_1} \right) \exp \left[ \frac{(E_t - E_p)/k_B T}{\gamma_0} \right]. \]  
(2-13)

\( n \) increases with \( E_p \) (as given by the Fermi-Dirac distribution function); therefore, \( c_n \) is large when \( E_p \) is large. When \( E_p \) is small, \( c_n \) is small. Unlike \( c_n \), \( \sigma_n \) and \( e_n \) are not dependent on \( E_p \); these are intrinsic characteristics of the defect state.

As alluded to above when describing the degeneracy of a defect state, each state can be populated by more than one electron. By applying equation (2-12), it can be shown that the electron population within a defect state increases with \( E_p \).

Blood and Orton\(^6\) show how, when \( E_p \) is high, a defect state charged doubly-positive when empty can be populated by up to three electrons; this fact was considered when investigating some of the implantation-caused effects described in Part 3.

Enhanced emission of electrons from defect states

With increasing electric field, \( E_t \) becomes effectively smaller (see figure 2.4). At a specific temperature, therefore, the thermal emission of electrons from the defect state is enhanced with increasing electric field; thus decreasing the number of trapped electrons (see equation (2-12)) and, hence, lowering the resistivity of the ion-implanted semiconductor. At high temperatures, a large current of electrons excited into the conduction band by this field-enhanced thermionic emission, or Poole-Frenkel emission\(^27\), can be induced at medium-to-high electric fields; this current is proportional to \( V \exp\left\{-e[E_t - (eV/W_t \pi \varepsilon_0 \varepsilon)^{1/2}]/k_B T\right\} \), where \( e \) is the charge of an electron, \( W_t \) is the thickness of the specimen, \( \varepsilon_0 \) is the permittivity of free space, and \( \varepsilon \) is the dielectric constant of the semiconductor.
Figure 2.4  Schematic diagrams of the two current-conduction mechanisms in ion-implanted semiconductors which involve lowering the barrier created by the bending of the conduction-band edge near the defects.
Chapter 2  Ion implantation for the electrical isolation of III-V semiconductor devices

Poole-Frenkel emission of electrons into the conduction band from the defect states is the preponderant current-limiting mechanism in damaged semiconductors at high temperatures and high electric fields. A current of electrons excited into the conduction band by field-enhanced ionisation of the defect states can be induced at medium-to-high electric fields; this current is proportional to \( (V)^2 \exp(-V_0/V) \), where \( V_0 \) is a function of the band-gap of the semiconductor, which increases slightly with decreasing temperature. Compared to Poole-Frenkel emission, field-enhanced ionisation is relatively independent of temperature because the ionisation process is actually the tunnelling of a trapped electron into the conduction band (see figure 2.4); therefore, at very low temperatures it is the preponderant current-limiting mechanism in a damaged semiconductor.

Post-implantation annealing

If the temperature of a sample is increased steadily then the concentration of defects will decrease; therefore, its resistivity returns eventually to the pre-implantation value. The annealing of implantation-created damage in GaAs involves three distinct stages: 'stage 1' occurs between ~100 and ~300°C and involves the recrystallisation of the GaAs if it was amorphised during the implantation process; 'stage 2', which occurs between ~300 and 600°C, involves the removal of complex point-defect structures such as divacancies, trivacancies and stacking faults; and 'stage 3', which occurs between ~600 and ~950°C, involves the removal of the dislocation loops and remaining point defects.

2.22 - Ion implantation to create chemically-compensated layers

This technique was used during the final stages of this work, and it involves the implantation of an element which, when heated to a suitable temperature, moves onto a lattice site to create chemical compensation. Usually this technique is thermally stable, i.e. the high-resistivity layer created by the implantation process is not removed by high-temperature annealing. Suitable elements for the creation of chemically-compensated layers of n-type GaAs are Be, C, Mg and Va; however, Be is implanted very rarely because the ion sources used are highly toxic. The dose of implanted ions necessary to chemically-compensate an n-type layer at a depth \( X \) is given by (as stated by Sze):

\[
\phi_{\text{com}} = \left[ (2\pi)^{0.5} \Delta R_p N_D \right] \frac{1}{\exp\left[-\frac{(X-R_p)/(2)^{0.5} \Delta R_p}{2} \right]} \]

(2-14)
where \( \phi_{\text{com}} \) is specified by the number of ions \( \text{cm}^2 \), and \( N_D \) is the donor density (atoms cm\(^{-3}\)). \( R_p \), the average projected-range of the implanted ions in the solid, is the projection of the average ion-range normal to the surface \( (R_n) \). \( \Delta R_p \) is the projected straggle of the implanted ions (the distribution of ions about \( R_p \)). During the work described in Parts 2 and 3, \( R_p \) and \( \Delta R_p \) were calculated using TRIM.

### 2.3 - The ranges of ions in gallium arsenide

\( R_p \) in equation (2-14) can be estimated using the equation

\[
R_p = \left( \frac{1}{N} \right) \int_0^E \frac{dE}{S} \quad (2-15)
\]

where \( S \) is the nuclear cross-section given by equation (2-3).

Figure 2.5a depicts the ion-energy dependence of the range in GaAs of protons, He\(^+\), Be\(^+\), B\(^+\), C\(^+\) and Mg\(^+\) ions; and figure 2.5b depicts the impurity distribution in GaAs after implantations of equal doses of four different ions. Note that with increasing range the number of near-surface impurities becomes less; this was an important consideration during the work described in subsequent chapters.

### 2.31 - Channelling

TRIM can calculate the average range of a heavy ion implanted into a crystal to an accuracy within \( \pm 5\% \). Measurements of the damage distribution created by lighter ions, e.g. 300keV protons\(^{31}\), indicate that TRIM is between only 10 and 15\% accurate for these ions. The larger inaccuracy which results when modelling the transport of light ions through a crystalline solid is caused by disregarding the occurrence of ion channelling\(^{12,32,33}\). Channelling occurs when ions are scattered into low-index crystallographic directions, along which they can travel to large depths without interacting with any target nuclei. To decrease the amount of channelling, the ions can easily be implanted at \( 7^\circ \) to the normal of the GaAs surface\(^{12}\): GaAs wafers are grown in the [001] direction, and, for the purposes of ion implantation, GaAs is effectively amorphous at \( 7^\circ \) from this direction.

### 2.4 - Ion implantation of aluminium gallium arsenide

The chapter so far has been primarily a description of ion implantation of
Figure 2.5  

a) The TRIM-calculated theoretical ranges of protons, He⁺, Be⁺, B⁺, C⁺ and Mg⁺ ions implanted into GaAs; and b) the TRIM-calculated impurity distribution in GaAs after the same dose of 30keV protons, 300keV protons, 1.3MeV C⁺ ions and 2MeV C⁺ ions.
GaAs, but all the principles described above are applicable equally to both n and p-type Al\_xGa\_1-xAs. If Al\_xGa\_1-xAs is implanted with ions then the usual defect states in the band-gap are observed, and the temperature stability of the post-implantation resistivity is almost identical to that of GaAs. Also, TRIM calculations indicate that for a specific implantation process the distribution of damage in Al\_xGa\_1-xAs is similar to that in GaAs - the only differences are that the overall amount of damage created is less in Al\_xGa\_1-xAs because its lattice binding energy is higher, and R_n is slightly greater in Al\_xGa\_1-xAs because of its lower crystal density (which decreases with x).

2.5 - Ion implantation of aluminium gallium arsenide/gallium arsenide heterostructures

There have been many investigations of the post-implantation optical characteristics of Al\_xGa\_1-xAs/GaAs heterostructures\textsuperscript{34-38}, but, to the knowledge of the author, very few investigations of the associated electrical characteristics\textsuperscript{39}. Most of these investigations were carried out to quantify and qualify the post-implantation enhancement of the anneal-induced interdiffusion of Al and Ga across the Al\_xGa\_1-xAs-GaAs interfaces within large superlattices.

2.5.1 - Damage distribution within superlattices

In ion-implanted Al\_xGa\_1-xAs/GaAs superlattices the GaAs layers are damaged more greatly because the lattice bond-strength increases greatly with x, and the small mismatch between the Al\_xGa\_1-xAs and GaAs lattices creates a small tensile strain in the GaAs. Interstitial loops, therefore, nucleate preponderantly in the GaAs layers of an ion-implanted Al\_xGa\_1-xAs/GaAs superlattice\textsuperscript{34-35}.

2.5.2 - Implantation-enhanced interdiffusion across interfaces

Even at temperatures higher than 800°C very little interdiffusion between Al and Ga atoms occurs across a well-defined interface. Many groups\textsuperscript{34-38} have discovered that after damaging the interface (using ion implantation) the amount of interdiffusion occurring during annealing at similar temperatures is several orders of magnitude greater; this is believed to be caused by the recombination of interstitial Al and Ga atoms with the implantation-created vacancies. Implantation-enhanced interdiffusion increases with damage, which, in turn, increases with both the ion dose and the ion mass. In other words, the interdiffusion increases with the
average distance between a vacancy and its associated interstitial atom.

2.6 - The ion accelerators used during this research

Three of the ion accelerators at the University of Surrey were used during the author's research, and each one is described below. The two highest-energy ion accelerators are capable of implanting a large variety of elements, and have excellent mass resolution and ion-beam purity; these are a result of the technical expertise at the EPSRC Central Facility for Ion-beam Technology based within the Department of Electronic and Electrical Engineering at the University of Surrey. This facility was commissioned in 1978, and for most of the years since it has been managed and directed by B.J. Sealy and K.G. Stephens.

2.6.1 - The 400kV accelerator

This ion accelerator can produce a very-high ion-beam current (800μA is a typical current when implanting Ar⁺ ions); therefore, it is used primarily for the high-dose implantations of Co⁺ and Fe⁺ ions into Si to synthesise the associated silicide layers (an important part of the research carried out by the Department of Electronic and Electrical Engineering at the University of Surrey). The 400kV accelerator, otherwise known as the Surrey high-energy ion-beam accelerator (SHEBA), is more than twenty years old and is planned to be replaced soon even though most of its original components have been either replaced or maintained well. It was used during some of the work described in Chapters 3, 5 and 6, all of which involved low-dose implantations of protons. Protons are easy to separate from other ions when monitoring the beam with the (low-quality) mass spectrometer incorporated into the 400kV accelerator; therefore, its poor mass resolution was not a problem. S. Hutchinson was its operator (with assistance from the author).

2.6.2 - The 500kV accelerator

The 500kV accelerator is capable of implanting ions having an energy as low as 25kV in an ion-beam current of up to 100μA. Its low-energy capability was utilised during the short project involving implant isolation of δ-doped materials, which is briefly described above and in the first publication listed on page iii. The 500kV accelerator was also used for some of the work described in Chapters 3 and 6 (R.M. Gwilliam was its operator).
2.63 - The 2MV accelerator

The newest of the three ion accelerators (it was installed in 1991), the 2MV accelerator was built originally as the prototype for a new design, but Surrey's remains the only one of its type in the world; hence its relatively-low reliability and serviceability (but these are improving quickly with the knowledge and experience of its technicians). Ion-beam currents of 50μA have been attained when using the 2MV accelerator, which was used during all the work described in Chapter 4 and some of the work described in Chapters 5 and 6 (R.J. Wilson was its operator).

2.7 - Summary

The relevant physics of the implantation processes described within the subsequent chapters has been summarised. The two complementary implant-isolation techniques which can create resistive layers within III-V semiconductors have been described, together with descriptions of their appropriate uses. The results obtained during the first ten months of the author's research, where variations of the ion-beam current were used to change the damage in a simple implant-isolated GaAs multilayer structure, were shown and described briefly. Also described were the annealing characteristics of ion-implanted III-V semiconductors, which involve the repairing of different types of defects during different stages. A brief summary of the investigations of ion-implanted AlGaAs/GaAs heterostructures reported to date was given. The three ion accelerators used during the work described in the subsequent chapters were described briefly.
2.8 - References

11. III-Vs Review, 8 no. 5 p. 4
22. Carried out by D.A. Ritchie and E.H. Linfield at the Cavendish Laboratory, Department of Physics, University of Cambridge.
23. Carried out by S. Gymer at the Cavendish Laboratory, Department of Physics, University of Cambridge.
Cambridge.


25 Measured by A.P. Churchill at the Cavendish Laboratory, Department of Physics, University of Cambridge.


PART 2

The Engineering Objective
Chapter 3

ION IMPLANTATION FOR THE THREE-DIMENSIONAL INTEGRATION OF SINGLE- AND DOUBLE-BARRIER DIODES: DAMAGE CREATION

3.1 - Introduction

As described in sections 1.2 and 1.3, by integrating DBDs with microwave-detector diodes, a low-surface-area high-performance integrated circuit could mix microwaves. This chapter describes the initial attempts at attaining one of the primary objectives of this research, namely the development of an implant isolation process where near-surface DBDs are implanted with ions to create a resistive layer beneath them (as part of a potential device integration technology where the wafer would be ion-implanted in selected areas only). A successful development of this process would allow the 3D integration of DBDs with other devices (see figure 3.1). Figure 3.2 depicts the layer structure with which the vertical integration of DBDs and microwave-detector diodes could be attained, and the implantation-created damage distribution necessary to create a resistive layer between the two types of diode. The theoretical damage distribution depicted in figure 3.2 is that created in GaAs by an implantation of 300keV protons: note the large difference between the amount of damage creation near the surface to that at much greater depths (see sub-section 2.2i). The objective of this work was to create a resistive layer at ~2.0μm by implanting protons through the double-barrier structure without causing irreparable damage to it. Experimentally this damage would be less, particularly near the surface, because of intrinsic annealing, which can be increased by carrying out the implantation process at 150°C or above.
Figure 3.1  A schematic of the mesa structure of a DBD integrated with an ASPAT diode at a greater depth. The required depth of the high-resistivity layer is depicted. To attain the 3D integration of diodes in the two levels of devices, the high-resistivity layer should be created between the two levels of devices only in selected areas of the wafer.
Damage created per ion (vacancies cm$^{-2}$)

Chapter 3  ION IMPLANTATION FOR THE THREE-DIMENSIONAL INTEGRATION OF .... DAMAGE CREATION

Figure 3.2  A schematic of the layer structure with which the 3D integration of DBDs and microwave-detector diodes could be attained, depicted together with the theoretical distribution of damage in GaAs created by an implantation of 300keV protons.
3.2 - Experimental procedure

The work described here was carried out using two samples\(^1\), grown by MBE, with obvious NDR at 295K. During the growth of the samples they were held firm inside the MBE chamber by coating the back of the substrate with indium, which melts at a temperature suitable for using it as an adhesive. Conveniently, the indium diffuses into the substrate; thus creating a ‘ready-made’ ohmic contact. Figure 3.3 depicts the layer structures of both samples.

3.21 - As-grown sample uniformity

Figure 3.4 depicts the forward-bias \(I(V)\) characteristics of eight as-grown specimens of a typical DBD wafer grown at the University of Nottingham for this work. Each specimen was located at a different distance from the centre of the wafer: the first and eighth specimens being 10mm and 22mm from the centre respectively. \(I_p\) increased with distance from the centre, but neither \(V_p\) nor the PVCR changed much. These results represent the excellent wafer uniformity\(^2\) of all the DBD samples grown at the University of Nottingham for this work.

3.22 - Photolithography and etching: sample NU1222

Conventional cleaning, wet-chemical etching and photolithography\(^4\) were used to prepare the specimens of sample NU1222, most of which had an area of approximately 0.5cm\(^2\) (after cleaving with a diamond scribe). Before etching mesas the specimens were washed in boiling methanol, boiling acetone and boiling isopropylalcohol in pyrex beakers on a hotplate - each wash took ten minutes. Immediately after being taken from the isopropylalcohol the specimens were rinsed in de-ionised water, and then blow-dried by a jet of \(N_2\) gas. Each specimen was then mounted onto a glass cover slip (using baked photoresist as an adhesive) because the indium-coated back-surface was not smooth enough for the creation of a vacuum when spin-coating the photoresist onto its top-surface, and when aligning the specimen for photolithography.

Before the photolithography, the specimens were placed on the hotplate, which was at a constant 100°C, to evaporate surface moisture. The first photolithographic step involved spin-coating at 6000rpm a 0.5\(\mu\)m-thick layer of AZ1505 photoresist, which was then soft-baked at 100°C for forty seconds. After the unmasked areas of photoresist were exposed to UV radiation for three seconds, the photoresist was developed in a 4:1 mixture of de-ionised water and AZ400
**Figure 3.3** The as-grown layer structures of the two samples investigated.
Figure 3.4  The probed forward-bias $I(V)$ characteristics of a typical Nottingham-grown DBD wafer at different radii.
photoresist-developer; this took approximately one minute, after which the specimens were rinsed in de-ionised water and blow-dried by the jet of N\textsubscript{2} gas. The photoresist was then hard-baked at 100°C for thirty minutes.

Most of the individual devices of NU1222, which had lateral dimensions between 50 and 140\textmu m, were etched to a depth of 0.65\textmu m in a 1:8:40 solution of H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O for 70 seconds (the depth of the mesas was measured using a talystep\textsuperscript{6}); this solution was prepared usually by adding 5cm\textsuperscript{3} of 99% H\textsubscript{2}SO\textsubscript{4} to 200cm\textsuperscript{3} of de-ionised water, a mixing process which cause an effervescent reaction to occur. The H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O solution was left for one hour to cool down to room temperature before 40cm\textsuperscript{3} of 30% H\textsubscript{2}O\textsubscript{2} was added. The etching process was then carried out immediately. After removing the photoresist in acetone (and removing the specimens from the cover slips), the specimens were washed as described above, and remounted on cover slips. For ten minutes the specimens were then placed on the hotplate, which was at a constant 100°C, to evaporate surface moisture before the second photolithography step was carried out.

The second photolithography step involved spin-coating at 6000rpm a 3\textmu m-thick layer of AZ4330 photoresist, which was then soft-baked at 100°C for forty seconds. After the unmasked areas of photoresist were exposed to UV radiation for three seconds, the photoresist was developed in a 3:1 mixture of de-ionised water and AZ400K; this took up to three minutes, after which the specimens were blow-dried by the jet of N\textsubscript{2} gas before the photoresist was hard-baked at 100°C for thirty minutes. Then the specimens, which were still mounted on cover slips, were mounted onto glass slides (using melted wax as an adhesive). Before ohmic contacts were evaporated\textsuperscript{6} onto the specimens, for thirty seconds they were dipped into a 1:10 mixture of NH\textsubscript{3}OH:H\textsubscript{2}O to remove any oxide layer. Then the samples were rinsed in de-ionised water, blow-dried in the jet of N\textsubscript{2} gas, and mounted inside the multi-crucible evaporator for ohmic-contact deposition. From the layer nearest the GaAs to the top, the ohmic contacts consisted of 10nm of Ge, 40nm of Au, 10nm of Ni and 140nm of Au.

3.23 - Photolithography and etching: sample NU168

The individual devices of sample NU168, which had diameters between 20 and 200\textmu m, were prepared elsewhere\textsuperscript{6}, but using a similar technique: the DBD specimens, each having an area of approximately 0.5cm\textsuperscript{2}, were etched to ~1.5\textmu m using a 1:1:1 solution of HBr:CH\textsubscript{3}COOH:K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. Ohmic contacts consisting of
0.22\(\mu\)m of AuInGe were then evaporated onto them.

3.24 - 'Lift-off' and alloying of ohmic contacts

On both samples the two sets of ohmic contacts were on the top surface of the specimens (the indium layer on the back surface of the substrate was used as a back contact only when measuring the sheet resistivity of the material below the mesas). By evaporating both sets of ohmic contacts onto the top surface of the specimens, and etching the mesas to depths within 2\(\mu\)m, none of the bias voltage during \(I(V)\) measurements will have been applied across the buried resistive layer, and the resulting \(I(V)\) characteristics will be those of the ion-implanted DBD only. After ‘lifting off’ the photoresist in boiling acetone, each specimen was blow-dried by a jet of \(N_2\) gas before being subjected to a 400°C/10s contact-alloying process inside an optical furnace\(^7\) (with which one could control both the ramping time and the peak temperature). To minimise surface oxidation during the contact-alloying process, \(N_2\) gas was passed through the specimen chamber of the optical furnace; this was started five minutes before the furnace was switched on.

3.25 - \(I(V)\) measurements

For preliminary 295K measurements the samples were probed, and the \(I(V)\) characteristics were displayed on a Telequipment curve tracer. Using a Kulicke & Soffa 4124 ultrasonic bonder with 1/1000 inch Au wire, and the specimen holder at a constant 130°C, some 0.1\(cm^2\) specimens were wire-bonded to eighteen-pin chip carriers for low-temperature \(I(V)\) measurements. Using a variable 5V power supply, a basic Keithley ammeter and the equivalent voltmeter, the \(I(V)\) data of each sample before proton implantation were obtained both at 295K and 77K. For convenience, during the later stages of this work, this simple \(I(V)\) measurement system was substituted for a Hewlett Packard 4156A Precision Semiconductor Parameter Analyser; most of the subsequent \(I(V)\) measurements were carried out using this.

Figure 3.5 depicts a schematic layout of the two \(I(V)\) data-acquisition systems, both of which involved pseudo-four-terminal measurements. These type of measurements involve measuring the voltage across two connections in parallel to the device, the two connections being as close to the device as possible; therefore, the series resistance of the cables along which the measured current flows is effectively negated. The \(I(V)\) measurements made prior to obtaining the ’4156A were not repeated because the simple \(I(V)\) measurement system was at least as accurate: the
Gold probes/sample holder to make a connection to the ohmic contacts/chip carrier.

Figure 3.5  Schematic wiring diagrams of the two $I(V)$ measurement systems.
Chapter 3  Ion implantation for the three-dimensional integration of damage creation

295K $I(V)$ characteristics of NU1222 obtained using the two measurement systems are depicted in figure 3.6. NU1222 was the most difficult sample to investigate because at a specific bias it had the lowest resistance relative to that of the complete circuit, but the two sets of data depicted in figure 3.6 are practically identical.

Apart from convenience, the other obvious advantage when using the '4156A was that a maximum of 1000 data-points per measurement could be obtained in only a few seconds: when using the simple $I(V)$ measurement system, approximately fifty data points could be obtained within ten minutes.

The probed $I(V)$ characteristics are depicted in the relevant graphs in section 3.3, and figure 3.7 depicts the 5K, 77K and 295K $I(V)$ characteristics of the wire-bonded specimens.

3.26 - Proton implantation

After the $I(V)$ measurements, some of the processed specimens were subjected to a room-temperature implantation of protons from the 400kV accelerator. To compensate for the presence of the 0.2μm-thick metal layers, which do not suffer persistent implantation-created damage, 325keV protons were used instead of 300keV protons. The proton-doses varied from $1 \times 10^{13}$ cm$^{-2}$ to $2 \times 10^{14}$ cm$^{-2}$, most of which were expected to be too low to create an adequate post-anneal buried resistive layer beneath the ion-implanted DBDs: these specimens were used during the preliminary investigations of the $I(V)$ characteristics before and after annealing, the results of which will be described below (Chapter 5 describes more detailed investigations of the electronic transport through these and other ion-implanted DBDs). The implantation of protons was carried out after the processing of the specimens because a post-implantation contact-alloying process will have annealed a large amount of the damage; thus preventing any pre-anneal investigations of the $I(V)$ characteristics. An ion-beam current of ~0.2μA was used, which should not have heated the specimens during the implantation process (any heating could have reduced the amount of damage created).

Using an ion-beam current of ~1μA from the 500kV accelerator, $3 \times 10^{14}$, $5 \times 10^{14}$ and $8 \times 10^{14}$ 300keV protons cm$^{-2}$ were implanted into unprocessed specimens of NU1222. To minimise the accumulation of near-surface damage during the implantation of protons into these specimens, they were heated to 150°C whilst fixed to the accelerator specimen-holder. The procedure used to prepare these specimens for $I(V)$ measurements was identical to that described above; however, to investigate...
Figure 3.6 The probed $I(V)$ characteristics of NU1222 measured with the simple $I(V)$ measurement system and the Hewlett Packard 4156A Precision Semiconductor Parameter Analyser.
Figure 3.7 The $I(V)$ characteristics of the two samples. The PVCR of each data set is shown in brackets. The asterisks mark the occurrence of 3D-2D resonant tunnelling of ballistic electrons.
the effectiveness of the proton implantation in creating a resistive layer in series with the double-barrier structure, some mesas were etched to 3.2μm (which took 330 seconds). The implantation-created damage at 2.0μm was not affected much by the contact-alloying process: after the alloying the sheet resistivity of the damaged material was still ~10^6Ω square^-1, which was the order-of-magnitude expected^8-12.

The ion beam of all the implantation processes was at 7° from the normal to the surface of the specimens (see sub-section 2.31).

3.3 - Results and discussion

Considering the material implanted with the doses of 1x10^13 and 2x10^13 protons cm^-2, although there was both an obvious and an expected degradation of the DC performance caused by the implantation of protons, figure 3.8 indicates that during room temperature I(V) measurements there was some occurrence of resonant tunnelling, the current density and abruptness of which decreased with increasing dose. The low currents and low-quality resonance characteristics depicted in figure 3.8 are caused primarily by the decrease of n in the contact layers, particularly the n-doped spacer layers. The degradation of the I(V) characteristics caused by ion implantation will be described in detail in Chapter 5.

3.31 - The anneal-induced recovery of the as-grown I(V) characteristics

The low-quality DC performance of the material is not representative of poor structural integrity of the Al_{0.4}Ga_{0.6}As barriers; these, it seems, were damaged very lightly by the implantation process. As figure 3.9 depicts, annealing the material implanted with these relatively-small dose of protons, at temperatures between 300 and 600°C for thirty seconds in steps of 100°C, resulted in an almost-complete recovery of the as-grown I(V) characteristics. The optical furnace used was the same as that described in sub-section 3.24, which made possible the use of a constant ramping-time for all programmed peak temperatures (the ramping time was always ~20s). At the temperatures used for the annealing processes there would be a) very little evaporation of either Ga or As from the surface of the specimens^13, and b) no measurable interdiffusion of Al and Ga within the ion-implanted double-barrier structure - the annealing processes would have done nothing more than repair the implantation-created defects, and, hence, increase n in the contact layers by freeing the trapped electrons.
Figure 3.8  The probed 295K reverse-bias $I(V)$ characteristics of NU168 after doses of $1\times10^{13}$ and $2\times10^{13}$ 325keV protons cm$^{-2}$. 
Figure 3.9  The probed 295K $I(V)$ characteristics of NU1222 (forward bias) and NU168 (reverse bias) after a dose of $1 \times 10^{13}$ 325keV protons cm$^{-2}$, and subsequent annealing for thirty seconds at the temperatures shown. The as-grown PVCRs are 2.2:1 and 2.6:1 for NU1222 and NU168 respectively, and 2.0:1 and 2.5:1 in the bottom-right graph.
It must be mentioned that 1) the recovery of the as-grown electrical characteristics of an ion-implanted semiconductor device having quantum length-scale layers had not been observed before this work was carried out, and 2) the ability of fully-fabricated mesas to withstand an anneal at 600°C had never been demonstrated before (recent work at the Massachusetts Institute of Technology demonstrated that fully-fabricated commercial GaAs VLSI circuitry can withstand extended durations at 500°C).

3.32 - Ion-dose dependent recovery of the as-grown \( I(V) \) characteristics

The almost-complete recovery of the as-grown 295K \( I(V) \) characteristics of the material implanted with higher doses of protons was attained after carrying out the same annealing process - figure 3.10a depicts the results of this when investigating NU1222. These results prove that there is a small decrease of both the recovered PVCR and the recovered peak current-density \( I_{pd} \) with an increase of proton-dose; this indicates that the effectiveness of rapid thermal-annealing decreases with ion-dose (which was expected). The effectiveness of rapid thermal-annealing at temperatures below 600°C was observed to decrease with proton dose: the post-500°C/30s anneal \( I(V) \) characteristics of the specimens implanted with the dose of \( 2 \times 10^{14} \) 325keV protons cm\(^{-2} \) were similar to the pre-anneal characteristics after the dose of \( 2 \times 10^{13} \) cm\(^{-2} \).

Figure 3.10b depicts both the 295K and 77K forward-bias \( I(V) \) characteristics of NU1222 after a dose of \( 2 \times 10^{13} \) 325keV protons cm\(^{-2} \), and annealing at 550°C for ten seconds (the equivalent reverse-bias \( I(V) \) characteristics were similar). The forward-bias 77K PVCR of this specimen was 8.2:1, which is approximately half the as-grown 77K PVCR. The equivalent \( I(V) \) characteristics of NU168, which were very different, will be described in Chapter 5.

3.33 - Enhancing the recovery of the as-grown \( I(V) \) characteristics

Figure 3.11a depicts the 295K \( I(V) \) characteristics of NU1222 after the higher-dose implantations of protons (carried out at 150°C), and annealing at 600°C for thirty seconds. Compared with the results depicted in figure 3.10a the recovery of the \( I(V) \) characteristics was improved, even though higher doses of protons were implanted. The improved recovery of the post-implantation \( I(V) \) characteristics is attributed primarily to carrying out the proton implantation at 150°C (as mentioned earlier, this should have minimised the accumulation of near-surface damage), but
Figure 3.10 The post-anneal $I(V)$ characteristics of NU1222 implanted with proton doses between $2 \times 10^{13} \text{cm}^{-2}$ and $2 \times 10^{14} \text{cm}^{-2}$. 
Figure 3.11 The post-anneal \(I(V)\) characteristics of NU1222 implanted with proton doses between \(3\times10^{14}\,\text{cm}^{-2}\) and \(8\times10^{14}\,\text{cm}^{-2}\).
the use of a larger ion-beam current during the high-temperature implantation processes may also have enhanced the amount of intrinsic annealing. In fact, the post-anneal $I_{pd}$ through the specimen implanted with the dose of $3\times10^{14}$ 300keV protons/cm$^2$ was slightly higher than the as-grown $I_{pd}$; the resistance of the ohmic contacts will have been reduced after the 600°C/30s anneal because the number of active Ge atoms$^{13}$ diffused into the emitter will have been increased. The data depicted in figure 3.11a also indicate that the recovery of the as-grown $I(V)$ characteristics is dependent on the dose of implanted protons, which is consistent with the results depicted in figure 3.10a. Figure 3.11b depicts the 295K and 77K $I(V)$ characteristics after the dose of $3\times10^{14}$ 300keV protons/cm$^2$ (the forward-bias PVCR was 2.1 and 13.2 at 295K and 77K respectively).

3.34 - The effectiveness of the implantation-and-anneal processes

When investigating the material implanted with the dose of $5\times10^{14}$ cm$^{-2}$ and annealed at 600°C for thirty seconds, there was no NDR observed during the $I(V)$ measurements of the specimens etched to a depth of 3.2μm; these data are consistent with there being a resistive layer in series with the DBD. At $V_p$ of the DBD etched to 0.65μm (0.55V), the average resistivity of the material below the first 0.65μm was calculated to be approximately four times greater. Assuming that the depth dependence of the resistivity is similar to that of the implantation-created damage, most of the added resistivity will be between the depths of 2.0 and 2.6μm. At 0.55V, therefore, the resistivity between those depths is estimated to between ten and fifteen times greater than that within the first 0.65μm (which is primarily the resistivity of the double-barrier structure). For the purposes of electrically-isolating the DBD from a device beneath it, this is inadequate.

Improving the effectiveness

The difference between the post-anneal resistivity at ~2μm and that near the surface of material implanted (at room temperature) with larger doses of 300keV protons ($1\times10^{15}$ and $5\times10^{15}$ cm$^{-2}$) or heavier ions (750keV He$^+$ and 2MeV B$^+$ ions - see the subsequent chapters) was no larger than that described above, even after using a higher-temperature stage 2 anneal together with a much shorter anneal duration (e.g.700°C/1s). More advanced post-implantation anneal processes, such as laser thermal-annealing$^{15}$, electron-beam thermal-annealing$^{15}$, and low-temperature minority-carrier injection$^{16-18}$, may be the only techniques which could anneal the
near-surface material without annealing the buried resistive layer.

By using the minority-carrier injection process\textsuperscript{16-18} just mentioned, the damage within an ion-implanted DBD could be annealed without annealing the material beneath it. The technique, usually carried out at 200°C, involves the injection of a large current of holes into the (illuminated) specimen, and then the subsequent recombination of each hole with an electron trapped within a defect; therefore, some p-type doping of the DBD wafer during growth would be necessary. The phonon released during a recombination process expedites the annealing of the defect from which it originated; thus enhancing the annealing process only in a highly localised volume of the damaged semiconductor.

At 250°C the stability of the damage created within the specimens of NU1222 implanted with a dose of 8x10\textsuperscript{14} 300keV protons cm\textsuperscript{-2} was investigated - a specimen was annealed at 250°C for one hour, and the pre- and post-anneal resistivity of this material were compared: they were calculated to be \(\sim 4 \times 10^6 \Omega \text{ square}^{-1}\) and \(\sim 6 \times 10^6 \Omega \text{ square}^{-1}\) respectively; this is consistent with the results reported by Pearton\textsuperscript{9}, and indicate that post-implantation anneal processes can decrease the amount of hopping conduction between defect states within the band-gap. If an ion-implanted DBD was subjected to the low-temperature annealing process described above, the damage within the diode mesa could be annealed whilst increasing the high-resistivity of the material at greater depths. No low-temperature annealing processes were attempted by the author. Instead, ion implantation (and annealing) to create a chemically-compensated layer beneath the DBDs was carried out; this is described in the next chapter.

3.35 - The post-anneal uniformity of ion-implanted specimens

Figure 3.12 depicts the probed 295K forward-bias \(I(V)\) characteristics of five identical specimens of NU168 (situated within 10mm of each other) which, after ohmic-contact deposition and alloying, were subjected to the dose of 4x10\textsuperscript{13} 325keV protons cm\textsuperscript{-2}, and a 550°C anneal for ten seconds: note that all five \(I(V)\) characteristics are almost identical; this is typical of all the implanted-and-annealed specimens of either sample investigated, and indicates that no non-uniformity is created by any of the implantation-and-anneal processes.

3.36 - The post-anneal quality of the ohmic contacts

The 600°C anneals used during all the above-mentioned work did not destroy
Figure 3.12  The probed 295K forward-bias $I(V)$ characteristics of five identical specimens of NU168 after an implantation of $4 \times 10^{13}$ 325keV protons cm$^2$, and a $500^o$C anneal for ten seconds. Note that the implantation process was carried out after ohmic-contact metallisation.
the ohmic contacts or cause any diffusion of donors through the double-barrier structure. Both before and after any annealing the specific contact-resistivity was usually ~10⁶Ω cm², which is the order-of-magnitude expected when using AuGe-based metal contacts on n-type GaAs (the contact resistivities were measured using the standard transmission-line technique). After annealing at temperatures above 520°C, the surface of the AuGeNi contacts became visibly rougher. The roughness of the surface was believed to be caused by the AuGeNi alloy agglomerating during the 600°C anneals. Consequently, wire-bonding to these AuGeNi contacts was very difficult. Much less agglomeration of the AuInGe contacts occurred during 600°C anneals, and subsequent wire-bonding to them was easy.

### 3.4 - Conclusions

The implantation of relatively-low doses of protons through DBDs destroys the I(V) characteristics of the diodes, but these can be recovered almost completely by annealing at and above 600°C. The double-barrier structures were damaged very lightly during the low-dose implantation processes used, but many of the Si donors had been effectively deactivated. This work is believed to be the first to observe the anneal-induced recovery of an ion-implanted electronic device containing quantum length-scale layers. The anneal-induced recovery of the as-grown I(V) characteristics of proton-implanted DBDs was improved by heating the diodes to 150°C during the implantation process. Indeed, the post-anneal $I_{pd}$ through the specimen implanted with a dose of 3x10¹⁴ 300keV protons cm⁻² was slightly higher than the as-grown $I_{pd}$. The creation of a resistive layer beneath the DBDs was observed, but was proved to be inadequate for the purposes of electrically-isolating the diode from another device beneath it. No non-uniformity across a specimen was created by the implantation-and-anneal processes. The implantation-created damage was proved to be stable at 250°C; this makes possible the effective use of a low-temperature annealing process which repairs the near-surface damage but does not repair the heavier damage at greater depths.
3.5 - References

1. Grown by M. Henini at the Department of Physics, University of Nottingham.
4. Carried out with the assistance of A.F. Royle at the Department of Electronic and Electrical Engineering, University of Surrey.
5. Carried out at the Department of Electronic and Electrical Engineering, University of Surrey.
6. Carried out by G. Hill at the Department of Electronic and Electrical Engineering, University of Sheffield.
7. Designed and built by R.M. Gwilliam at the Department of Electronic and Electrical Engineering, University of Surrey.
19. R.M. Gwilliam (private communication).
Chapter 4

ION IMPLANTATION FOR THE THREE-DIMENSIONAL INTEGRATION OF SINGLE- AND DOUBLE-BARRIER DIODES: CHEMICAL COMPENSATION

4.1 - Introduction

This chapter describes the second set of attempts at creating an electrically-insulating layer ~2μm below a near-surface double-barrier structure. Implantations of either C⁺ ions or Mg⁺⁺ ions to create a chemically-compensated resistive layer were carried out. The work described in this chapter was somewhat more tentative that described in Chapter 3: the double-barrier structures were damaged much more heavily during these more-powerful implantation processes and during the subsequent annealing to electrically activate the C and Mg atoms. The results obtained during investigations of Mg⁺⁺-implanted AlGaAs/GaAs superlattices¹, however, proved that little interdiffusion of Al and Ga across the heterojunctions occurs during both the implantation process and the subsequent annealing; therefore, it was hoped that the implanted-and-annealed DBDs would have similar I(V) characteristics to the as-grown characteristics (assuming that the density of acceptors within the double-barrier structure was too low to change the characteristics). The results obtained during investigations of the ease with which implanted Mg atoms in GaAs could be electrically activated²³ proved that there was some justification for believing that the resistivity of the chemically-compensated layers beneath the DBD would be much more resistive than the damaged layers described in Chapter 3.

During all the implantation processes most of the specimens were at a high
temperature to minimise near-surface damage, and the ion beam was at 7° from the normal to the surface of the specimens (see sub-section 2.3i).

4.11 - The DBD samples used

NU1222 and three other structurally-related samples were investigated; these three other samples were called NU1331, NU1332 and NU1333. Figures 4.1 and 4.2 depict their as-grown layer structures and $I(V)$ characteristics: note that the layer structure of both NU1332 and NU1333 were very asymmetric (the configuration of a QWITT diode), whereas NU1331 had a symmetric layer structure (both spacer layers were very thick). The differences between the $I(V)$ characteristics of the four samples are explained in the Appendix.

4.2 - Carbon implantation

To reach a depth of ~2μm within GaAs, C+ ions have to be accelerated to 2MeV (see figure 4.3a); this was the energy used, which meant that the 2MV accelerator had to be used at its limit. The lowest possible dose of 2MeV C+ ions was implanted, i.e. it was assumed that the anneal-induced activation of the implanted C atoms would be 100%; this was an unreasonable assumption, but if the double-barrier structure withstood this implantation-and-anneal process then higher doses would be implanted subsequently.

4.21 - Theoretical procedure

Equation (2-14) was used to calculate the dose of 2MeV C+ ions necessary to chemically-compensate $2 \times 10^{18}$ Si atoms cm$^{-3}$. TRIM calculated that $R_p$ of 2MeV C+ ions in GaAs is 2.1μm, and that $\Delta R_p$ is 0.32μm. A dose of $1.6 \times 10^{14}$ 2MeV C+ ions cm$^{-2}$ was calculated to be necessary. To create a thicker layer of chemically-compensated GaAs (assuming 100% activation of the C atoms), and possibly a p-type layer at ~2.1μm, a dose of $2.2 \times 10^{14}$ ions cm$^{-2}$ was implanted (see figure 4.3a). At least part of any thin p-type layer created beneath the DBDs would be depleted of holes because of the presence of the two p-n junctions.

4.22 - 2MeV C+ implantation

Using a 0.1μA ion-beam current generated by the 2MeV accelerator, the dose of 2MeV C+ ions calculated above was implanted into three different 0.5cm$^2$
Chapter 4  **ION IMPLANTATION FOR THE THREE-DIMENSIONAL INTEGRATION OF CHEMICAL COMPENSATION**

### Table 4.1

<table>
<thead>
<tr>
<th>Layer Structure</th>
<th>Doping Level</th>
<th>Sample Code</th>
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<tbody>
<tr>
<td>0.4μm GaAs</td>
<td>2E18 n+ doped</td>
<td>NU1331 X = 100</td>
</tr>
<tr>
<td>50nm GaAs</td>
<td>2E17 n doped</td>
<td>NU1332 X = 10</td>
</tr>
<tr>
<td>50nm GaAs</td>
<td>2E16 n doped</td>
<td>NU1333 X = 20</td>
</tr>
<tr>
<td>Xnm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.7nm AlGaAs (x=0.40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1nm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.7nm AlGaAs (x=0.40)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120nm GaAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50nm GaAs</td>
<td>2E16 n doped</td>
<td></td>
</tr>
<tr>
<td>50nm GaAs</td>
<td>2E17 n doped</td>
<td></td>
</tr>
<tr>
<td>2μm GaAs</td>
<td>2E18 n+ doped</td>
<td></td>
</tr>
</tbody>
</table>

**n+ GaAs substrate**

Figure 4.1  The as-grown layer structure of three of the samples investigated, and the as-grown $I(V)$ characteristics of NU1331. The numbers in brackets are the forward- and reverse-bias PVCRs.
Figure 4.2  The as-grown $I(V)$ characteristics of both NU1332 and NU1333. The numbers in brackets are the forward- and reverse-bias PVCRs.
Figure 4.3  a) The theoretical distribution of C atoms after an implantation of 2.2x10^{14} 2MeV C^+ ions cm^2, and b) the post-anneal $I(V)$ characteristics of the C^+-implanted specimens of NU1222.
specimens of NU1222: one of which was at room temperature during the implantation process, the second heated to 150°C and the other to 285°C.

4.23 - Post-implantation sample preparation

After the implantation processes the specimens were capped with 50nm of Si$_3$N$_4$, which was used to prevent the evaporation of either Ga or As from the surface of the specimen during the subsequent anneal. During the deposition of the Si$_3$N$_4$ cap the specimens were at a maximum of 300°C for ten minutes. The work of other groups indicated that a 950°C anneal for ten seconds would activate ~20% of the implanted C atoms. As will be described in section 4.5, anneals at temperatures higher than 800°C degrade the composition of even as-grown Al$_x$Ga$_{1-x}$As/GaAs heterostructures (this was also mentioned in section 2.5), but the 950°C anneal was attempted with the intention of using lower-temperature anneals subsequent to success of the 950°C anneal.

After the annealing process, the Si$_3$N$_4$ cap was removed in a 48% HF solution (this took anything between five and thirty minutes). The samples were then washed in de-ionised water, and blow-dried in a jet of N$_2$ gas before the first few surface layers of GaAs were removed by a fifteen-second bathing in a 1:8:40 solution of H$_2$SO$_4$:H$_2$O$_2$:H$_2$ (which was prepared as described in sub-section 4.21); this was carried out to ensure that the GaAs surface was devoid of residual Si$_3$N$_4$, which would prevent the making of ohmic contact between the AuGeNi and GaAs. Metallised mesas were fabricated on the specimens by using the processes described in sub-sections 3.22 and 3.24 (where the top and bottom ohmic contacts were on the top-surface and above the resistive layer).

4.24 - Results and discussion

Figure 4.3b depicts typical $I(V)$ characteristics of the fully-processed C$^+$-implanted specimens; these results are independent of the specimen temperature during the implantation process: the very powerful 950°C post-implantation anneal ostensibly negated the importance of heating the specimen holder of the ion accelerator during implantation.

Degraded $I(V)$ characteristics

Even after implantation of this lowest-possible dose of 2MeV C$^+$ ions, the post-anneal 295K $I(V)$ characteristics of the DBDs were much inferior to the
as-grown characteristics: the valley-current density ($I_{vd}$) was higher after implantation-and-annealing; this was also true at 77K but to a lesser extent. During the 950°C anneal the double-barrier structure was damaged probably by 1) anneal-enhanced interdiffusion of Al and Ga across the Al$_{0.4}$Ga$_{0.6}$As-GaAs interfaces, and 2) diffusion of Si into the double-barrier structure. The presence of a small number of C acceptors near the surface should not have resulted in such a large degradation of the $I(V)$ characteristics: both the emitter spacer-layer barrier and the confined energy-state between the barriers will have been made somewhat higher, thus increasing $V_p$, but the PVCR should not have been degraded to such an extent$^{8,9}$.

Compared to the as-grown $I(V)$ characteristics at both 295K and 77K, the post-implantation-and-anneal $I(V)$ characteristics at 77K were degraded much less than those at 295K; this is consistent with the effects caused by 'freeze-out' of the donors having diffused into the double-barrier structure during annealing.

The effectiveness of the implantation-and-annealing

The post-anneal $I(V)$ characteristics of C$^+$-implanted DBDs having 3.2µm-deep mesas were very similar to those depicted in figure 4.3b, i.e. there was apparently no resistive layer buried beneath the DBDs; therefore, this implantation-and-anneal process was, not surprisingly, completely ineffective in creating a resistive layer beneath the diodes. Implanting a higher dose of C$^+$ ions will have increased the number of activated C atoms, but there would also have been more anneal-induced Al$_{0.4}$Ga$_{0.6}$As-GaAs interdiffusion and Si diffusion into the double-barrier structure; therefore, no higher-dose implantations and/or more powerful anneals were attempted.

4.3 - Magnesium implantation

During annealing, implanted Mg atoms in GaAs are much easier to activate than implanted C atoms$^{5,6}$: lower temperatures and shorter durations can be used to attain a specific electrical activation; therefore, it was decided to attempt Mg implantation whilst hoping that the increase of implantation-created damage would be less than the decrease of anneal-induced degradation (there will have been less implantation-enhanced Al$_{0.4}$Ga$_{0.6}$As-GaAs interdiffusion at the lower anneal temperatures used). To reach a depth of ~2.1µm within GaAs, Mg$^+$ ions have to be accelerated to 2.6MeV (see figure 4.4), which was beyond the capabilities of the 2MV
Figure 4.4 The theoretical distribution of Mg atoms in GaAs after each of the doses of 1.3MV Mg$^{++}$ ions. Inset $b$ depicts the theoretical amount of damage created by the lowest dose of Mg$^{++}$ ions and $2.2\times10^{14}$ 2MeV C$^+$ ions cm$^{-2}$. 
accelerator; therefore, 1.3MV Mg++ ions were implanted instead. Both the mass resolution and ion-beam purity within the 2MV accelerator were good enough to ensure that less than 1% of the implanted ions were 1.3MeV C⁺ ions, a large amount of which will have caused much extra damage within a micron below the surface (as indicated by the results depicted in figure 2.5).

### 4.3.1 - Theoretical procedure

Equation (2-14) was used to calculate the doses of 1.3MV Mg⁺⁺ ions necessary to chemically-compensate 2x10¹⁸ Si atoms cm⁻³. TRIM calculated that ΔR_p of 1.3MV Mg⁺⁺ ions in GaAs is 0.36μm. Assuming 100% electrical activation of the implanted atoms, a dose of 1.8x10¹⁴ 1.3MV Mg⁺⁺ ions cm⁻² was calculated to be necessary. To create a thicker layer of chemically-compensated GaAs (and possibly a thin p-type layer also) 2.5x10¹⁴ Mg⁺⁺ ions cm⁻² were implanted (see inset a of figure 4.4). Figure 4.4 depicts the theoretical distribution of Mg atoms in GaAs after implantation of each of the six different doses of 1.3MV Mg⁺⁺ ions. The choice of doses was made assuming that the post-anneal electrical activation of Mg atoms would be between 50% and 100%, the estimation of which was reasonable³.

Figure 4.5 depicts both the theoretical density of displaced Al atoms and the Mg density within an Al₀.₄Ga₀.₆As single-barrier structure after implantation of the highest dose of 1.3MV Mg⁺⁺ ions (calculated by TRIM); these data indicate that at most 5% of the Al atoms in the experimental double-barrier structures would be displaced, but that very few would be displaced to a layer either side of the barriers (before annealing). The density of active Mg atoms may be enough to change the double-barrier structure and possibly the n-doped spacer layers into low-doped p-type material, the effect of which would be to increase V_p. The NDR of the Mg⁺⁺-implanted samples was not expected to be degraded severely by the presence of the Mg acceptors⁸⁹, but the remnant damage created by the Mg⁺⁺ implantation (after subsequent annealing) was expected to degrade the I(V) characteristics somewhat.

#### Possible amorphisation of GaAs

Assuming that \( (E_d)_{GaAs} = 20 \text{eV}, N_{GaAs} = 4.4 \times 10^{22} \text{ cm}^{-3} \), and that \( [(dE/dX)_n]_{GaAs} \) calculated using TRIM was correct, \( \phi_{GaAs} \) of equation (2-6) was calculated and is depicted in figure 4.6 as a function of energy of Mg⁺⁺ ions. \( \phi_{GaAs} \) as a function of energy of the four other ions used during the work described in Chapters 3 to 6 is depicted also. The six doses of Mg⁺⁺ ions described above, and all the other implantation
Figure 4.5 The theoretical distribution of both the Al displacements and the Mg atoms in a single $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ layer below a 0.5 $\mu$m GaAs layer after an implantation of $5\times10^{14}$ 1.3MV Mg$^{++}$ ions cm$^{-2}$. 

Atomic density of Al in $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As} = 8.8\times10^{21}$ cm$^{-3}$
Figure 4.6  The minimum ion-doses necessary to amorphise GaAs (as a function of the energy of five different ions).
processes described in Parts 2 and 3, should not have amorphised the GaAs.

4.32 - 1.3MV Mg$^{++}$ Implantation

Each of the six doses of 1.3MV Mg$^{++}$ ions described above were implanted into many specimens of NU133x. A 0.1μA ion-beam current and a specimen temperature of 280°C were used during the implantation of all six doses.

4.33 - Post-implantation sample preparation

After Mg$^{++}$ implantation the quarter-wafers of NU133x were cleaved into 1cm$^2$ specimens. All these specimens were then capped with 50nm of Si$_3$N$_4$ to prevent the evaporation of either Ga or As from their surface during the subsequent anneals. The work of Patel and Sealy$^9$ indicated that rapid thermal-annealing at temperatures between 700°C and 950°C would activate most of the implanted Mg atoms, and prevent considerable Mg diffusion. Very rapid anneals (where $t$ was less than 5s) between 700°C and 800°C inclusive were carried out. Anneals at temperatures greater than 800°C were not carried out because of the desired minimisation of implantation-enhanced interdiffusion of Al and Ga across the Al$_{0.4}$Ga$_{0.6}$As-GaAs-interfaces. After the annealing process the Si$_3$N$_4$ capping layer was removed as described in sub-section 4.23. The specimens were then prepared as described in sub-sections 3.22 and 3.24 (except that the mesas were etched to a depth of 0.8μm, which took 80s).

Mg$^{++}$ implantation and $C(V)$ profiling of a bulk n-type GaAs sample

Two of the six doses described above (2.8x10$^{14}$ ions cm$^{-2}$ and 3.6x10$^{14}$ ions cm$^{-2}$) were each implanted into a quarter-wafer of a bulk-grown Si-doped GaAs sample, which is referred to hereafter as RMG1. After the post-implantation sample preparation described above (minus the etching and metallisation of diode mesas), each specimen of RMG1 was subjected to electrochemical capacitance(voltage), e$C(V)$, profiling$^{10,12}$ of the net carrier density ($N^*$) as a function of $X$.

All $C(V)$ profiling techniques$^{11,14}$ use a Schottky contact to create a depletion layer in the semiconductor. $N^*(X)$ at the edge of the depletion layer is calculated using the equation

$$N^*(X) = C^3/\varepsilon_o\varepsilon A^2e(dC/dV) \text{ where}$$

$$X = \varepsilon\varepsilon_0 A/C.$$

(4-1)

(4-2)
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The capacitance of a depletion layer in an n-type semiconductor decreases with negative voltage between the Schottky diode and the semiconductor; therefore, \( dC/dV \) and, hence, \( N^* \) will be negative. In p-type semiconductors the capacitance of a depletion layer decreases with positive bias applied at the Schottky contact; therefore, \( dC/dV \) and, hence, \( N^* \) will be positive. \( C \) and \( dC/dV \) are obtained by using a voltage modulated by a low frequency (several kHz).

The maximum \( X \) at which measurements can be made is limited by the reverse breakdown voltage of the Schottky diode; this is a problem particularly when the semiconductor has a high \( N^* \). \( eC(V) \) measurements circumvent this problem by using an electrolyte-semiconductor interface to form a Schottky contact with the semiconductor. When biased appropriately, i.e. more highly, the electrolyte is also used to etch the semiconductor surface. Charge is transferred across the semiconductor-electrolyte interface, where, in a system used correctly, the transfer of electrons to the electrolyte from the conduction band of the semiconductor is balanced by the transfer of holes from the valence band. The etching (dissolution) reaction when investigating GaAs is

\[
\text{GaAs + six holes} \rightarrow \text{Ga}^{3+} + \text{As}^{3+}.
\]

In p-type semiconductors there are enough holes to attain etching, but to create enough holes in an n-type semiconductor it must be illuminated by light having a wavelength less than the band-gap. The four-stage cycle for obtaining a depth distribution of \( N^* \) are 1) obtaining the \( I(V) \) data, from which the range of bias voltages for \( C(V) \) measurements is obtained; 2) obtaining the \( C(V) \) data, from which the bias necessary to attain etching is obtained; 3) measuring the depletion length; and 4) etching (stage 1 is then repeated, and so on). Obviously the etching rate increases with the etching current; therefore, the etched depth can be calculated by using Faraday's law of electrolysis:

\[
X_e = \left[ \frac{M_w}{z} C_p e \right] \int_0^t I_e \, dt
\]

where \( X_e \) is the etched depth, \( I_e \) is the etching current, \( g \) and \( M_w \) are the density and the molecular weight of the semiconductor respectively, \( z \) is the valence of the resulting ions (see the dissolution reaction above) and \( C_p \) is the Faraday constant.
4.34 - Results and discussion 1: eC(V) measurements

Figure 4.7 depicts some of the results obtained during the eC(V) measurements. After the implantation of \(2.8 \times 10^{14}\) Mg\(^{++}\) ions cm\(^{-2}\), the eC(V) data indicate that 70% of the Si dopants within 1\(\mu\)m of the GaAs surface can be reactivated by a 740°C/5s anneal (the as-grown donor density \(1.2 \times 10^{18}\) cm\(^{-3}\) is marked by the dashed line). As figure 4.7 indicates, the 740°C/5s anneal activated a significant number of implanted Mg atoms; hence the p-type layer below 1\(\mu\)m. Considering the quantitative characteristics of this eC(V) data, if one estimates that between 50 and 70% of the Si atoms at that depth were reactivated by the anneal, which is a very reasonable estimate, then the presence of a p-type layer indicates that at least \(6.1 \times 10^{17}\) Mg atoms cm\(^{-3}\) were active; this is approximately 35% of that required to chemically compensate the n\(^{+}\)-layer beneath the double-barrier structure of NU133x (see figure 4.4). Specimens annealed at 800°C were also investigated - unfortunately no meaningful data were obtained (a meaningful set of eC(V) data obtained when measuring more than one specimen is extremely difficult to carry out successfully because the equipment set-up parameters required for a specific specimen are almost always different to those required for another). The data depicted in figure 4.7 does nevertheless prove that a layer of n-type GaAs far below the surface can be transformed into a p-type layer by an implantation-and-anneal process (without decreasing the near-surface n-type doping greatly).

Note that the p-type layer is somewhat closer to the surface than the peak of the Mg distribution depicted in figure 4.4; this is consistent with Mg diffusion towards the surface during the anneal. Anneals at higher temperatures will have caused more Mg diffusion, which would be undesirable. The duration of a higher temperature anneal used to repair more implantation-created defects and/or activate more Mg would have to be kept very short (e.g. one second) to minimise the diffusion of Mg atoms into the near-surface layers. Note the meaningless data near the extremes of the p-type layer; these data are probably an artifact caused by the presence of the p-n junctions. Just beyond the p-type layer, with increasing depth the reactivated number of Si atoms decreased to a minimum (at \(\sim 2.5\mu\)m) before increasing to the as-grown density. The depth of this minimum is consistent with the depth of the implantation-created damage peak.

4.35 - Results and discussion 2: \(I(V)\) measurements

The \(I(V)\) characteristics of NU1332 after implantation of \(2.5 \times 10^{14}\) 1.3MV Mg\(^{++}\)
Figure 4.7  $N^+$ in RMG1 after implantation of $2.8 \times 10^{14}$ 1.3MV Mg$^{++}$ ions cm$^2$, and annealing for five seconds at 740°C.
ions cm\(^{-2}\), and annealing at 800°C for one second, are depicted in figure 4.8a: note the very small current density and the complete absence of NDR, both of which prove that the 800°C/1s anneal repaired too few of the defects to attain the recovery of the as-grown \(I(V)\) characteristics of this material (which was implanted with the lowest dose of ions). Despite the probable anneal-induced reactivation of a considerable number of Si donors, as indicated by the data depicted in figure 4.7, the presence of the many remaining defects greatly degraded the electron transport through the implanted-and-annealed double-barrier structure. Chapter 5 describes the large extent to which current conduction through a typical DBD is degraded by the presence of even a few defects.

Annealing the same material again for thirty seconds at 515°C repaired a few more of the defects, and the \(I(V)\) characteristics improved somewhat: note the (low quality) NDR in reverse bias. Subsequent annealing did not improve the \(I(V)\) characteristics any more. To repair more of the implantation-created damage, it was not circumspect to use a more powerful process (higher temperature and/or longer time) than the 800°C/1s anneal. As will be explained in section 4.5, at 800°C or above there occurs a measurable amount of Si diffusion and interdiffusion of Al\(_x\)Ga\(_{1-x}\)As and GaAs even in as-grown Al\(_x\)Ga\(_{1-x}\)As/GaAs heterostructures. In an ion-implanted Al\(_x\)Ga\(_{1-x}\)As/GaAs heterostructure annealed at the same temperatures, Si diffusion and interdiffusion of Al\(_x\)Ga\(_{1-x}\)As and GaAs would be much enhanced\(^{15}\). Therefore, higher-temperature anneals were not attempted because, even though many more of the defects would be repaired, the \(I(V)\) characteristics of the DBDs would be degraded considerably (see figure 4.3b).

It is concluded that high-energy Mg\(^{++}\) implantation to create a chemically-compensated layer buried beneath the DBDs is much too destructive to be the basis for the three-dimensional integration of DBDs with microwave-detector diodes. A feasible alternative involving the creation of much less damage, and, hence the use of more effective post-implantation anneal, is described in section 4.4.

Near-perfect PVCR after implantation-and-annealing

Despite the failure of the C\(^+\) and Mg\(^{++}\)-implantation processes to create a buried resistive layer beneath good-quality DBDs, the \(I(V)\) measurements of many different Mg\(^{++}\)-implanted-and-annealed DBDs was to some avail. Figure 4.8b depicts the \(I(V)\) characteristics of a specimen of NU1331 implanted with 2.5x10\(^{14}\) 1.3MV ions cm\(^{-2}\), and annealed at 700°C for one second. These 'one-off' \(I(V)\) characteristics
Figure 4.8  The $I(V)$ characteristics of NU133x before and after the implantation-and-anneal processes written in the legends.
are remarkable because they are qualitatively almost identical to the as-grown $I(V)$ characteristics (included for comparison), but $I_{pd}$ is two orders-of-magnitude less. As will be described in Chapter 5, $V_p$ of a double-barrier structure in series with a damaged layer, i.e. a relatively-high resistance, is larger because more of the bias exists across the added resistance; this is proved by the results depicted in figures 3.8 to 3.11, which also prove that the PVCR is degraded by the presence of implantation-created damage. The near-perfect PVCR and $V_p$ of the $I(V)$ characteristics depicted in figure 4.8b are consistent only with an apparent decrease of the cross-sectional area of as-grown material within this DBD mesa. As Chapter 6 describes in much detail, this is indeed what happened.

4.4 - Boron (and beryllium) implantation

Several unprocessed specimens of NU1332 were implanted, at room temperature, with $5 \times 10^{13}$ 2MeV B$^+$ ions cm$^{-2}$. After the specimen-preparation processes described in sub-sections 3.23 and 3.24, the $I(V)$ characteristics of the B$^+$-implanted DBDs were investigated after annealing at only 600°C for various short durations. Figure 4.9 shows that these relatively low-power anneals partly recovered the as-grown DC performance of the DBDs. Also depicted in figure 4.9 are the results obtained during double-crystal x-ray diffraction (XRD) investigations of the same material: the peak of the ‘rocking curve’ was made broader by ion implantation because the lattice constant throughout the defective crystal was less uniform than that throughout the as-grown crystal, but the abruptness of the peak was partly recovered by the short 600°C anneals. With more powerful annealing, the as-grown $I(V)$ characteristics and rocking curve should have recovered completely. If most of the damage created by a room-temperature implantation of B$^+$ ions can be annealed at only 600°C (or not much above), then so can the damage created by a high-temperature implantation of Be$^+$ ions; these are smaller and, hence, less damaging. Chemical compensation of an n$^+$-doped layer beneath a DBD should be possible when using Be$^+$ implantation, but, very importantly, without degrading the $I(V)$ characteristics of the DBD.

Despite the toxic hazard described in Chapter 2, some integrated-circuit manufacturers do implant Be$^+$ ions into GaAs because 1) these small ions create little damage to the GaAs and 2) Be is a very easily-activated acceptor (even more so than Mg). Figure 4.10 depicts the depth dependence of both the p-type dopant
Figure 4.9  The XRD rocking curves and $I(V)$ characteristics of NU1332 both before and after implantation of $5 \times 10^{13}$ 2MeV B⁺ ions cm⁻², and annealing at $600^\circ$C for the durations written in the legends.
Figure 4.10 The theoretical distribution of vacancies and implanted p-type dopant atoms in GaAs after a dose of $2 \times 10^{14}$ 2.6MeV Mg$^+$ ions cm$^2$, and $1.4 \times 10^{14}$ 1.2MeV Be$^+$ ions cm$^2$. 
density and the vacancy density in GaAs after implantations of $2.5 \times 10^{14}$ 2.6MeV Mg+ ions cm$^{-2}$, and $1.4 \times 10^{14}$ 1.2MeV Be+ ions cm$^{-2}$. The Be+ implantation is completely superior: there are much fewer vacancies because the Be+ ion is much lighter; there are fewer p-type dopants near the surface because the Be distribution is more abrupt; and the necessary ion energy is much less. If the DBDs described in sub-sections 4.2 and 4.3 were implanted with 1.2MeV Be+ ions instead of 2MeV C+ ions or 1.3MV Mg++ ions, their post-anneal DC performance will have been much superior: much less damage will have been created; thus necessitating a much less powerful post-implantation anneal. The results depicted in figure 4.9 indicate that an 800°C/1s anneal should repair most if not all of the defects within a DBD implanted, at high temperature, with high-energy Be+ ions, but should not cause detrimental enhancement of Al and Ga interdiffusion across the Al$_x$Ga$_{1-x}$As-GaAs interfaces. Raiston et al$^{18}$ carried out room-temperature implantations of Be+ ions into Al$_{0.3}$Ga$_{0.7}$As/GaAs superlattices, where the Be+ dose was more than ten times larger than that mentioned above. After annealing their samples at 660°C for four hours, they carried out transmission electron microscopy to investigate the superlattice integrity: no evidence of Al$_{0.3}$Ga$_{0.7}$As/GaAs intermixing was detected.

Unfortunately for the author, several years ago the EPSRC Central Facility for Ion Beam Technology at Surrey banned the implantation of Be+ ions within its laboratories because of the toxic hazard. If a research group elsewhere has access to a pure beam of high-energy Be+ ions then they ought to implant them through double-barrier structures because their post-anneal $I(V)$ characteristics and RF performance will be interesting (but both expensive and very dangerous to obtain).

4.5 - Post-anneal DC performance of ASPAT diodes

If a high-energy Be+-implantation-and-anneal process succeeded in creating a resistive layer buried beneath high-quality DBDs, the post-anneal performance of the microwave-detector diodes to be grown beneath the DBDs (and beneath the resistive layer) should be investigated. A wafer having the layer structure of a high-performance ASPAT diode was grown$^{19}$, and its as-grown $I(V)$ characteristics at various distances from the centre of the wafer were investigated (as part of a project to investigate the commercial ‘manufacturability’ of this single-barrier structure$^{20}$). The as-grown ASPAT diodes were fabricated using the process described in sub-sections 3.22 and 3.24 (except that the mesas were etched to 1.2μm, which took
120s). Wilkinson et al\textsuperscript{20} describe the differences between the $I(V)$ characteristics at different radial positions, and all the other important results of their manufacturability investigations.

Several unprocessed specimens from the same wafer were then prepared for annealing by capping them with 50nm of Si$_3$N$_4$ to prevent the evaporation of either Ga or As from their surfaces. The anneals used were, logically, similar to those described in sub-section 4.33, i.e one-second anneals at either 750°C or 800°C. Sub-section 4.23 describes how the Si$_3$N$_4$ was deposited, and then removed after annealing. The post-anneal specimens were fabricated as described above, and then their $I(V)$ characteristics were investigated.

4.51 - Results and discussion

Figure 4.11 depicts the as-grown and post-anneal $I(V)$ characteristics of the ASPAT diodes, together with their as-grown layer structure. For clarity, much $I(V)$ data are omitted because most of the as-grown data obtained between the two positional extremes were almost identical to that obtained at 12mm from the wafer edge; and, similarly, the post-anneal data obtained between 6 and 10mm from the wafer edge differed very little (no post-anneal data were obtained beyond those two extremes). The results depicted in figure 4.10 indicate that ASPAT diodes are suitable for integration with ion-implanted DBDs: after the 750°C anneal the $I(V)$ characteristics of the ASPAT diodes were unchanged; and after the 800°C anneal the $I(V)$ characteristics were not degraded qualitatively, although the current density in both forward and reverse bias was somewhat larger. At the anneal temperatures used, the distribution of Si donors and the composition of the AlAs layer should have changed only very slightly\textsuperscript{15}: such a small change was measurable after annealing at 800°C because of the sensitivity of quantum-mechanical tunnelling to variations of material composition\textsuperscript{20}. The layers of an ASPAT diode would, therefore, be degraded considerably if a thermal process more powerful than an 800°C/1s anneal was used to repair an ion-implanted DBD grown above the ASPAT diode; this is why it was not expedient to attempt such a thermal process during the work described in sections 4.2 and 4.3.

4.6 - Conclusions

The as-grown DC performance of DBDs implanted with high-energy B$^+$ ions
Figure 4.11 The as-grown layer structure of the ASPAT-diode wafer, together with its as-grown and post-anneal $I(V)$ characteristics.
was recovered considerably by rapid thermal-annealing for short durations at a relatively-low temperature (600°C). The damage created by high-energy Be⁺ implantation should not, therefore, necessitate the use of anneals involving the use of temperatures higher than 800°C, at which it was proved that destructive changes to AlₓGa₁₋ₓAs/GaAs heterostructures occur measurably; thus barring the use of implantation-and-anneal processes necessitating higher-temperature anneals (such as any of the C⁺- and Mg⁺-implantation processes described in this chapter). High-energy Be⁺ implantation should, after annealing, cause chemical compensation of part of the n⁺-doped material beneath a DBD; thus creating a semi-insulating layer which could isolate the DBD from an ASPAT diode beneath the semi-insulation - the fabrication of the high-performance microwave-mixer circuit described in sections 1.2 and 3.1 will then be possible (in fact, a p-type layer buried beneath a thick 70%-reactivated n⁺-layer was created by annealing some of the Mg⁺-implanted material). The successful fabrication of a high-performance integrated circuit which can mix microwaves, consisting of DBDs integrated with ASPAT diodes at a greater depth, depends only on the resources and the will of a research group with access to high-energy Be⁺ ions.
Chapter 4

ION IMPLANTATION FOR THE THREE-DIMENSIONAL INTEGRATION OF...CHEMICAL COMPENSATION

4.7 - REFERENCES

4. Grown by M. Henini at the Department of Physics, University of Nottingham.
7. Carried out by V.F. Power at the Department of Electronic and Electrical Engineering, University of Surrey.
10. Carried out with the assistance of R.M. Gwilliam at the Department of Electronic and Electrical Engineering, University of Surrey.
PART 3

Resonant tunnelling through ion-implanted double-barrier structures
Chapter 5

THE ELECTRONIC PERFORMANCE OF IMPLANTED-AND-ANNEALED DOUBLE-BARRIER DIODES

5.1 - Introduction
Chapters 3 and 4 described electrical investigations of DBDs which were implanted-and-annealed in an attempt to create a resistive layer beneath them. Chapter 5 describes more detailed investigations of the electronic transport through implanted-and-annealed near-surface DBDs: understanding the physics of the electronic transport through such a structure would facilitate the designing of a DBD which performed better after one of the implantation-and-anneal processes described in Chapters 3 and 4. Some theoretical work was also carried out in conjunction with the experimental measurements; this involved modelling implantation-caused changes to the conduction-band edge above and below a DBD.

5.2 - Experimental procedure
NU168 and NU1333 were the DBD samples investigated, which are described in Chapters 3 and 4 respectively. The table on page 92 lists the implantation processes used, all of which were carried out at room temperature. None of the ion-beam currents used during these implantation processes would have heated the specimens considerably. Once again, the ion beam was at 7° from the normal to the surface of the specimens (see sub-section 2.3.1). Figure 5.1 depicts the theoretical distribution of damage created by each of the implantation processes.
Figure 5.1  The theoretical distributions of damage created by each of the implantation processes used here (calculated by TRIM).
### 5.21 - Post-implantation specimen preparation and \( I(V) \) measurements

The processing used to prepare the specimens for \( I(V) \) measurements is described in sub-sections 3.23 and 3.24. The 325keV proton-implantation processes were carried out after the mesas used for the \( I(V) \) measurements were etched, whereas the other two implantations were carried out before the etching of the mesas (the 400°C contact-alloying process would have annealed the very-light damage created by the 325keV proton-implantation process). The optical annealing furnace, Kulicke & Soffa gold-wire bonder, and the apparatus and procedure used during \( I(V) \) measurements were exactly the same as those described in Chapter 3.

### 5.3 - Results and discussion 1: pre-anneal DC performance

This section primarily describes the effects of ion implantation of \( 1 \times 10^{13} \) and \( 2 \times 10^{13} \) 325keV protons cm\(^{-2} \) into NU168, but the other implantation processes described above are discussed also.

### 5.3.1 - The conduction-band edge

As stated in sub-section 2.21, the number of trapped electrons in a defective semiconductor is negligible when \( n \) is much larger than \( N_t \). As indicated by figure 5.1, \( n \) will have been much larger than \( N_t \) in the n\(^+ \) contacts after implantation of \( 1 \times 10^{13} \) 325keV protons cm\(^{-2} \); therefore, the conductivity of this material will not have been much different to that of the equivalent as-grown material. To prove this,
metallised mesas of a bulk GaAs sample doped with $2 \times 10^{18}$ Si atoms cm$^{-3}$ were fabricated using the techniques described in sub-sections 3.21 and 3.23, and the resistivity of the GaAs was measured before and after implantation of $1 \times 10^{18}$ 325 keV protons cm$^{-2}$: a resistivity of $\sim 10^3 \Omega \text{cm}$ was measured before and after implantation, which was the order of magnitude expected. The slight decrease of $n$ caused by ion implantation will have, as stated by the Fermi-Dirac distribution function, decreased $E_F$ therein very slightly.

Figure 5.1 indicates that a room-temperature implantation of $1 \times 10^{13}$ 325 keV protons cm$^{-2}$ creates $\sim 1.7 \times 10^{17}$ vacancies cm$^{-2}$ at the depth of the graded-doped spacer layer in the emitter. Even if only half the associated defect states were electron traps then $N_t$ was at least four-times larger than the maximum $n$ in that layer. When $N_t$ is much larger than $n$, most of the once-free electrons are trapped within the defects states; thus creating semi-insulation because there are almost no free electrons with which to transfer charge. The 50 nm-thick graded-doped spacer layers will therefore have been highly resistive after ion implantation.

Conduction band modelling

The creation of $1 \times 10^{17}$ point defects cm$^{-3}$ should not have changed the profile of the conduction-band edge of NU168 considerably. The principle of this was simulated theoretically by using a self-consistent Poisson-Schrodinger solver developed by Syme to model the (single-barrier) ASPAT diode. The conduction-band edge of a single-barrier structure having variable $n$ in the contact layers was modelled, and the results obtained are depicted in figure 5.2. Obviously the changes to the conduction-band edge caused by space-charge accumulation between the two barriers during resonant tunnelling is not included in Syme’s program, but the space-charge effects caused by the presence of ionised donor atoms in the n-doped contact layers are included; therefore, the author’s use of Syme’s program to model a single-barrier structure having variable $n$ instead of the equivalent double-barrier structure was not inappropriate. The Poisson equation Syme uses is

$$\frac{d^2\phi}{dz^2} = \left[ \frac{|e|}{\varepsilon \varepsilon_0} \right] (N_D - n)$$  \hspace{1cm} (5-1)

where $z$ is the direction of current flow (all the other quantities are described in the glossary on page xv). There are two unknowns in equation (5-1): $n$ and $\phi$. The simulation starts by obtaining $\phi$ by using the Thomas-Fermi approximation. $\phi$ is
Bias voltage= 0.8V

- - - $E_F$ within emitter of structure 1
- - - c.b.e of structure 1
- - - $E_F$ within emitter of structure 2
- - - c.b.e. of structure 2

Layer structure:
- 0.5μm $n^+$-doped GaAs
- 50nm n-doped GaAs
- 3nm undoped GaAs
- 10nm undoped AlAs
- 3nm undoped GaAs
- 50nm n-doped GaAs
- 0.5μm n$^+$-doped GaAs

- $n^+$ doping in structure 1 = $2 \times 10^{18}$ cm$^{-3}$
- $n$ doping in structure 1 = $1 \times 10^{16}$ cm$^{-3}$
- $n^+$ doping in structure 2 = $1.7 \times 10^{18}$ cm$^{-3}$
- $n$ doping in structure 2 = $5 \times 10^{14}$ cm$^{-3}$

Figure 5.2 The conduction-band edge of a single-barrier structure having variable $n$ in each of the n-doped layers (which were modelled on those of NU168).
then inserted into the 1D Schrodinger equation, which is used to obtain the wavefunctions of any quantised electron states in the accumulation layer. The result of this calculation is inserted into the equation

\[ n = \frac{|\psi|^2 (m^*k_B^2T/\pi\hbar^2)^{1/2}}{\ln 1 + \exp[(E_F - E_i)/k_B^2T]} \]  

(5-2)

where \( \psi \) is the 1D electron envelope function, and \( E_i \) is the energy of the quantised state \( i \). The result of this equation is inserted in equation (5-1), and then the entire process is repeated by using the Thomas-Fermi approximation to calculate the new value of \( \phi \). The process is repeated until convergence is attained. From the emitter contact to the AlAs layer, \( E_F \) is assumed to be the same as that within the emitter contact. Within the AlAs layer, \( E_F \) is assumed to be decreased by half the bias voltage. Below the AlAs layer, \( E_F \) is assumed to be decreased again by the other half of the bias voltage. See Syme \(^4\) for more details about the simulation.

The n-type layer structure and ‘as-grown’ doping of the modelled AlAs/GaAs single-barrier structure were varied to be very similar to that of NU168, but the graded-doped n-type layers were modelled as a single layer doped with \( 1 \times 10^{16} \) Si atoms cm\(^{-3}\) (this was the average as-grown Si density in these layers). The post-implantation free-electron density in the n\(^+\) contacts was calculated to be between \( 1.8 \times 10^{18} \) and \( 1.95 \times 10^{18} \) cm\(^{-3}\), assuming that each of the electron-trapping defect states within the n\(^+\) contacts trapped between one and three electrons\(^3\) (figure 5.1 shows that the density of point-defects in the n\(^+\) contacts was \( 1 \times 10^{17} \) cm\(^{-3}\)). As mentioned above, \( n \) in the graded-doped layers will have been decreased greatly by the implantation process. It was assumed during the theoretical simulation that \( n \) in the post-implantation graded-doped layers was as low as the ‘background’ donor density\(^7\) in epitaxially-grown undoped GaAs, i.e. between \( 1 \times 10^{14} \) and \( 5 \times 10^{14} \) cm\(^{-3}\). The results depicted in figure 5.2 show that proton implantation caused little change to the conduction-band edge at a specific bias, but \( E_F \) was decreased slightly relative to the bottom of the accumulation layer (very similar results were obtained for all free-electron densities in the n\(^+\) contacts between \( 1.5 \times 10^{18} \) and \( 2 \times 10^{18} \) cm\(^{-3}\)).

The results described above were obtained assuming that \( E_F \) within the graded-doped spacer layers was not ‘pinned’ by the presence of defect states near the middle of the band-gap\(^8\); this can occur when \( N_t \) is much greater than \( n \), and when most of the electron-trapping defect states in ion-implanted GaAs are approximately half-way between the conduction-band and valence-band edges\(^8\). If
such a pinning of $E_F$ occurred within the post-implantation graded-doped spacer layers then the results obtained by the theoretical simulation described above would be inconsistent: the emitter spacer-layer barrier would be much higher than that depicted in figure 5.2 because $E_F$ in the graded-doped layers would be $\sim 0.7$eV below the conduction-band edge, i.e. $\sim 0.6$eV lower than that calculated by the modelling. If the post-implantation emitter spacer-layer barrier was indeed 0.6eV higher than that depicted in figure 5.2 then $V_p$ after implantation would be at least 1V higher than the as-grown $V_p$ (the increase of $V_p$ would be approximately twice the additional height of the emitter spacer-layer barrier because more or less half the bias voltage across a DBD is applied across the collector$^9$).

5.32 - Electron transport

Figures 3.8, 3.9 and 5.3 show that the post-implantation $I(V)$ characteristics are completely different to the as-grown characteristics: note that after implantation $I_{pd}$ is much lower, $I_{pd}$ decreases with temperature, the PVCR of the main resonance at 295K is much lower, and the PVCR has a very unusual temperature dependence because of the existence of a second resonance peak at low temperatures. However, $V_p$ is only 0.3V larger after the implantation process. $E_F$ within the graded-doped spacer layers was, therefore, not pinned to an energy in the middle of the band-gap, and the results depicted in figure 5.2 are meaningful.

The slight increase of $V_p$ with ion implantation is partly attributable to the fact that $E_F$ in the n$^+$ contacts was slightly lower relative to the energy of the confined state between the barriers after implantation (see figure 5.2). The decrease of $I_{pd}$ is partly attributable to inelastic scattering of resonant-tunnelling electrons by the $2 \times 10^5$ vacancies nm$^{-3}$ within both the accumulation layer and the double-barrier structure: this small amount of scattering will have destroyed the coherence of the resonant-tunnelling process of a very few electrons; thus decreasing $I_{pd}$ slightly because of partial reflection of the electron wavefunction, and, hence, causing transmission of fewer electrons at resonance$^{5,9}$. This scattering process will also have decreased the PVCR slightly because not all the incident electrons having a kinetic energy degenerate with $E_{0\text{con}}$ will have tunnelled resonantly at $V_p$.

5.33 - Charge-transfer from the n$^+$ contacts to the double-barrier structure

As described in sub-section 1.23, the current density at a specific bias across an ASPAT diode or a DBD is limited by the conductivity of the emitter spacer layer.
Figure 5.3  The $I(V)$ characteristics of NU168 after implantation of $1 \times 10^{18} 325\text{keV}$ protons cm$^{-2}$. 
Most of the differences between the as-grown and post-implantation $I(V)$ characteristics are attributed to the resistive characteristics of the graded-doped spacer layers after ion implantation. The increased $V_p$ after ion implantation was caused primarily by the fact that the DBDs were more resistive, particularly the graded-doped spacer layers; therefore, a larger bias was necessary to attain a specific electric field across the double-barrier structure. The obvious occurrence of a resonance peak at 295K (resonance ‘a’) indicates that some charge transfer between the n+ contacts and the double-barrier structure was occurring at that temperature, but its magnitude at a specific bias was much less, and its temperature dependence was completely unlike that of an as-grown specimen.

5.34 - Decrease of $I_{pd}$ with temperature

The temperature dependence of the post-implantation DC characteristics is similar to that of 3D-2D resonant tunnelling of ballistic electrons\(^8,10\) (see sub-section 1.32) where the number of populated quasi-continuous 3D emitter states decreases with temperature. However, if a large proportion of the resonance current depicted in figure 5.3 was formed of ballistic electrons then the $I(V)$ characteristics after implantation of $2 \times 10^{18}$ 325keV protons cm\(^{-2}\) would also include a prominent resonance current of ballistic electrons because the free-electron density within the n+ contacts of this material will also have been very high ($\sim 1 \times 10^{18}$ cm\(^{-2}\)): figure 3.8 shows that such a resonance was not observed. Also, the presence of defect states in the graded-doped spacer layers and the double-barrier structure after implantation of either dose will have inelastically scattered many ballistic electrons; thus thermalising them into the accumulation layer. Furthermore, a prominent resonance of ballistic electrons after ion implantation would still be observable after annealing some of the defects; however, the only resonance observed after the initial stages of annealing was the recovered main resonance of electrons originating from the quasi-2D states in the accumulation layer (see figure 3.9). Also, the hypothesis that the post-implantation main-resonance current was formed primarily of ballistic electrons explains the temperature dependence of $I_{pd}$ but does not explain the occurrence of a second resonance peak (resonance ‘b’) at low temperatures.

Field-enhanced emission of electrons from defect states

The temperature dependence of the post-implantation $I_{pd}$ is also similar to that of a typical ion-implanted semiconductor\(^11\), in which the conductivity decreases
with decreasing $e_n$ from defect states (see sub-section 2.21). Figure 3.8 shows that after a dose of $2 \times 10^{13}$ 325keV protons cm$^{-2}$, the qualitative characteristics of the $I(V)$ data are very similar to those of a damaged semiconductor$^{11-13}$. There was, however, an indication of resonant tunnelling at $\sim 1$V, which is a higher $V_p$ than that depicted in figure 5.3; this is consistent with the resistance of the DBD increasing with damage, and $E_F$ decreasing with increasing $N_t$.

The $I(V)$ data obtained when investigating DBDs implanted with even higher doses had similar qualitative DC characteristics but there was no indication of resonant tunnelling, and the ‘current-breakdown’ voltage increased with damage. After the 750keV He$^+$ implantation, which should have removed all the free electrons in the n$^+$ contacts, the current-breakdown voltage was larger than 35V; this is consistent with the results obtained by Sze$^{11}$, who described how the dielectric breakdown of a damaged semiconductor increases with increasing damage-associated resistivity.

Poole-Frenkel emission

After ion implantation, Poole-Frenkel emission of electrons into the conduction band from the defect states$^{11-14}$ is proposed to have limited the conductivity of the graded-doped spacer layer at 295K; this mechanism, which has not been observed before when investigating DBDs, is described in sub-section 2.21.

Figure 5.4 depicts ln($I$) as a function of $1/T$, at four fixed bias voltages across NU168 after implantation of $1 \times 10^{13}$ 325keV protons cm$^{-2}$. Note that the datasets obtained at 0.6V and 0.8V have two distinct components, each of which represents a different current-conduction mechanism. The current originating from Poole-Frenkel emission from defect states is given by (see sub-section 2.21)

\[
I = V \exp[-e(E_t'(eV/W_n\pi e)\mu q/k_BT)], \quad \text{or} \quad (5-3)
\]

\[
I = (\text{Constant}) \exp[-E_t/k_BT] \quad \text{at a fixed bias.} \quad (5-4)
\]

By taking natural logs, equation (5-4) becomes

\[
\ln I = [-E_t/k_BT] \quad \text{or} \quad (5-5)
\]

\[-E_t = k_B \ln I/(1/T). \quad (5-6)\]
Figure 5.4  \( \ln(I) \) as a function of \( 1/T \) (at four fixed bias voltages) of the data depicted in figure 5.3. The inset depicts \( \ln(I) \), of the data depicted in figure 3.8, as a function of \( V^{1/2} \).
Therefore, if Poole-Frenkel emission was the current-limiting mechanism in the ion-implanted DBDs then $E_t$ can be calculated at a specific bias by plotting a graph of $\ln(I)$ as a function of $1/T$ - the dataset of which should be a straight line\textsuperscript{11-13}.

As depicted in figure 5.4, at high temperatures the gradient of the two lowest-bias datasets and that obtained at $V_p$ is indeed very straight, which is a strong indication that the current-limiting mechanism in these conditions was Poole-Frenkel emission. $E_t$ at 0.6V and 0.8V was 0.15eV and 0.08eV respectively, which is consistent with the decreasing of $E_t$ with increasing bias (see figure 2.4). The magnitude of $E_t$ at both bias voltages is low, which indicates that $E_t$ at zero bias, i.e. the actual depth of the defect state, was also low (but somewhat higher than 0.15eV); this is consistent with the work of Yuba et al\textsuperscript{15}, who discovered a relatively high density of defect states at only ~0.3eV below the conduction-band edge of GaAs implanted with between $1 \times 10^{11}$ and $1 \times 10^{14}$ 60keV protons cm\textsuperscript{-2}.

Note that the transmission probability of thermally-emitted electrons through the double-barrier structure at a specific bias will have changed very slightly with temperature because of the changing profile of the conduction-band edge, and the increasing number of available collector states; however, as depicted in figure 5.4, $\ln(I)$ at $V_p$ decreased linearly with $1/T$; thus indicating that $I_{pd}$ was limited primarily by Poole-Frenkel emission.

The inset of figure 5.4 depicts $\ln(I)$ as a function of $V^{1/2}$. As described by equation (5-3), the current of electrons emitted into the conduction band by Poole-Frenkel emission from defect states is proportional to $\exp(V^{1/2})$. Such a current should therefore be a straight line when depicted in the inset of figure 5.4. At a bias lower than $V_p$, the two datasets are indeed straight lines with very similar gradients; this is another strong indication that the current-limiting mechanism in these conditions was Poole-Frenkel emission. Quantitative analysis of such data obtained when investigating simple electronic devices can elucidate\textsuperscript{11,14} the magnitude of $\varepsilon$; however, with increasing bias the change of transmission probability through the double-barrier structure, and the non-linear increase of electric field at a specific depth\textsuperscript{16,17} invalidate such analysis of the data depicted in the inset of figure 5.4.

The much lower $I_{pd}$ after proton implantation is consistent with the presence of defect states within the graded-doped spacer layers: as described above, the current of ballistic electrons will have been much less after implantation. Also, after proton implantation the presence of empty defect states...
within the graded-doped spacer layers will have slowed-down and trapped many of the thermalised electrons diffusing from the $n^+$ emitter-contact to the double-barrier structure when biased. Furthermore, as depicted in figure 5.4, the height of the emitter spacer-layer barrier relative to $E_F$ was somewhat greater after proton implantation (this will have decreased the thermionic emission of electrons over the spacer-layer barrier from the $n^+$ contact).

**Field-enhanced ionisation**

Figure 5.4 shows that the gradient of the dataset obtained at 1.2V is very different to that of the other two: figure 5.3 shows that the higher-bias resonance (resonance $b$) occurs in these conditions. Resonance $b$ was still observable at very low temperatures, at which Poole-Frenkel emission does not occur considerably; hence the disappearance of resonance $a$ with decreasing temperature. Indeed, below 25K resonance $b$ was apparently independent of temperature. The ‘peak’ current density of resonance $b$ was a superposition of its own current with $I_{vd}$ of resonance $a$; hence its ostensible decrease with temperature and its temperature independence below 25K (at which resonance $a$ was unobservable). In other words the current-density decrease of resonance $b$ with temperature was dependent on that of resonance $a$, but resonance $b$ was actually independent of temperature. Resonance $b$ is attributed to resonant tunnelling of electrons excited into the conduction band of the graded-doped spacer layer by field-enhanced ionisation of the defect states, a current-limiting mechanism which is independent of temperature$^{11}$.

**Hopping conduction**

At low temperatures, the gradient of the three datasets depicted in figure 5.4 is almost identical, which indicates that the activation energy of this current-conduction mechanism, where $I$ was very low, was independent of electric field. Furthermore, $\ln(I)$ changed relatively little with decreasing temperature (where $\ln(I)$ at very low temperatures was proportional to $T^{0.4}$); these facts are consistent with hopping conduction of electrons between defect states$^{11,13,18}$. A more detailed analysis of this current in the ion-implanted DBDs was not carried out because its magnitude was negligible.

**5.35 - The PVCR**

Consider the PVCR at 295K: with increasing bias the very large increase of
the number of electrons excited into the conduction band by Poole-Frenkel emission will have lowered the PVCR because there were many more electrons available for conduction (and tunnelling) at bias voltages higher than $V_p$. The same reasoning is applied when describing the 5K PVCR: the bias-dependence of field-enhanced ionisation (see sub-section 2.21) is such that with increasing bias there is a large increase of electrons in the conduction band. The increase of PVCR with decreasing temperature between 295K and 210K is consistent with the increasing abruptness of the distribution of the states within the accumulation layer (c.f. the temperature dependence of the as-grown PVCR). The ostensible decrease of PVCR (of resonance $a$) below 210K was caused by the increasing prominence of resonance $b$.

5.36 - Asymmetric $I(V)$ characteristics

The asymmetry between the forward- and reverse-bias $I(V)$ characteristics of NU168 was more prominent after proton implantation. The as-grown $I(V)$ characteristics of NU168 were asymmetric: $I_p$ in forward bias was slightly larger than that in reverse bias; this is consistent with the forward-bias emitter being n$^+$-doped slightly more highly than the collector (the reverse-bias emitter). After proton implantation the magnitude of $N_t$ below the double-barrier structure will have been slightly higher than that above it (see figure 5.1); therefore, the number of trapped electrons within the forward-bias emitter will have been relatively less than that within the collector. Consequently, after proton implantation there will have been a bigger relative difference between the magnitude of $n$ within the emitter and that within the collector; hence the more prominent asymmetry of the $I(V)$ characteristics.

5.37 - Secondary resonances

Tunnelling from the confined energy-state between the barriers through defect states within the collector barrier would not have occurred because $E_t$ in ion-implanted Al$_{0.4}$Ga$_{0.6}$As is usually not less than 0.5eV below its conduction-band edge and, therefore, more than or similar to ~0.2eV below the conduction band-edge of the GaAs layer between the barriers.

The small resonance at a lower bias than the main resonance is unobservable after ion implantation; this small resonance is attributed to 3D-2D resonant tunnelling of ballistic electrons (see figure 3.7). The inelastic scattering of ballistic electrons caused by compositional defects within both the emitter and the double-barrier structure will have decreased the resonance current of these
electrons; this has already been described in sub-section 5.34.

5.38 - Proton implantation of NU1333

Figure 5.5 depicts the reverse-bias $I(V)$ characteristics of NU1333 after implantation of $1 \times 10^{12}$, $3 \times 10^{12}$ and $1 \times 10^{13}$ 325keV protons cm$^{-2}$. Compared to the as-grown $I(V)$ characteristics depicted in figure 4.2, the post-implantation DC performance of NU1333 was much inferior even after the lowest dose of protons, which was a tenth of that implanted into NU168 (see figures 5.1 and 5.3). Figure 5.1 indicates that this smallest dose of protons will have created enough defect states within the spacer layers doped with $2 \times 10^{16}$ Si atoms cm$^{-3}$ to have trapped many but not all the free electrons (figure 4.1 depicts the as-grown layer structure of NU1333). The occurrence of both LOP-assisted resonant tunnelling at 77K and resonant tunnelling from the uppermost sub-band within the accumulation layer at 295K were still observable after this implantation process.

The doses of $3 \times 10^{12}$ and $1 \times 10^{13}$ 325keV protons cm$^{-2}$, which greatly degraded the $I(V)$ characteristics, will have caused the trapping of a large proportion of the free electrons in all the n-doped spacer layers: note that the $I(V)$ characteristics of NU168 after the dose of $1 \times 10^{13}$ 325keV protons cm$^{-2}$ were degraded much less.

The high sensitivity of NU1333 to the effects of ion implantation is probably a result of the creation of many defect states in the (thick) layer of GaAs between the n* contacts and the double-barrier structure: the total thickness of this layer is 340nm ($4 \times 50$nm+$20$nm+$120$nm), whereas in NU168 it is only 105nm ($2 \times [50$nm$+2.5$nm$]$). The high sensitivity of the other very similar QWITT-diode sample, NU1332, to implantation-created damage was observed after the high-dose 1.3MV Mg$^{++}$ implantations described in section 4.3: figure 4.8a shows that the $I(V)$ characteristics after annealing were much inferior to the as-grown characteristics; this indicates, together with the $eC(V)$ data depicted in figure 4.7, that a high density of defect states remained after annealing. If a QWITT diode is to be used in the microwave-mixer circuit described on the first page of Chapter 3, the post-implantation anneal must be highly efficient at repairing most if not all the defects.

5.4 - Results and discussion 2: post-anneal $I(V)$ characteristics of ion-implanted DBDs

Similar results to those depicted in figure 5.3 were obtained during $I(V)$
Figure 5.5 The reverse-bias $I(V)$ and $[dI/dV](V)$ characteristics of NU1333 after implantation of the proton doses written in the legends. The asterisks mark the occurrence of resonant tunnelling from the uppermost sub-band.
measurements of NU168 after implantation of $4 \times 10^{13} 325\text{keV} \text{protons cm}^{-2}$, but only after annealing for one second at $400^\circ\text{C}$ to anneal some of the damage (see figure 5.6): note that resonance $b$ was independent of temperature to a much larger extent than that depicted in figure 5.2. At a specific temperature, $I_{vd}$ of resonance $a$ depicted in the top-left graph of figure 5.6 was much lower than that depicted in figure 5.3. Furthermore, $I_{pd}$ of resonance $b$ depicted in figure 5.6 was 50% larger than that depicted in figure 5.2. $I_{pd}$ of resonance $b$ depicted in figure 5.6 will therefore have been less dependent on temperature than that of figure 5.2. In fact, resonance $b$ depicted in figure 5.6 was almost completely independent of temperature; this adds credence to the proposal that it was limited by field-enhanced ionisation of defect states.

With subsequent 1s anneals at higher temperatures the number of defect states within the graded-doped spacer layers decreased, the disorder within the Al$_{0.4}$Ga$_{0.6}$As barriers was repaired, and, hence, the $I(V)$ characteristics improved. Note that the 77K forward-bias PVCRs after annealing at 500°C and 550°C were 11.2:1 and 15.8:1 respectively (the reverse-bias PVCRs were similar).

Figure 5.7 depicts the post-600°C-anneal forward-bias $I(V)$ characteristics after a dose of $8 \times 10^{14} 300\text{keV} \text{protons cm}^{-2}$: note that $I_{pd}$ of the specimens annealed for the two shortest durations decreased before beginning to increase at 240K (see figure 5.8); this indicates that some Poole-Frenkel emission of electrons into the conduction band from the remaining defect states was still occurring at high temperatures. Compare the as-grown PVCRs at both 295K and 77K to those after annealing for the three longest durations.

Figures 5.6 and 5.7 show that, even after the most powerful anneals, many of the point defects in the n-doped layers had not been repaired. After implantation of $8 \times 10^{14} 300\text{keV} \text{protons}$, and annealing at 600°C for 120s, the 77K $I_{pd}$ was only ~35% of the as-grown $I_{pd}$; the 295K PVCR was ~85% of the as-grown PVCR; and, as figure 5.8 shows, with decreasing temperature the increase of $I_{pd}$ was less than the increase of the as-grown $I_{pd}$. These facts indicate that a considerable amount of Poole-Frenkel emission was occurring from the (many) remaining defects, even though the conductivity of the graded-doped spacer layer above the emitter barrier had improved greatly with annealing.

### 5.41 - Less-prominent 3D-2D resonant tunnelling

Figures 5.6 and 5.7 show that the 3D-2D resonance current of ballistic
The electronic performance of implanted-and-annealed double-barrier diodes

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295K</td>
<td>[Graph A]</td>
</tr>
<tr>
<td>125K</td>
<td>[Graph B]</td>
</tr>
<tr>
<td>77K</td>
<td>[Graph C]</td>
</tr>
<tr>
<td>10K</td>
<td>[Graph D]</td>
</tr>
</tbody>
</table>

**Figure 5.6** The forward-bias I(V) characteristics of NU168 after a dose of $4 \times 10^{13}$ 325keV protons cm$^{-2}$, and annealing in the conditions written in the graphs. The asterisk marks an observable occurrence of 3D-2D resonance.
Figure 5.7  The forward-bias $I(V)$ characteristics of NU168 after a dose of $8 \times 10^{14}$ 300keV protons cm$^2$, and annealing at 600°C for the durations written in the legends. The numbers written in brackets are the PVCRs. The asterisks mark the observable occurrence of 3D-2D resonant tunnelling.
Figure 5.8 The temperature dependence of the $I(V)$ characteristics depicted in figure 5.7. The post-implantation-and-anneal peak- and valley-current densities were normalised to the 295K as-grown data. The dotted lines between the data points are guides to the eye.
electrons at low bias was much less prominent at 295K, and was unobservable at low temperatures. It seems as though the scattering of ballistic electrons was still very considerable after annealing; this is also consistent with the statement made above that even after annealing there were still many remaining defects. Hot electrons are inelastically scattered very efficiently by defect states and ionised impurities; therefore, it is not surprising that the 3D-2D resonance current of ballistic electrons was still much less prominent after annealing.

5.42 - Larger-than-as-grown PVCR at 77K

Figures 5.6 and 5.7 also show that at low temperatures a remarkable difference between the electronic transport through the implanted-and-annealed DBDs and that through as-grown diodes became apparent: the 77K PVCR of some implanted-and-annealed specimens was between 50 and 100% larger than the as-grown 77K PVCR, even though the associated 295K PVCR was smaller. Each of the He⁺-implanted specimens of NU168 which were annealed for ninety seconds at 600°C also had 5K and 77K PVCRs which were approximately twice the as-grown PVCRs. When investigating the change of both the as-grown and the post-implantation-and-anneal I(V) characteristics with decreasing temperature (see figure 5.8) it was obvious that a greater decrease of \( I_{\text{vd}} \) occurred after implantation-and-annealing. With decreasing temperature, the increase of \( I_{\text{pd}} \) was somewhat less after implantation-and-annealing (see the third paragraph on page 106).

The proposed causes of the increased low-temperature PVCR

Assuming the most powerful anneals repaired between a third and a half of the electron-trapping defect states (a reasonable estimate when considering the pre- and post-implantation-and-anneal values of \( I_{\text{pd}} \)), the conduction-band edge of the same variable-\( n \) single-barrier structure described in sub-section 5.31 was modelled - the results obtained are depicted in figure 5.9. Assuming that each of the remaining electron-trapping defect states within the \( n^+ \) contacts trapped between one and three electrons, the post-implantation free-electron density in the \( n^+ \) contacts was estimated to have been between \( 1.9 \times 10^{18} \) and \( 2.0 \times 10^{18} \) cm\(^{-3} \), and the n-doping in the annealed spacer layer was assumed to be \( 4 \times 10^{25} \) cm\(^{-2} \). The bias voltage applied across the theoretical ‘ion-implanted’ structure was slightly larger than the bias across the ‘as-grown’ structure; this was carried out to model the increased bias necessary to create a specific electric field across an implanted-and-annealed
Figure 5.9 The conduction-band edge of a single-barrier structure having variable $n$ in each of the $n$-doped layers (which were modelled on those of NU168).
double-barrier structure.

Note that in figure 5.9 the electrostatic geometry of the accumulation layer within the two modelled structures was almost identical; this was true for many different combinations of n+- and n-doping within the modelled ‘ion-implanted’ structure. Consequently, within the accumulation layer of an implanted-and-annealed DBD the number of quasi-2D states therein, their energy spacing and spatial width will have been very similar to those within an as-grown DBD. Therefore, the post-implantation-and-anneal accumulation layer was just as 2D-like (the modelling described above showed that there would actually have been only one quasi-2D sub-band within the accumulation layer both before and after implantation-and-annealing; this is consistent with the results obtained during magnetic-field investigations\textsuperscript{22} of a sample almost identical to NU168). As described above, the resonance current of 3D-2D ballistic electrons is less prominent after implantation-and-annealing; therefore, the main-resonance peak of DBDs would have been, surprisingly, more 2D-like after the implantation-and-annealing processes described above.

However, as described above, even after annealing there would still have been many defect states from which Poole-Frenkel emission could occur at high temperatures; hence the lower-quality 295K $I(V)$ characteristics after implantation-and-annealing. The 295K PVCR after implantation-and-annealing is lower than the as-grown PVCR because with increasing bias the very large increase of the number of electrons excited into the conduction band by Poole-Frenkel emission will have lowered the PVCR, i.e. there were many more electrons available for conduction (and tunnelling) at bias voltages higher than $V_p$. At much lower temperatures, Poole-Frenkel emission, one of the primary causes of the decreased high-temperature PVCR after ion implantation, will have occurred much less\textsuperscript{11-13} (see figure 5.4). Field-enhanced ionisation will have occurred at low temperatures, but the current induced by it was, as depicted in figures 5.3 and 5.6, much less than that induced by Poole-Frenkel emission. Consequently, the more 2D-like resonant tunnelling after implantation-and-annealing will have been more prominent at low temperatures. It is proposed that the combination of there being 1) much less Poole-Frenkel emission at low temperatures, 2) a very low current induced by field-enhanced ionisation and 3) a more 2D-like main-resonance peak within some of the implanted-and-annealed specimens is a primary cause of their larger-than-as-grown low temperature PVCRs. This proposal is somewhat speculative, but 295K
and 77K $I(V)$ measurements of equivalent specimens fabricated from NU1222 added credence to it: within as-grown specimens of NU1222 there was 1) only a very small occurrence of 3D-2D resonant tunnelling of ballistic electrons at 295K, and 2) no observable occurrence of 3D-2D resonant tunnelling at 77K. In other words, the as-grown $I(V)$ characteristics of NU1222 were much more 2D-like than those of NU168; therefore, after implantation-and-annealing the low-temperature PVCR of NU1222 was not expected to be increased to the same extent. Figures 3.10a and 3.11a depict the best $I(V)$ characteristics of NU1222 observed after implantation-and-annealing: note that the PVCR at 77K was never larger than the as-grown PVCR at 77K.

There was no observed LOP-assisted resonant tunnelling within NU168 after implantation-and-annealing; this was unexpected because the theoretical modelling described above indicates that $E_{Facc} - E_{0acc}$ would not be much different in the two structures (see sub-section 1.32). It is possible theoretically that a considerable amount of the LOP-assisted resonant tunnelling that occurred within the as-grown specimens of NU168 (see figure 5.7) was caused by the inelastic scattering of ballistic electrons, not those originating from the accumulation layer - as described above, the resonance current of ballistic electrons was much less prominent after implantation-and-annealing. The absence of LOP-assisted resonant tunnelling would obviously increase the PVCR because less of the electrons would tunnel through the double-barrier structure at a bias other than $V_p$. Furthermore, no LOP-assisted resonant-tunnelling was observed when investigating any specimen of NU1222 at low temperature; therefore, the implantation-caused changes to any LOP-assisted resonant tunnelling in this sample would be unobservable. Note that, as mentioned above, the PVCR of NU1222 after implantation-and-annealing was never larger than the as-grown PVCR.

5.5 - Conclusions

Despite the complexity of resonant tunnelling through a double-barrier structure, simple theoretical and experimental measurements (as distinct from much more complex techniques, e.g. magneto-tunnelling spectroscopy) proved to be useful for investigating the changes to the electronic transport caused by implantation-and-annealing. At high temperatures the electronic transport through lightly damaged DBDs was shown to be degraded considerably: no 3D-2D resonant-
tunnelling of ballistic electrons was observed, $V_p$ was somewhat higher, and both the PVCR and $I_{pd}$ of the main resonance were much lower. There was much empirical evidence that the transfer of charge across the n-doped emitter spacer-layer was the current-limiting mechanism after ion implantation. The $I(V)$ characteristics of a DBD sample with very thick spacer layers (NU1333) were degraded to a very large extent by the implantation of very small doses of protons; thus explaining the extreme degradation of the $I(V)$ characteristics of the very-similar specimens described in sub-section 4.35.

After implantation of low doses of protons, with decreasing temperature the current density at a specific bias decreased with the Poole-Frenkel emission of electrons into the conduction band from the defect states within the emitter spacer layer. At low temperatures a current-conduction mechanism for which the activation energy was independent of bias was observed after implantation-and-annealing. The magnitude and temperature dependence of this very small current were consistent with hopping conduction of electrons between defect states. In the same specimens at very low temperatures, the occurrence of Poole-Frenkel emission was not observable, but a resonant-tunnelling current limited by field-enhanced ionisation was observed at a relatively high bias. Resonant tunnelling of electrons excited into the conduction band from the defect states via field-enhanced ionisation also occurred within more-heavy damaged specimens, but was observable only after rapid thermal annealing. Poole-Frenkel emission of electrons into the conduction band from the defect states also occurred within these specimens at high temperatures, and will have been one of the primary causes of the low-quality PVCRs even after annealing for short durations at 600°C.

Subjecting the ion-implanted DBDs to powerful anneals repaired the electron-trapping defects and, hence, greatly improved the $I(V)$ characteristics, but the 295K PVCR was still somewhat lower than the as-grown PVCR. At 77K a 3D-2D resonance current of ballistic electrons was observable within as-grown specimens, but was unobservable within implanted-and-annealed specimens; this was attributed to the increased amount of inelastic scattering of these electrons in the presence of many defects.

It is proposed that at low temperatures the absence of 3D-2D resonant tunnelling of ballistic electrons within implanted-and-annealed specimens, together with the negligible occurrence of Poole-Frenkel emission, was a primary cause of the larger-than-as-grown PVCRs at low temperatures. LOP-assisted resonant
tunnelling was not observable after implantation-and-annealing; this also contributed to the increase of the PVCR at low temperatures. In a DBD sample in which there occurred no observable 3D-2D resonant tunnelling of ballistic electrons at 77K, and no observable LOP-assisted resonant tunnelling at 77K, no increase of the 77K PVCR was caused by implantation-and-annealing.
5.6 - References

2. M.J. Kelly - "Low Dimensional Semiconductors: Materials, Physics, Technology, Devices" (Oxford University Press, 1995)
7. M. Henini (private communication).
Chapter 6

MULTI-STAGE ANNEALING OF
ION-IMPLIED DOUBLE-BARRIER DIODES

6.1 - Introduction
This chapter describes the anneal-induced structural changes within ion-implanted DBDs. This was, intrinsically, an investigation of the annealing characteristics of GaAs\textsuperscript{1,2} where resonant tunnelling was used for the first time as a probe of the large-scale structural changes, i.e. this was not an investigation of defect-state energies, defect types, defect complexity, or defect density. \( I(V) \) measurements at various temperatures were made between each annealing stage. Some of the implanted-and-annealed specimens were subjected to low-temperature AC measurements, the reasons for which will be described below.

6.2 - Experimental Procedure
NU168 and NU1222 were the two samples investigated during this work - their layer structure and as-grown \( I(V) \) characteristics are depicted in figures 3.3 and 3.7 respectively.

6.21 - Ion implantation
The table overleaf lists the implantation processes used. The proton-implantations were carried out after the metallised mesas used for the \( I(V) \) measurements were fabricated (see sub-section 3.26), whereas the other implantations were carried out before the fabrication of the devices. None of the
ion-beam currents used would have heated the specimens considerably. All the implantation processes were carried out at room temperature, and, once again, the ion-beam was at 7° from the normal to the surface of the specimens (see sub-section 2.31). Figure 5.1 depicts the theoretical distribution of damage created by each of the implantation processes used here.

<table>
<thead>
<tr>
<th>Dose, energy and ion</th>
<th>Ion-beam current</th>
<th>Ion accelerator</th>
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<tr>
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<td>400kV</td>
</tr>
<tr>
<td>2x10¹³ 325keV protons cm⁻²</td>
<td>0.2µA</td>
<td>400kV</td>
</tr>
<tr>
<td>8x10¹³ 325keV protons cm⁻²</td>
<td>0.2µA</td>
<td>400kV</td>
</tr>
<tr>
<td>* 8x10¹⁴ 300keV protons cm⁻²</td>
<td>2.0µA</td>
<td>500kV</td>
</tr>
<tr>
<td>* 1x10¹⁴ 750keV He⁺ ions cm⁻²</td>
<td>25nA</td>
<td>2MV</td>
</tr>
</tbody>
</table>

* Not implanted into NU1222

6.22 - Post-implantation sample preparation and I(V) measurements

Chapter 3 describes the processing used to prepare the specimens of both samples for I(V) measurements, the optical annealing furnace, the Kulicke & Soffa gold-wire bonder and the apparatus and procedure used during the I(V) measurements.

6.23 - AC measurements

These experiments were carried out³ to measure the bias-dependent capacitance of an as-grown specimen and an implanted-and-annealed specimen having very unusual I(V) characteristics: after very rapid high-temperature anneals the I(V) characteristics of NU168 were similar qualitatively to the as-grown characteristics, but \( I_{pd} \) was orders-of-magnitude smaller. At high bias these I(V) characteristics included a resonance peak similar to resonance ‘a’ depicted in figure 5.3, i.e. low-quality resonant tunnelling through damaged material. The I(V) characteristics of many other implanted-and-annealed specimens also included a low-current ‘as-grown’ resonance. It was hoped that the bias-dependance of their low-temperature capacitance would add credence to a model which describes the origin of both the ‘as-grown’ and high-bias resonant-tunnelling characteristics.
6.3 - Results and discussion

Figure 6.1 depicts the 295K reverse-bias $I(V)$ characteristics of NU168 both before and after implantation with $2 \times 10^{13}$ 325keV protons cm$^{-2}$, and annealing for ten seconds at temperatures between 300 and 550°C in steps of 50°C. The qualitative and quantitative characteristics of the pre-anneal $I(V)$ data are described in sub-section 5.32. The post-anneal $I(V)$ data will now be described.

6.3.1 - Multi-stage annealing

The post-anneal data demonstrate the multi-stage annealing$^1$ of defects in ion-implanted GaAs: the anneals at temperatures up to 350°C resulted in a large improvement of the DC performance because, as deduced from the literature$^1$ and sub-section 2.21, complex defects such as divacancies and trivacancies in the graded-doped spacer layers (see sub-section 5.32) were annealed (stage 2 annealing); between 350 and 400°C there was very little change in the DC performance because there were very few remaining complex defects in the graded-doped layers to anneal, and the temperature was not high enough to repair the GaAs completely. The remaining point defects were not removed until anneals at 450°C were used (stage 3 annealing); hence the large improvements of the DC performance during these anneals (the high-resistivity of ion-implanted semiconductors is caused primarily by the presence of point defects$^2$). Stage 1 annealing would not have occurred because the dose of implanted protons was three orders-of-magnitude too small to amorphise$^3$ the GaAs (see figure 4.6). Also, the density of implantation-created defects was orders-of-magnitude too small to cause the creation of any dislocations during the implantation or the subsequent annealing$^4$.

The results depicted in figure 6.1 were reproduced easily using other specimens of NU168, and the equivalent specimens of NU1222. To the knowledge of the author, this work was the first electrical investigation of multi-stage annealing in ion-implanted III-V semiconductor structures within which the primary current-conduction mechanism is quantum-mechanical tunnelling through a heterostructure, where the damage therein was created primarily by electronic stopping of long-range ions (where $N_t$ was $\sim 5 \times 10^5$ nm$^{-3}$).

6.3.2 - Very rapid high-temperature annealing

Figure 6.2 depicts the $I(V)$ characteristics of proton-implanted specimens of NU168 which were subjected to a dose of $8 \times 10^{13}$ 325keV protons cm$^{-2}$, and
Figure 6.1 The \( I(V) \) characteristics of NU168 after implantation of \(2 \times 10^{13} \) 300keV protons cm\(^{-2}\), and annealing for ten seconds at the temperatures written in the legends.
Figure 6.2  The reverse-bias probed $I(V)$ characteristics of NU168 at 295K after a dose of $8 \times 10^{13}$ 325keV protons cm$^{-2}$, and annealing in the conditions written in the legends. The equivalent as-grown $I(V)$ characteristics are included for comparison. The arrows depict the change of the two resonances with increased annealing. The inset depicts the $[dI/dV](V)$ characteristics of sets ‘1’ and ‘3’.
subsequent annealing at various temperatures. The pre-anneal $I(V)$ characteristics are similar qualitatively to those depicted in figure 6.1; however, the current density was much less because the density of vacancies was four-times greater.

After annealing at 500°C for three seconds, the low-bias $I(V)$ characteristics of several specimens were similar qualitatively to the as-grown characteristics, but the current density was two orders-of-magnitude lower. $I_{pd}$ through the 500°C/3s-annealed material differed greatly from one specimen to the next: it differed between that of set ‘1’ and set ‘2’ depicted in figure 6.2, i.e. from being unmeasurably small to $2.3\text{A cm}^2$. At higher bias a resonance similar to that of resonance $a$ depicted in figure 5.3 was observed at all temperatures.

Both the main graph and inset $a$ of figure 6.3 prove that from 295K to 77K the low-bias resonance changed in an identical manner to that of the as-grown main-resonance, i.e. $I_{pd}$ doubled and $I_{vd}$ halved; therefore, the 77K PVCR was identical to the as-grown 77K PVCR. A lower-bias resonance of electrons originating from quasi-continuous 3D emitter states was observed at both 295K and 77K, and LOP-assisted resonant tunnelling was observed at both 77K and 4.2K (see figure 6.3). Inset $b$ depicts the high-bias resonance through the damaged material changing with temperature in an identical manner to that of resonance $a$ depicted in figure 5.3, i.e. its current density decreasing with temperature. At 77K a higher-bias resonance similar to that of resonance $b$ depicted in figure 5.3 was also observed, together with another resonance at an even higher bias (the origin of this third high-bias resonance was not ascertained).

**Clustering of defects**

The model proposed to explain the results depicted in figures 6.2 and 6.3; and also those depicted in figure 4.7b; is based on the creation of clusters of defects surrounded by percolation paths of as-grown material through the whole depth of the graded-doped spacer layers and the undoped layers (see figure 6.4). If this model is appropriate then defect clusters will also have been created in the n+ contacts, but after annealing their presence would be unobservable because $N_t$ therein will have been much smaller than $n$ (figure 5.1 depicts the pre-anneal defect density). Considering the similarity between $I_{pd}$ of resonance $a$ depicted in figure 5.3, and that of the higher-bias resonance depicted in figure 6.3, the post-anneal $N_t$ within the defect clusters was very similar to the pre-anneal $N_t$ in the bulk GaAs of the specimens implanted with $1\times10^{18}$ 325keV ions cm$^2$. 
Figure 6.3  The forward-bias $I(V)$ characteristics of wire-bonded specimens of NU168 after a dose of $8 \times 10^{13}$ 325keV protons cm$^2$, and annealing for three seconds at 500°C. The large arrow depicts the change of the first higher-bias resonance with decreasing temperature.
Figure 6.4  A schematic of an implanted-and-annealed DBD mesa within which there are many clusters of defects surrounded by percolation paths of as-grown material.
The cross-section of as-grown material within the mesa depicted in figure 6.4 would be decreased; therefore, $I_p$ would be lower but both the PVCR and $V_p$ would be unchanged because both $E_p$ in the n' contacts and the free-electron density in the graded-doped spacer layers would be the same as those in unimplanted material. The difference between the low-bias resonance current from one mesa to the next is consistent with local differences in annealing and, hence, differences in the volume of percolation paths in the graded-doped spacer layers.

Very simple modelling

The PVCR of the 295K low-bias resonance depicted in figure 6.3 was smaller than that of the 295K main resonance of as-grown specimens (1.8:1 c.f. 2.6:1). The rate at which the current density increased just beyond the 295K low-bias resonance depicted in figure 6.3 was larger than that beyond the main-resonance of as-grown specimens. Both differences resulted from there having been, just beyond the low-bias resonance, a considerable current through the defect clusters; this can be modelled very simply but quite accurately by scaling down the as-grown $I(V)$ characteristics to the extent that $I_p$ is equal to that of the low-bias resonance, and adding it to the post-500°C anneal $I(V)$ characteristics without the low-bias resonance. Figure 6.5a depicts the results obtained from carrying out this simple modelling: note the similarity between the modelled low-bias resonance and that observed experimentally.

At 77K the low-bias $I(V)$ characteristics were qualitatively almost identical to the as-grown characteristics because at low bias the current through the defect clusters was very much smaller than that through the percolation paths - at a specific bias the current density through the damaged GaAs decreased with temperature (see sub-section 5.32).

Annealing at higher temperatures resulted in the recovery of the resonance through the defect clusters, and the disappearance of the low-bias resonance, as depicted in both the main graph and the inset of figure 6.2: the low-bias resonance through any percolation paths remaining after each anneal will have become unmeasurable with the increasing current through the damaged material.

Clustering of defects within more-heavily damaged material

After annealing for one second at 600°C, the $I(V)$ characteristics of many specimens implanted with the doses of 300keV protons or 750keV He⁺ ions had a
Figure 6.5  a) The experimental and modelled forward-bias $I(V)$ characteristics of NU168 after a dose of $8 \times 10^{13}$ 325keV protons cm$^2$, and annealing for three seconds at 500°C; and b) the reverse-bias probed $I(V)$ characteristics at 295K both before and after the He$^+$-implantation-and-anneal process. The numbers written in brackets are the PVCRs.
low-bias resonance similar qualitatively to the as-grown main-resonance, but did not have any higher-bias resonances (see figure 6.5b): the current density flowing through the defect clusters of this material would have been very small because of the greater amount and complexity of damage created by the He⁺ implantation. Again, the low-bias $I_{pd}$ differed much from one DBD to the next. Low-temperature DC measurements of these specimens proved that the temperature dependence of their $I(V)$ characteristics was similar to that of the as-grown characteristics. Figure 6.5b shows that the low-bias resonance was not observable after annealing this material for ten seconds, and that the subsequent anneal-induced recovery of the as-grown $I(V)$ characteristics proceeded as expected (see sub-section 3.3i).

**AC measurements**

As mentioned earlier, to investigate the electrical characteristics further, a Hewlett Packard 4275A LCR analyser was used to ascertain the bias-dependent capacitance of an as-grown specimen, and the implanted-and-annealed specimen whose $I(V)$ characteristics are depicted in figure 6.3. It is very important to note that a direct quantitative comparison between the $C(V)$ characteristics of the two diodes was allowed because the mesas of both had a diameter of 200μm. Figure 6.6 depicts the results obtained during these measurements, which were carried out assuming that the equivalent circuit of the DBD was a capacitance in parallel with a resistance. Using a 4MHz 5mV$_{pp}$ modulating signal, the $C(V)$ measurements were carried out only at low bias because the sensitivity of these measurements decreases with conductivity of the specimen ($G$) when above ~1mS.

No as-grown $C(V)$ characteristics could be obtained at 295K, even at low bias because $G$ was too high (it was much higher than 1mS); however, low-bias measurements were possible at 77K. The top graph of figure 6.6 depicts the results of these measurements: note the decreasing capacitance with increasing bias, which is consistent with results obtained by Leadbeater et al when investigating the $C(V)$ characteristics of an as-grown DBD. At low bias the capacitance of an as-grown DBD decreases because of the increasing thickness of the depletion layer beyond the collector barrier: the increasing charge between the barriers, an effect which increases the capacitance, is negligible at low bias.

The low-bias capacitance of an as-grown DBD can be given by

$$C_n = (\varepsilon \varepsilon_0 A_n)/d_n$$  \hspace{1cm} (6-1)
Figure 6.6  The $C(V)$ characteristics of two 200μm-diameter specimens of NU168 - an as-grown specimen and the specimen whose $I(V)$ characteristics are depicted in figure 6.3.
where \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constant of GaAs and the permittivity of free space respectively, \( A_a \) is the cross-sectional area of the diode, and \( d_a \) is its capacitative thickness (the effective thickness of the dielectric). \( d_a \) is assumed to be the thickness of the depletion layer below the second barrier plus the thickness of the double-barrier structure (16nm); the effective source of electrons within this structure is the accumulation layer contiguous to the first barrier; therefore, during C(V) measurements the n-type layer and the graded-doped spacer layer above the accumulation layer are relatively unimportant. However, the quantum stand-off distance\(^{15} \), which is the distance between the emitter barrier and the peak of the electron distribution within the accumulation layer, must be considered; this distance is 10nm typically. Within the as-grown specimen of NU168 at low bias, the depletion layer was assumed to be the thickness of the graded-doped spacer layer (50nm) plus the thickness of the intrinsic spacer layer (2.5nm). The total capacitative thickness of the as-grown specimen was, therefore, 2.5nm + 50nm + 16nm + 10nm. While using this value with equation (6-1) to calculate the capacitance of an as-grown DBD, a low-bias as-grown capacitance of 45pF was calculated; this is similar to the low-bias result obtained experimentally (51pF). Another as-grown DBD which had a mesa diameter of 100\( \mu \)m (and, therefore, \( A_x0.25 \)) had a low-bias capacitance of 12pF, which is consistent with the other experimental result.

Within the ion-implanted DBD at low bias, the total capacitance \( (C_i) \) was assumed to be equal to the capacitance of the damaged material \( (C_c) \) plus the parallel capacitance of the percolation paths of as-grown material \( (C_p) \). \( C_p \) is equal to \( (A_p/A_a)C_a \), where \( A_p/A_a \) is the fraction of \( A_a \) occupied by the percolation paths; therefore, \( C_i \) is equal to

\[
C_i = FC_a + (1-F)C_c
\]

where \( F \) is equal to \( A_p/A_a \). \( F \) can be calculated by dividing \( I_{pd} \) of the low-bias resonance by that of the main resonance of the as-grown specimen. The capacitative thickness of the percolation paths was assumed to be equal to the as-grown capacitative thickness, i.e. \( d_a \). Within the defect clusters the capacitative thickness \( (d_c) \) was assumed to be the total thickness of the layers between the n-type doped contacts (121nm): the quasi-continuous 3D states in the n-type emitter were assumed to be the only considerable source of electrons in the defect clusters at low bias because any accumulation layer created at low bias will have been populated by almost no
electrons, especially at 77K (see sub-section 5.32); therefore,

\[ C_i = \frac{\varepsilon_0 (A_a - A_p)}{d_p} \]  

(6-3)

because the 52.5nm of GaAs either side of the double-barrier structure would have been electrically important during \( C(V) \) measurements. \( C_i \) was calculated to be 28pF, which is quite consistent with the experimental data. The most probable cause of the difference between the calculated and experimental values of \( C_i \) is an underestimation of \( d_p \), which may have extended into the \( n^+ \)-doped layers. Figure 6.6 shows that the low-bias \( C_i \) was practically constant with increasing bias; this is consistent with the fact that within the defect clusters, the layers beneath the double-barrier structure were depleted of free electrons even at zero bias because most of them were trapped within defect states.

As the bias was increased up to the first (3D-2D) resonance, the presence of the percolation paths of as-grown material then became obvious: \( C_i \) began to decrease with the increase of \( d_p \) within the percolation paths. Increasing the bias further caused \( C_i \) to increase because of the high rate of charge accumulation when the bias is almost at the resonance voltage of the 3D-2D tunnelling. The magnitude of the change of \( C_i \) near the 3D-2D resonance, and the sudden decrease of \( C_i \) beyond this resonance could have been caused only by a sudden detrimental increase of \( G \); therefore, the data obtained at this and higher bias are meaningless.

Low-bias DC measurements at 4.2K: resonant tunnelling through donor states

The AC experiments described above corroborated the model explaining the existence of percolation paths of as-grown material within the specimen whose \( I(V) \) characteristics are depicted in figure 6.3; however, neither the number of percolation paths nor their average diameter were quantified. After calculating \( F \), which equals 3.9A cm\(^2/630A \) cm\(^2\) = 0.006, the total area of the percolation paths of as-grown material was calculated to be 189\( \mu \)m\(^2\). At the limit of there being only one (circular shaped) percolation path, it is easy to calculate that its diameter would be 15\( \mu \)m. If there were twenty-five percolation paths of as-grown material, their average diameter would be only 3\( \mu \)m. If the typical diameter of the percolation paths was less than or not much greater than 5\( \mu \)m, resonant tunnelling through different donor states\(^{16}\) between the barriers should have been observable at low bias and at low temperatures (less than 20K usually). A donor between the barriers creates a
localised potential well having confined states associated with it, through which resonant tunnelling can occur; these donor states having a lower energy than the main-resonance confined state. Low-bias resonance through donor states within a double-barrier structure can be observed if the number of different donor states is small; therefore, the resonances are observable most easily when investigating a DBD with a very small cross-sectional area (less than 30\(\mu\)m\(^2\) usually). Within a large-area DBD there might be many different donors between the barriers, each having their own energy state which is indistinct amongst the many others.

\(I(V)\) measurements at 4.2K were carried out to investigate whether resonant tunnelling through donor states was observable, the results of which are depicted in figure 6.7. To decrease the effects of extrinsic noise (and intrinsic noise - see below), the \(I(V)\) measurements were carried out using the longest integration time-per-measurement that the H.P. 4156A was capable of (2s).

The results depicted in figure 6.7, which were highly reproducible, indicate that resonant tunnelling through at least two different donor states occurred: the resonance characteristics at very-low bias were quite prominent, but were very broad because the experimental \(I(V)\) characteristics were a superposition of those through many percolation paths of as-grown material. No very-low bias resonances were observed when investigating as-grown specimens of NU168. With increasing temperature the very-low bias resonance characteristics very quickly became unobservable, which is consistent with the results obtained previously\(^{16}\). The results depicted in figure 6.7 were obtained when the DBD was reverse biased - the forward-bias characteristics were similar, but the indications of resonance were somewhat less prominent; this asymmetry is consistent with the few donors being, on average, not exactly half-way between the barriers.

Low-bias DC measurements at 4.2K: single-electron switching

Defect states at or near \(E_p\) can trap and thermally emit electrons with a temperature-dependent frequency (see sub-section 2.21); thus creating an intrinsic noise. When the current through the conducting path of a device is low enough, this emission and trapping of electrons, which is known as ‘single-electron switching’\(^{17}\), can be observed. Single-electron switching was observed during room-temperature \(I(V)\) measurements of DBDs where the conducting path between the barriers was a quantum dot\(^{18}\) with a minimum lateral dimension of 0.1\(\mu\)m, and where \(I_p\) was similar to that of the percolation-path DBD specimen.
Figure 6.7  The 4.2K reverse-bias $I(V)$ and $[dI/dV](V)$ characteristics of the percolation-path specimen.
At a constant bias voltage of either 0.8V or 0.85V, both of which are in the region of $I_s$, the current through the percolation-path specimen was measured for a maximum of 30s in 10ms intervals of $t$ (which equates to 3000 measurements per temperature). The data indicate that single-electron switching did occur at 4.2K, as depicted in figure 6.8, which indicates that some of the percolation paths of as-grown material may have had sub-micron diameters. Distinct single-electron switching was not observable at 77K and 295K, which is consistent with the results obtained by Ralls et al\textsuperscript{17}: more electrons (in many percolation paths) will have had enough energy to switch and, therefore, any individual occurrences of switching will have been indistinct. Note also that single-electron switching was not observed at any bias when investigating specimens of the same material without ostensibly having any percolation paths, or when investigating as-grown specimens; this confirms the fact that the single-electron switching was occurring within the percolation paths of as-grown material.

6.4 - Conclusions
Resonant tunnelling through ion-implanted Al\textsubscript{0.4}Ga\textsubscript{0.6}As/GaAs DBDs was used to probe the large-scale structural changes during rapid thermal-annealing. Multi-stage annealing of damage in III-V semiconductors was demonstrated by the multi-stage recovery of the as-grown resonant tunnelling. The $I(V)$ characteristics of the ion-implanted double-barrier diodes after very rapid high-temperature anneals were similar qualitatively to the as-grown characteristics, but $I_{pd}$ was two orders-of-magnitude lower. The creation of percolation paths of as-grown material (which surrounded clusters of defects) during these rapid anneals was proposed to explain this. The evidence of multi-stage annealing and defect clustering was corroborated by the results obtained during low-temperature $I(V)$ measurements and $C(V)$ measurements: the temperature dependance of the low-bias resonance was identical to the as-grown main resonance; and with increasing bias the capacitance of the defect clusters was preponderant until a relatively large current flowed through the percolation paths of as-grown material. Resonant tunnelling through donor states and single-electron switching were observed at 4.2K; these observations indicate that the typical diameter of the percolation paths was less than five microns, and that some of the percolation paths may have had sub-micron diameters.
Figure 6.8 The 4.2K $I(t,V)$ characteristics of the percolation-path specimen biased at the voltages written in the graphs.
6.5 - REFERENCES

3. Carried out by the author with the assistance of L. Eaves and T.J. Foster, Department of Physics, University of Nottingham, U.K.
PART 4

Discussions and Conclusions
Chapter 7

WHAT NEXT?

7.1 - Introduction (or ‘inspiration and encouragement’)

Soon after the principal research of this PhD was commenced (about a year after the PhD itself was commenced) a respected and much-liked academic member of staff at Surrey commented intelligently that worldwide there were many research groups attempting to fabricate 3D integrated circuitry of electronic devices, but that none of them would be doing, or had done, anything similar to the work described in this thesis: he was alluding to the fact that attempting to implant high-energy ions through a fragile nanoscale heterostructure was a seemingly absurd thing to do. At that time, very few people would have disagreed with him. The author himself was not without his own doubts regarding the potential abilities of high-energy ion implantation through semiconductor multilayers.

Three months later, the results depicted in figure 3.9 were obtained. These $I(V)$ characteristics were certainly not the first to be observed when carrying out DC measurements on ion-implanted DBDs, but they were the first which confirmed that the original idea of implanting high-energy ions through a double-barrier structure should be pursued over a longer timescale; hence the submission of this thesis for examination two years later. There are many more experiments involving ion-implanted DBDs which ought to be carried out, and this chapter is a compilation of suggestions for such future work.

7.2 - Chapters 3 and 4

Ion implantation of DBDs fabricated from other semiconductors: the
highest-performance DBDs manufactured to date were fabricated using more exotic III-V semiconductors than Al$_x$Ga$_{1-x}$As/GaAs. If the low-temperature annealing process described in Chapter 3 and/or the Be$^+$-implantation process described in Chapter 4 were successful when fabricating and processing Al$_x$Ga$_{1-x}$As/GaAs DBDs, it would be very important to develop equivalent processes for the materials described in the literature.

**Fabrication of a mixer-circuit:** when a successful implantation-and-anneal process has been developed, and the RF characterisation of implanted-and-annealed DBDs and annealed ASPAT diodes has been carried out successfully, a wafer including the layer structure of an ASPAT diode two-to-three microns below that of a DBD should be grown. The successfully-developed implantation process should then be carried out in selected areas of this two-level wafer; this is the basis for fabricating the microwave-mixer circuit described in Chapters 1 and 3. To prove that growing such a wafer was possible, sample A1034 was designed by the author and grown at the Cavendish Laboratory in Cambridge: figure 7.1 depicts its layer structure and $I(V)$ characteristics (of both the DBD and the ASPAT diode). Note that the PVCR of the DBD is much smaller than that of the double-barrier structures grown at the University of Nottingham. The two obvious reasons for this are 1) the fraction of Al in the barriers is smaller; therefore, the barriers are lower, and 2) the distribution of donors near the double-barrier structure is such that no considerable accumulation layer is formed when biased; therefore, the main-resonance peak will be very 3D-like. The inferior DC performance of the DBD is not caused by defective growth of the very thick epilayers below it: its PVCR and $I_{pd}$ are very similar to those of a (very similar) double-barrier structure investigated by Tewordt et al. Nevertheless, this design of DBD does not have a good enough performance for use within the microwave-mixer circuit.

### 7.3 - Chapter 5

**Modelling the $I(V)$ characteristics of ion-implanted DBDs:** it would be expedient to expand a theoretical procedure used to model the $I(V)$ characteristics of a DBD to also model the effects of ion implantation (e.g. increased inelastic scattering, Poole-Frenkel emission at high temperatures, field-enhanced ionisation at low temperatures, and decreased prominence of 3D-2D resonance after
Figure 7.1  The as-grown $I(V)$ characteristics of both multilayer tunnel devices within A1034, and the layer structure of the wafer.
The successful formulation and subsequent expansion of such a complete procedure would probably necessitate the whole duration of a three-year MPhil/PhD project.

**High B-field DC measurements of implanted-and-annealed DBDs: I(V,B) measurements, where B||I, have been used to differentiate between 3D-2D and 2D-2D resonant tunnelling when 3D-2D resonant tunnelling was indistinct during zero-B I(V) measurements**. The results obtained during 4.2K I(V,B) measurements of implanted-and-annealed DBDs should indicate the extent to which the 3D-2D resonance current therein is suppressed; these results might also provide evidence for the proposed cause of the larger-than-as-grown PVCRs at low temperatures.

**7.4 - Chapter 6**

*Magnetotunnelling spectroscopy of donor states*: the very-low bias resonance characteristics depicted in figure 6.7 were those of a diode specimen having a diameter of 200 µm, and 189 µm² of as-grown material in the form of percolation paths surrounding defect clusters. Within an equivalent but smaller implanted-and-annealed DBD (which could have a diameter less than one micron), there would be approximately the same density of as-grown material but, obviously, a smaller number of percolation paths. The very-low bias resonance characteristics of such a smaller specimen, therefore, would probably be much more abrupt; thus facilitating investigations, using the technique used by Dellow et al. and Sakai et al., of the energy levels of the donor states confined between the barriers.

*Measuring the activation energy of single-electron switching*: within the hypothetical specimen described above, it would also be easier to investigate single-electron switching: the activation energy of the original defects can be calculated when, at many temperatures, the average duration of both the ‘on’ state and the ‘off’ state have been measured. Ralls et al. describe the method used to calculate the activation energy of the switching defect states.

**7.5 - The final words**
The work carried out by any of the countless research groups involved with
improving the performance and/or the commercial applicability of double-barrier diodes, which includes the tentative work described in this thesis, will not be exploited commercially until the manufacture and characterisation of multilayer tunnel diodes improves greatly. The work carried out partly by the author to investigate the manufacturability of even the simplest multilayer tunnel diodes proved that such devices are not manufacturable when using present-day semiconductor growth, characterisation, and modelling techniques16.

The invention of ‘closed-loop’ epitaxial growth of multilayer semiconductors17 has brought closer the day when such materials could be manufactured repeatedly and routinely within stringent tolerances; however, as mentioned above, both the modelling and the characterisation of the electrical performance of devices fabricated from such materials will have to be advanced similarly. Perhaps within twenty years the first commercial quantum-well injection transit-time diodes will be manufactured and sold as high-efficiency microwave generators. If these diodes are to be manufactured commercially, it is realistic to believe that ion implantation will be used during their manufacture: very recently there were several publications describing the successful use of ion implantation during the fabrication of advanced devices and integrated circuits18-21 to be used within commercial high-frequency communication systems. After more than thirty years since its first commercial use, ion implantation is now acknowledged to be an expedient technique to be used during the manufacture of such high-frequency systems. Perhaps it will be no more than another thirty years before high-energy ions are implanted through the active layers of advanced high-frequency devices as part of a commercial process used to integrate the devices three-dimensionally.
Chapter 7

7.7 - References

8. Carried out by D.A. Ritchie and E.H. Linfield at the Cavendish Laboratory, Department of Physics, University of Cambridge.
18. III-Vs Review, 8 no. 5 p. 4
Appendix

NU1222, NU1331, NU1332, and NU1333 all had the same designed double-barrier structure, but their $I(V)$ characteristics differed greatly. NU1222 was a symmetric structure, and NU1331 was almost symmetric but its spacer layers were much thicker (see the modelled conduction-band edges in figure A.1a). The layer structure of NU1331 was, therefore, more resistive; hence its larger $V_p$. With increasing emitter spacer-layer thickness, the current-limiting caused by thermionic emission of electrons over the emitter spacer-layer barrier becomes more prominent; hence the smaller $I_{pd}$ of NU1331.

Consider the forward-bias $I(V)$ characteristics of NU1331, NU1332 and NU1333: $V_p$ did not increase much with increasing emitter spacer-layer thickness because most of the bias was across the relatively resistive depletion layer; this had the same thickness within each sample. In reverse bias, the voltage required to bring the confined energy-state between the barriers down to $E_f$ acc increased with the thickness of the depletion layer; this was thinnest in NU1332, and thickest in NU1331. At a specific reverse bias both the height and the thickness of the emitter spacer-layer barrier were the same within each sample, as depicted in figure A.1b. The increasing $I_{pd}$ with structural symmetry of NU133x could not be elucidated by the modelling of their conduction-band edges (it is unlikely that the increase of $I_{pd}$ with symmetry is caused by unintentional doping differences).

The well-defined accumulation layer within NU1331, NU1332 and NU1333 was populated by several quasi-2D sub-bands; hence the obvious occurrence of secondary resonances at low bias. The lowest-bias secondary resonance was attributed to 3D-2D resonant tunnelling.

References
Figure A.1  

a) The modelled conduction-band edge of both NU1222 and NU1331 in forward bias, and b) the modelled conduction-band edge of both NU1331 and NU1332 in the same reverse bias. Each double barrier was actually modelled as a thick single barrier, and then the double-barrier structure was drawn in schematically (but accurately).