Preparation of Pyramidal Textured GaP p-n Junctions and Their Applications to Alpha Radio-Voltaic Cells (ARVCs)

Xiangyang Mei

A thesis submitted in conformity with the requirements of the degree of Master of Applied Science

The Department of Metallurgy and Materials Science

University of Toronto

© Copyright by Xiangyang Mei 1997
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author’s permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.
To my parents, my wife and son.
ABSTRACT

A new GaP pyramidal textured p-n junction (PTJ) was developed for improving the conversion efficiency of alpha radio voltaic cells (ARVCs). The pyramidal textured surfaces were prepared using photolithographic masking followed by wet chemical etching on n-type GaP (111) B surfaces. Surface morphology evolution as a function of etching time was investigated on patterned GaP substrates. Liquid phase epitaxy (LPE) growth of p-type GaP layers was carried out on the pyramidal textured substrates to form the PTJ. The LPE layer evolution for different growth time was also investigated to study LPE growth behavior on textured substrates. Field emission scanning electron microscopy (FE-SEM) studies on PTJ structure devices showed that sharp PTJ interfaces with flat surfaces were realized. Electron beam induced current (EBIC) analysis proved that collection current follows the PTJ interface with an obvious increase in collection area compared to that of flat junctions. I-V studies revealed that very low leakage currents were achieved for p-n junctions formed with Mg doped p-type epilayers on both pyramidal and flat GaP substrates. Alpha radiation tests confirmed a significant (~100%) increase of the conversion efficiency for the ARVCs with PTJ structures compared to those with flat junctions.
ACKNOWLEDGMENTS

First of all, I have to thank my supervisor, Professor Harry E. Ruda, for his trust in me by giving me the chance to work on this research project. His support and encouragement have helped me to overcome whatever the difficulties I met in my research work and in my school life. I am very grateful for his teaching on semiconductor material growth and characterization, which greatly enriched my knowledge in this field and increased my ability to deal with the problems in the research works. I also appreciate very much his guidance for solving technical problems related to LPE growth and characterization of epilayers and devices, and developing new device structures.

I would like to express my acknowledgments to Dr. Lech Jedral for his pioneering work on alpha radio voltaic cells and accomplishments on setting the related equipment for this research project; to Dr. Tatiana Berdinskihk for her collaboration on the studies of etching evolution on patterned GaP substrates and on SEM and EBIC analysis; to Professor Ben Yacobi for his guidance on Monte Carlo simulations and other advise and suggestions for this project; to our EMG group team member Dr. Yuichi Masaki, Dr. Zhong Ling Peng, Mr. Manoj Prasad, Mr. Genmao Chen and others for their help, advice and valuable discussions.

I would also like to thank Dr. Margaret Buchanan of the National Research Council of Canada for her help on photolithographic masking, F. Neub and S. Boccia from the Department of Metallurgy and Material Science for their help on SEM and EBIC measurements.
## Contents:

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Introduction</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 2</td>
<td>Basic principles of ARVCs</td>
<td>5</td>
</tr>
<tr>
<td>Chapter 3</td>
<td>Simulation of alpha particle irradiation of GaP and design of GaP ARVCs</td>
<td>11</td>
</tr>
<tr>
<td>3.1</td>
<td>Simulation of alpha particle irradiation of GaP</td>
<td>11</td>
</tr>
<tr>
<td>3.2</td>
<td>Alpha irradiation generated current in GaP p-n junction devices</td>
<td>18</td>
</tr>
<tr>
<td>3.3</td>
<td>Design of GaP ARVCs</td>
<td>22</td>
</tr>
<tr>
<td>Chapter 4</td>
<td>Fabrication of GaP ARVCs</td>
<td>28</td>
</tr>
<tr>
<td>4.1</td>
<td>Polishing of GaP substrates</td>
<td>28</td>
</tr>
<tr>
<td>4.2</td>
<td>Pyramidal substrate preparation</td>
<td>30</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Photolithographic masking</td>
<td>30</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Wet chemical etching</td>
<td>33</td>
</tr>
<tr>
<td>4.3</td>
<td>Liquid phase epitaxial growth of GaP layers</td>
<td>44</td>
</tr>
<tr>
<td>4.3.1</td>
<td>GaP LPE growth mechanism</td>
<td>44</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Doping in the GaP layers</td>
<td>49</td>
</tr>
<tr>
<td>4.3.3</td>
<td>LPE system and growth procedures</td>
<td>50</td>
</tr>
<tr>
<td>4.4</td>
<td>Metal contacts</td>
<td>56</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Evaporation</td>
<td>56</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Rapid thermal annealing</td>
<td>58</td>
</tr>
</tbody>
</table>
Chapter 1  Introduction

A radio voltaic cell (RVC) is a device that generates electrical power using the decay energy of radio isotopes. Because of the advantages of long life, high energy density, high reliability and maintenance-free operation, RVCs are very attractive power supply options for applications in space travel, satellites, deep sea and arctic explorations and cardiac heart pacers. Currently used radio-isotopic batteries are mainly thermo-electric and thermo-ionic radio-isotopic batteries. These radio-isotopic batteries use indirect thermal conversion, and the conversion efficiencies are usually less than 8% [1-1]. However, RVCs can directly convert the radiation energy from radio-isotopes to electrical energy. Because of direct conversion, RVC has the potential of realizing much higher conversion efficiencies compared with thermal radio-isotopic batteries. Theoretical conversion efficiency limits vary for different semiconductor materials. Taking Si as an example, its average ionization energy is 3.62eV for generating an electron-hole(e-h) pair, the maximum output voltage is about 0.7V, resulting in a theoretical energy conversion efficiency limit of 19.2%.

The first radio voltaic cell was demonstrated in Sarnoff Laboratories by P. Papport et al. In 1956 [1-2]. They observed electron-voltaic effect in Si and Ge p-n junctions irradiated with high energy electrons (beta rays) emitted from $^{90}$Sr. These devices were called beta cells. In 1972, L. C. Olson et al. [1-3] further developed the beta cell in attempting to realize a long life battery using natural decay energy from radio isotopes. Because of the limitation of semiconductor technologies during that pioneering time, the
radio voltaic conversion efficiencies of these beta cells were very low, which dimmed the practical applications of radio voltaic cells. As a matter of fact, hardly any research effort on RVCs was found in the following one and half decades.

Since 1989, radio voltaic cells have been gaining attention again. One fact that motivated the radio voltaic research is the availability of large quantities of tritium as a radiation source which arises as a waste from nuclear power plants. Tritium emits beta particles with average energy of 6 keV, a maximum energy of 18.6 keV and a half life of 12.3 years. Using tritium as an energy source for making long life batteries is a very promising way to consume tritium nuclear waste. Moreover, tritium is a desirable radiation source for radio voltaic cells since tritium possesses a relatively small health risk as it is not readily absorbed by the human body[1-4].

Another driving force for RVC research comes from the highly developed semiconductor technology. One has a wide choice of semiconductor materials and related device fabrication technologies for building RVCs. As compared with Si and Ge, III-V semiconductor materials such as GaP are available and are superior choices to Si and Ge for fabricating RVCs. GaP has an energy band gap of 2.26 eV at room temperature, much higher than that of Si and Ge. Due to the high energy band gap, GaP RVCs can achieve higher output voltages compared with Si and Ge, which means that one generated e-h pair can contribute more electrical power. Higher energy band gap is also helpful in minimizing leakage currents for p-n junction devices. This is especially important for RVCs because the generated current level is usually very low for RVCs due to low incident power flux of radio isotopes. Self absorption however limits the available
power flux from both beta and alpha radio isotopes. The current density generated by radio isotopes are usually of the order of only about micro-amps per square centimeter.

R. J. Walko and coworkers from Sandia National Laboratories reported tritium fueled beta cells using both GaP p-n junction and Schottky barrier devices in 1991[1-5]. They used both liquid phase epitaxy (LPE) and metal-organic chemical vapor deposition (MOCVD) techniques for GaP device fabrication. Using a tritium source with a power density of about 10 μW/cm², they realized a short circuit current of 1 μA, an open circuit voltage of ~ 1 V and a maximum output power of 0.7 μW. The conversion efficiency was about 7%, which was a very encouraging result.

Their experimental results also showed that LPE samples had less impurity incorporation than MOCVD samples. Radio voltaic cells fabricated using LPE technique had better performance than those fabricated using MOCVD. Since RVCs are low excitation conversion devices, reducing the impurity related leakage current is very important. Their results indicated that LPE is a better technique for RVC device fabrication. Moreover, since LPE system is relatively simpler than MOCVD, the LPE process is less costly. LPE is also much less hazardous than MOCVD process since no toxic gases are required for LPE growth.

Alpha particles have much higher energy than beta rays, so that alpha radio isotopes can provide higher energy/weight ratio devices than beta sources. Alpha isotopes usually have very long half lives. For example, $^{241}$Am has a half life of more than 400 years. Alpha isotopes are solids, which can potentially be integrated with semiconductor devices to reach low weight and small volume. Moreover, alpha particles have relatively small health risks to humans since they can not penetrate human skin, and can be easily
sealed. Solid form sources are relatively easy to handle and have less environmental problems. The above features of alpha particles and alpha radio isotopes make alpha radio voltaic cells (ARVCs) more attractive than beta counterparts, especially for space applications. In addition alpha sources, such as $^{241}$Am, are commonly used in a number of commercial applications such as smoke detectors, where they have gained widespread acceptance. High efficiency ARVC devices can also be used as room temperature alpha particle detectors. T. Wang et al. reported that conversion efficiency of Si based ARVC could be over 16% according to their simulation results[1-6]. However, no practical device was reported to our knowledge.

Since alpha particles usually have very high energy, around several MeV, radiation damage is a serious concern for ARVCs. Semiconductors such as Si show poor immunity to the high energy alpha particle bombardments. Therefore, excellent radiation hard materials are required to build ARVC devices. III-V semiconductors, such as InP, GaInP and GaP, have been shown to have far superior radiation hardness than Si[1-7,8,9]. GaP has demonstrated excellent radiation hardness in beta-RVCs [1-5, 9]. Moreover, the large band gap of GaP is crucial to realize a very low leakage current, which is also critical for ARVCs because of the low generation current due to low incident power flux for alpha sources.

In this work, we demonstrated the design and fabrication of ARVCs using GaP p-n junction structures. LPE was used to prepare high quality GaP epilayers on GaP (111)B substrates. Since the minority carrier diffusion length is much shorter than the alpha radiation penetration depth, a special pyramidal textured p-n junction (PTJ) interface structure was designed to increase the collection volume of the generated e-h pairs. This
PTJ structure was successfully realized using LPE growth on pyramidal GaP substrates prepared through photo-lithographic masking and wet chemical etching. Detailed discussion and experimental results on GaP ARVC design, fabrication, LPE layer and device characterization and alpha cell performance, are presented in the following chapters.

Chapter 2 Basic principles of ARVCs

2.1 General mechanism of ARVCs

Similar to semiconductor solar cells, ARVCs also use semiconductor p-n junction structures to convert alpha radiation energy to electrical energy[2-1]. A schematic diagram of the device design is shown in Fig.1. In the p-n junction device, there is a built-in

![Diagram of a p-n junction ARVC](image)

Figure 1 An illustrative diagram of a p-n junction ARVC.

voltage $V_{bi}$ between p and n type regions as shown in Fig. 2, which results from the diffusion of electrons from n-type to p-type region and holes from p-type to n-type region. This built-in voltage creates an electric field in the depletion region in the
direction perpendicular to the junction from the n-type side to the p-type side. When alpha particles irradiate the semiconductor surface, they can penetrate through the p-n junction as long as the junction depth is smaller than alpha particle range. The high

![Energy band diagram of p-n junction ARVC.](image)

energy alpha particles will excite the electrons from valence band to the conduction band in both p and n regions, resulting in e-h pair generations in p- and n-type regions. The excited electrons in p-type region can diffuse to the edge of the depletion region and then be swept into n-type region by the built-in electric field of the p-n junction. Similarly, the excited holes in n-type region can flow into the p-type region. Under the short circuit conditions, the flows of generated electrons and holes result in an electrical current called short circuit current $I_{SC}$, which is the radiation generated current. In the case of open circuit conditions, the generated electrons and holes will accumulate in the n- and the p-type region, respectively, which produce a net output voltage called the open circuit voltage $V_{OC}$. The output current and voltage usually follow a form as shown in Fig.3.

There is a maximum output power $P_m = I_m V_m$, and a fill factor $FF$ can be introduced as:
\[ FF = \frac{P_m}{I_{SC} V_{OC}} \quad (2-1) \]

to represent the relation between \( P_m \) with \( I_{SC} \) and \( V_{OC} \). The conversion efficiency should be the ratio between maximum output power and the incident power \( P_\alpha \) of alpha particles, which can be expressed as:

\[ \eta = \frac{P_m}{P_\alpha} = \frac{I_{SC} V_{OC} FF}{P_\alpha} \quad (2-2) \]

### 2.2 Alpha radiation effects in semiconductors

From the general mechanism of ARVCs discussed above, one can see that the first important issue is how the alpha particles interact with semiconductor material to generate e-h pairs. When a high energy alpha particle irradiates a semiconductor, it losses its energy while penetrating into the semiconductor mainly through three basic processes. First, it is scattered by the electrons of semiconductor atoms. The electrons can get enough energy to escape from the trapping of their bonded atoms to become free electrons, leaving behind ionized atoms. The positive charges on these ionized atoms are called holes. This process is radiation induced ionization that produces e-h pairs suitable
for radio voltaic conversion. Secondly, alpha particles can interact with the atoms of the semiconductor material passed through and lose some energy to the atoms, resulting in lattice vibrations. This is a thermal process which is not useful to radio voltaic conversion because the lost energy only produces heat. Thirdly, since the alpha particle has a very high energy, it can displace atoms from their original positions, and hence create radiation induced defects. This process is damaging because the radiation induced defects can act as traps for excited carriers and degrade the device performance. Beside understanding how the alpha particle losses its energy, one should also know the spatial distribution of these energy losses. Detailed discussions of these factors are presented in Chapter 3.

2.3 Derivations of theoretical performance of alpha radio-voltaic cells

Under alpha particle irradiation, a semiconductor p-n junction device (as shown in Fig.1) can collect radiation generated electrons and holes to produce current and voltage as discussed above. The equivalent circuit under irradiation is shown in Fig. 4, where a constant-current source $I_{SC}$ is shown in parallel with an un-irradiated p-n junction diode. The source current $I_{SC}$ is produced by the alpha particle irradiation; $R_L$ is the load resistance.

![Figure 4](image-url)  The equivalent circuit of an ARVC.
The I-V characteristics of circuit shown in Fig. 4 are given by:

\[ I = I_s (e^{\frac{qV}{nkT}} - 1) - I_{SC} \]  \hspace{1cm} (2-3)

where \( q \) is the electron charge, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( I_s \) is the reverse saturation current and \( n \) is the ideality factor of the p-n junction diode.

The reverse saturation current \( I_S \) for an ideal p-n junction diode can be expressed as:

\[ I_s = I_{SC}/A = qN_cN_v [N_A^{-1}(D_n/\tau_n)^{1/2} + N_D^{-1}(D_p/\tau_p)^{1/2}]e^{\frac{-E_g}{kT}} \]  \hspace{1cm} (2-4)

where \( A \) is the junction area, \( N_C \) and \( N_V \) are the conduction band and valence band density of states, respectively; \( N_A \) and \( N_D \) are the acceptor and donor concentrations, respectively; \( D_n \) and \( D_p \) are the electron diffusion coefficient in p-type region and hole diffusion coefficient in n-type region, respectively; and \( \tau_n \) and \( \tau_p \) are the minority carrier life time of electrons and holes, respectively.

From Eq. (2-3), the open circuit voltage \( (I = 0) \) can be obtained as

\[ V_{OC} = \frac{(nkT/q)}{ln(I_{SC}/I_s + 1)} \approx \frac{(nkT/q)}{ln(I_{SC}/I_s)} \]  \hspace{1cm} (2-5)

The approximation is based on the fact that \( I_{SC}/I_s \gg 1 \), which can usually be satisfied. \( V_{OC} \) increases logarithmically with \( I_{SC} \) for a junction with a reverse saturation current \( I_s \). This means that increasing generation current helps to increase the output voltage. For a given generated current \( I_{SC} \), \( V_{OC} \) increases logarithmically with decreasing \( I_s \), and it also depends on the ideality factor \( n \). The output power is given by:

\[ P = IV = I_s V (e^{\frac{qV}{nkT}} - 1) - I_{SC}V \]  \hspace{1cm} (2-6)

The maximum output power can be obtained from Eq. (2-6) under the condition of \( dP/dV=0 \). The output voltage \( V_m \) and current \( I_m \) for maximum output power are:

\[ V_m = \frac{(nkT/q)}{ln[(I_{SC}/I_s + 1)/(1+qV_m/nkT)]} \approx \frac{V_{OC}}{nkT/q} \ln(1+qV_m/nkT) \]  \hspace{1cm} (2-7)
\[ I_m = (I_s q V_m / n k T) e^{q V_m / n k T} \approx I_{SC} \left[ 1 - (n k T / q V_m) \right] \]  \hspace{1cm} (2-8)

Then the maximum output power \( P_m \) is:

\[ P_m = I_m V_m \approx I_{SC} \left[ V_{oc} - (n k T / q) \ln(1+q V_m / n k T) - (n k T / q) \right] = I_{SC} (E_m / q) \]  \hspace{1cm} (2-9)

where

\[ E_m = q \left[ V_{oc} - (n k T / q) \ln(1+q V_m / n k T) - (n k T / q) \right] \]  \hspace{1cm} (2-10)

The energy \( E_m \) corresponds to the electrical energy produced from one e-h pair generated by the incident alpha particle. The conversion efficiency \( \eta \) is:

\[ \eta = P_m / P_a = I_{SC} (E_m / q) / P_a = I_{SC} \left\{ V_{oc} - (n k T / q) \ln[1+(q V_m / n k T)] - (n k T / q) \right\} / P_a \]  \hspace{1cm} (2-11)

The fill factor \( FF \) is:

\[ FF = I_m V_m / I_{SC} V_{oc} = 1 - (n k T / q V_{oc}) \ln[1+(q V_m / n k T)] - (n k T / q V_{oc}) \]  \hspace{1cm} (2-12)

From Eq. (2-10), one can see that electrical energy \( E_m \) contributed by an e-h pair is mainly determined by open circuit voltage \( V_{oc} \) since \( k T / q < V_{oc} \) and the second and the third terms have much smaller values than \( V_{oc} \). \( V_{oc} \) is directly related to the reverse saturation current \( J_s \), which depends on the semiconductor properties (e.g., \( \tau, D \) etc.), and the ideality factor \( n \). To obtain higher \( E_m \), the p-n junction device should have as low a \( J_s \) as possible. To satisfy these requirements, GaP has significant advantages over Si because its band gap is twice that of Si. Theoretical \( J_s \) for a GaP p-n junction will be much lower than that of a corresponding Si junction, based on equation (2-4).

The conversion efficiency depends not only on \( E_m \), but also on \( I_{SC} \), as can be seen from equation (2-11). \( I_{SC} \) is determined by how many e-h pairs can be collected by the p-n junction. The dependence of \( I_{SC} \) on the e-h pair generation rate and the device properties is discussed in chapter 3.
Chapter 3  Simulation of alpha particle irradiation of 
GaP and Design of GaP ARVCs

3.1 Simulation of alpha particle irradiation of GaP

In order to design GaP ARVCs, it is very important to know the distribution of alpha irradiation effects in GaP. As discussed in the previous chapter, there are three major effects of alpha particle irradiation in a semiconductor material (i.e., ionizing, heating and vacancy creation effects). The distributions of these effects in GaP material are studied using Monte Carlo simulations.

The Monte Carlo program TRIM [3-1] is a very powerful program for simulating irradiation effects of ions in different materials. This program allows a wide range of choices of particle ion types, energies and target materials. It can give a lively visual image of an ion particle penetrating into a target material. Alpha irradiation of GaP with and without a thin gold contact coating were simulated for comparison.

The alpha particle source is $^{241}$Am, which emits alpha particle with energy of 5.5MeV. Since there is a thin Ti layer to seal the source, actual emitted alpha particle energy is about 4.6 MeV. According to this fact, 4.6MeV alpha particles were used for the simulation. Typically, 3000 alpha particles were used to describe a point source for each simulation process.
Figs. 5 show the TRIM simulation results of alpha particle tracks in GaP with 0.1μm Au contact layer. The side view tracks are shown in Figs. 5 (a) to (c), and the top view in Figs.5(d). From the side view of the tracks, we can see that alpha particles travel in almost straight paths near the surface. The lateral dimensions of the tracks increase as alpha particles penetrate into the GaP. The largest lateral straggling dimension is about 1μm, which occurs near the end of the alpha particle range. The maximum range of alpha particle in GaP is 17 μm.
The ionization energy loss track is shown in Fig. 6. Near the surface, there is a thin region which has a higher energy loss rate than in the rest of the material. This high energy loss rate corresponds to energy losses in the Au layer since Au has a much higher density than GaP. The ionization energy loss rate increases as the alpha particles penetrate through the GaP, and reaches a maximum rate of about 38 eV/Angstrom/Ion at a depth of about 14μm. This increase in the energy loss rate is understandable since the scattering probability increases with the penetration depth as seen from the alpha path tracks shown in Figs.5. The ionization energy loss rate then decreases dramatically until finally all the alpha particles are stopped at a depth of about 17 μm.

![Graph showing energy loss vs. penetration depth]

Figure 6. Distribution of alpha particle energy losses through ionization in the GaP with a 0.1Au contact layer.

The ionization energy loss of alpha particles shown in Fig.6 corresponds to the generation of e-h pairs in the GaP. To generate one e-h pair, the average energy cost can be estimated using the empirical relationship of Klein [3-2],
\[ E_c = \left( \frac{14}{5} \right) E_g + K_i \quad (3-1) \]

where \( E_g \) is the band gap of the semiconductor and \( K_i \) is \( \sim 0.75 \text{eV} \). For GaP, the average energy required to generate an e-h pair is about 7 eV according to Eq.(3-1) and using the band gap of GaP. The ionization energy loss rate shown in Fig. 6 can be converted to e-h pair generation function in GaP as shown in Fig. 7. The distribution shape is identical to that in Fig. 6, but the values and the units are different.

![Graph showing the distribution of alpha generated e-h pairs in GaP with a 0.1 \mu m Au contact layer.](image)

Figure 7 Alpha particle generated e-h pair distribution in GaP with a 0.1 \mu m Au contact layer.

The distribution of the vacancies produced by alpha particles in GaP is shown in Fig. 8. Surprisingly, most of the vacancies are created near the end of the trip of alpha particles, within a 2 \mu m region before alpha particles stop. The reason for this behavior is probably that inelastic scattering events of alpha particle with GaP atoms are much higher for alpha particles with low momentum than those with high momentum. The
distribution of the stopped alpha particles has very similar shape and position to the peak of the vacancy distribution, which is clear by comparing Fig.9 with Fig.8.

According to the TRIM calculation results, each alpha particle losses 99.67% of its energy to GaP atoms, 0.1% to create vacancies and 0.23% to create phonons (or produce heat). This means that 99.67% of alpha energy can be used to produce e-h pairs. For GaP, each alpha particle having an energy of 4.6 MeV is able to produce 655,000 e-h pairs. Only 0.1% of the alpha particle energy is used in vacancy production, corresponding to each alpha particle creating about 300 vacancies in GaP. However, the damaging effect can still be significant since most of the vacancies are located in a very narrow band of only about 2 μm, and the vacancies will accumulate over the exposure time. The vacancy density can reach very high concentration in this major damage range after certain period of exposure time. The thermal effect due to alpha irradiation is not

![Vacancy distribution graph](image)

**Figure 8** Distribution of vacancies created by alpha particles in GaP.
sufficiently significant to be considered since the power density of alpha particle source is usually very low and only 0.23% of alpha particle energy is transferred to heat.

The distribution of ionization energy loss of alpha particles of GaP without a Au contact layer is shown in Fig. 10. One can see that this distribution is very similar to that of GaP coated with 0.1 μm Au. The peak position is only shifted by ~0.2 μm, and so is the stopping depth. This means that the thin layer metal contact has a very minor influence on e-h pair generation in the GaP material. Actually, the energy loss in 0.1 μm Au layer is only about 1% of the total energy loss of alpha particles. The distribution of the vacancies created by alpha particles in GaP without metal coating is shown in Fig. 11, which is also very similar to that with 0.1 μm Au layer.
Figure 10. The distribution of ionization energy losses of alpha particles in GaP without a metal contact.

Figure 11. The distribution of vacancies created by alpha particles in GaP without a metal coating.
3.2 Alpha irradiation generated current in GaP p-n junction devices

As discussed in chapter 2, the radiation generated current $I_{SC}$ is the most important parameter for ARVCs. Once $I_{SC}$ is obtained, the other parameters, i.e. $V_{oc}$, FF and $\eta$, can be derived from the equations (2-3), (2-9) and (2-10) as long as the reverse saturation of the p-n junction $I_S$ is known. $I_S$ is a basic parameter of a p-n junction device, which can be measured from the dark I-V characteristics of the device.

$I_{SC}$ is determined by e-h pair generation rate and semiconductor material properties, such as $\tau$, $D$ etc. The e-h pair generation rate profile of alpha particles as shown in Fig. 7 is very different from that for solar photons in solar cells. The latter can be approximated by an exponential decay curve (with depth), while the former is a slowly increasing curve. For simplicity in deriving how $I_{SC}$ depends on the generation rate and device properties, we assume the generation rate for a unit area and depth is a constant $G$, which does not change with the depth in the semiconductor (in the e-h pair generation region).

A p-n junction device diagram along alpha particle penetration direction is illustrated in Fig. 12. The p-n junction is located at a position of $X_j$ with a depletion

![Diagram of p-n junction](image)

Fig. 12 An illustrative diagram of p-n junction ARVC.
width of \( W \). The positions of \( X_p \) and \( X_n \) are the end of the p-region and the start of the n-region, respectively. Under low injection condition, the one dimensional steady-state continuity equations are:

\[
G_n - (n_p - n_{po})/\tau_n + (1/q)dJ_n/dx = 0
\]

for electrons in p-type semiconductors and

\[
G_p - (p_n - p_{no})/\tau_p - (1/q)dJ_p/dx = 0
\]

for holes in the n-type semiconductors, where \( G_n \) and \( G_p \) are the electron and hole generation rate, respectively, \( G_n = G_p = G \) according to constant generation rate assumption; \( n_p \) and \( p_n \) the minority carrier densities of electrons in p-type and holes in n-type semiconductors, respectively, and \( n_{po} \) and \( p_{no} \) corresponding the equilibrium conditions without alpha excitation. The current density equations are

\[
J_n = q\mu_n n_p E + qD_n d^n_p/dx
\]

\[
J_p = q\mu_p p_n E - qD_p d^p_n/dx
\]

where \( E \) is the electric field intensity and \( \mu_n \) and \( \mu_p \) are electron and hole mobility, respectively. For an abrupt p-n junction with constant doping concentration on each side of the junction, the electric field outside the depletion region can be neglected, so the first terms in Eqs. (3-4) and (3-5) are negligible.

In the case of a p- on n-type junction as shown in Fig. 12 with a p-type front, Eqs. (3-3) and (3-1) can be combined to yield an expression for the top side of the junction:

\[
G - (n_p - n_{po})/\tau_n + D_n d^2 n_p/dx^2 = 0
\]

Since \( G \) and \( n_{po} \) do not change with distance \( x \), we introduce the variable \( Y \),

\[
Y = n_p - n_{po} - G \tau_n
\]
Substituting Eq. (3-7) into Eq. (3-6), we get:

$$D_n \frac{d^2 Y}{dx^2} - \frac{Y}{\tau_n} = 0 \quad \text{(3-8)}$$

The general solution of Eq. (3-8) is:

$$Y = A_0 \text{Cosh} \left( \frac{x}{L_n} \right) + B_0 \text{Sinh} \left( \frac{x}{L_n} \right) \quad \text{(3-9)}$$

where $L_n$ is the minority carrier electron diffusion length in the p-type region, which equals $(D_n \tau_n)^{1/2}$; $A_0$ and $B_0$ are constants determined by boundary conditions. Using Eq. (3-7) again, we get:

$$n_p - n_{po} = A_0 \text{Cosh} \left( \frac{x}{L_n} \right) + B_0 \text{Sinh} \left( \frac{x}{L_n} \right) + G\tau_n \quad \text{(3-10)}$$

At the surface, the surface recombination velocity is $S_n$. The excess carriers recombine with a velocity of $S_n$, so:

$$D_0 \frac{d(n_p - n_{po})}{dx} = -S_n (n_p - n_{po}) \quad \text{at } x = 0 \quad \text{(3-11)}$$

At the depletion edge, the excess carrier density is small due to the strong electric field in the depletion region, so

$$n_p - n_{po} \approx 0 \quad \text{at } x = X_j. \quad \text{(3-12)}$$

Using the boundary conditions (3-11) and (3-12) in Eq. (3-10), $A_0$ and $B_0$ can be obtained from the following two equations,

$$D_n B_0 / L_n = -S_n (A_0 + G\tau_n) \quad \text{(3-13)}$$

$$A_0 \text{Cosh} \left( \frac{X_j}{L_n} \right) + B_0 \text{Sinh} \left( \frac{X_j}{L_n} \right) + G\tau_n = 0 \quad \text{(3-14)}$$

Solving Eqs. (3-13) and (3-14), we get:

$$A_0 = - \frac{G\tau_n \left[ 1 - (L_n S_n / D_n) \text{Sinh} (X_j / L_n) \right]}{\text{Cosh} (X_j / L_n) - (L_n S_n / D_n) \text{Sinh} (X_j / L_n)} \quad \text{(3-15)}$$

$$B_0 = \frac{G\tau_n}{D_n} \frac{L_n S_n}{1 - \text{Cosh} (X_j / L_n)} \quad \text{(3-16)}$$
The radiation induced current density at the depletion edge is

\[ J_n = qD_\alpha \frac{dn_p}{dx}X_j \]  

(3-17)

By combining Eqs. (3-10), (3-15), (3-16) and (3-17), the final expression of this current density can be obtained as

\[ J_n = -qGL_n + qGL_n \frac{(1 + L_n S_n / D_n) \exp(-X_j / L_n) - (L_n S_n / D_n)}{\cosh (X_j / L_n) - (L_n S_n / D_n) \sinh (X_j / L_n)} \]  

(3-18)

For the case \( X_j >> L_n \), (this condition is satisfied by GaP since its minority diffusion lengths are much shorter than the alpha particle projection depth), the second term in Eq. (3-18) can be neglected, resulting in

\[ J_n = -qGL_n \]  

(3-19)

Using the same procedures, the current density at the n-type side depletion edge can be derived as

\[ J_p = -qGL_p \]  

(3-20)

The simple expressions of (3-19) and (3-20) illustrate an important physical principle of the ARVCs, which is that the alpha radiation generated current mainly arises from the region within a minority carrier diffusion length. The negative sign represents the fact that current direction is against the x axis in Fig. 12.

In the depletion region, the electric field is generally very high, so the generated carriers can be swept out of the depletion region before they recombine. The generated current density in the depletion region is

\[ J_{dr} = -qGW \]  

(3-21)

The total generated current density is the sum of the above three parts, \( J_n \), \( J_p \) and \( J_{dr} \), which is approximately:
\[ J_{SC} = -qG(L_n + L_p + W). \]

(3-22)

The depletion width \( W \) is usually very small, typically only about 0.1 \( \mu m \). Therefore, the alpha particle generated current is directly controlled by the minority diffusion lengths of electrons and holes \((L_n, L_p)\). The longer diffusion lengths result in a larger current collection range.

### 3.3 Design of GaP ARVCs

GaP is a good candidate material for ARVCs because of the reasons mentioned in Chapter 1. However, there is a serious problem with using GaP material to achieve good conversion efficiency for ARVCs. This problem is associated with the relatively short minority carrier diffusion lengths of electrons and holes in p- and n-type GaP compared with the alpha particle generation range of e-h pairs. According to the simulation results shown in Fig.7, the alpha particle generation range of e-h pairs in GaP is around 17 \( \mu m \). However, the minority diffusion lengths of electrons and holes of GaP are only about 1 to 2 \( \mu m \)[3-2] for normal doping concentrations \((\sim 10^{17} \text{ cm}^{-3})\). This indicates that only a small portion of the generation range can be used to collect e-h pairs to produce current according to Eq.(3-22). How to increase the current collection is very critical to improve the efficiency of GaP ARVCs.

Since the minority carrier diffusion length is a basic property of a semiconductor, it does not have too much room for improvement. The objective of increasing the current collection efficiency is to increase current collection volume. Instead of improving the material properties, an alternative way to improve collection efficiency is to change the device structure.
In order to increase the e-h pair collection volume, one might first consider using a multi-junction structure as shown in Fig 13. Principally, this structure can cover the whole generation range as long as each layer is close to one corresponding minority diffusion length and the total active region thickness is about the same with the generation depth. However, there are many technical difficulties which will limit the improvements of practical ARVC device performances. One problem is current mismatch, which is very difficult to control when the number of p-n junctions exceeds three. The current mismatch directly causes current loss because the p-n junctions are in series connection. Moreover, there is a reverse n-p junction at the connection of two adjacent p-n junctions. In order to decrease current loss due to the reverse junction, a very thin highly doped tunneling layer should be introduced at each reverse junction site. This is also very difficult to realize technically, especially using LPE. Due to the above difficulties, it is very easy to lose more efficiency than to gain. As a matter of fact, it is hard to find a tandem solar cell with three or more junctions that exhibits significant increase of conversion efficiency over a single junction cell, despite having a much higher theoretical efficiency.

Figure 13. Cross-sectional diagram for a multi p-n junction device.
Instead of using flat p-n junctions, we developed a new p-n junction structure with a textured junction interface as illustrated in Fig.14. With this kind of structure, the current collection should follow the textured p-n junction interface. If this textured p-n junction is put in the alpha generation region, the current collection area can be increased significantly by adjusting the geometric dimensions of the textured structure profiles. This increase of the collection area will result in a significant increase of current collection volume if the minority carrier diffusion lengths are not affected by the textured p-n junction interface.

![Textured p-n junction interface](image)

**Figure 14.** An illustrative diagram of textured p-n junction structure device.

We designed a pyramidal textured p-n junction (PTJ) interface structure as shown in Fig.15. The p-n junction interface is composed of periodically arranged pyramidal surfaces. Assume that each pyramid has square top and bottom facets with dimensions of $a_1$ and $a_2$, respectively, and the height of each pyramid is $h$; the pyramids are arranged in both $x$ and $y$ directions with the same period of $W_p$.
Fig. 15  Diagrams of periodically arranged pyramids.  (a) three dimensional diagram of pyramids, (b) top view diagram of periodic arrangements of pyramids.

The surface area of each pyramid is:

\[ A_p = a_1^2 + 2 \left( a_1 + a_2 \right) \left[ h^2 + \frac{(a_2-a_1)^2}{4} \right]^{1/2} \]  \hspace{1cm} (3-23)

For each period, the total surface area is:

\[ A_T = a_1^2 + 2 \left( a_1 + a_2 \right) \left[ h^2 + \frac{(a_2-a_1)^2}{4} \right]^{1/2} + W_p^2 - a_2^2 \]  \hspace{1cm} (3-24)

Without pyramid, the flat surface area for one period is \( W_p^2 \). The area ratio between pyramidal surface and flat surface is:
According to Eq. (3-25), the ratio $R$ of areas with and without pyramids increases with the height $h$, and decreases with the period length $W_p$. The dependence of $R$ with $a_1$ and $a_2$ is somewhat complicated. Table 3-1 gives out some calculated results of $R$ under different values of parameters $h$, $a_1$, $a_2$ and $W_p$.

**Table 3-1. Calculated $R$ under different $a_1$, $a_2$, $h$ and $W_p$.**

<table>
<thead>
<tr>
<th>$a_1$ (μm)</th>
<th>$h$ (μm)</th>
<th>$a_2$ (μm)</th>
<th>$W_p$ (μm)</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6</td>
<td>10</td>
<td>18</td>
<td>1.32</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>10</td>
<td>15</td>
<td>1.46</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>10</td>
<td>18</td>
<td>1.40</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>10</td>
<td>15</td>
<td>1.57</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>10</td>
<td>18</td>
<td>1.48</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>10</td>
<td>15</td>
<td>1.69</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>8</td>
<td>12</td>
<td>2.04</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>6</td>
<td>10</td>
<td>2.40</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>4</td>
<td>6</td>
<td>3.35</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

If PTJ interface is within the electron-hole pair generation region, the generation current is total area times the current generation density given out in Eq. (3-22). Since the diffusion lengths and the depletion width is small, the current ratio between a pyramidal and flat junction is approximately given by $R$. According to the TRIM
simulation results, the total penetration depth of alpha particles in GaP with a 0.1 μm gold coating is about 17μm. For an ideal case, suppose $a_1 = a_2 = 2 \mu m$, $W_p = 4 \mu m$, and the height $h = 15 \mu m$; the diffusion lengths for both electrons and holes are 1μm; the current collection region can effectively cover the whole volume of the 17 μm generation depth, as indicated in Fig. 16. This means the new textured p-n junction structure can totally overcome the basic material property limitations, and realize a 100% collection of alpha particle generated current. We believe this structure is also very useful for solar cells whose minority carrier diffusion lengths are shorter than the photon absorption depth, such as polycrystalline Si solar cells whose minority carrier diffusion lengths are much shorter than the photon absorption depth.

The general pyramidal surface profile as shown in Figs. 15 can be realized using photolithography masking followed by wet chemical etching. We demonstrated this work in this project, as discussed in chapter 4. The PTJ structure can be realized using LPE
growth on a pyramidal textured surface. This was realized for the first time in our work. Detailed discussions about LPE growth of PTJ structure is also presented in Chapter 4.

Wet chemical etching is not feasible for realizing the surface pattern shown in Fig. 16 due to the problem of undercutting. However, this pattern is achievable using plasma dry etching, which is a technique widely used in semiconductor IC industry for achieving etching profiles without undercutting effects.

Chapter 4 Fabrication of GaP ARVCs

4.1 Polishing of GaP substrates

The substrates that we used for GaP ARVC fabrication were commercial sulfur(S) doped n-type GaP (111) with a doping concentration of $\sim 5 \times 10^{17}$ cm$^{-3}$ from Sumitomo Metal Mining Co. The substrate thickness is 0.3 mm. The reason we chose the (111) orientation of GaP substrates is discussed in section 4.2. The GaP substrates needed to be polished to remove the wafer cutting undulations and surface roughness. Basically, there are two kinds of methods to polish the GaP substrates. One is mechanical polishing, and the other is chemical polishing. We tried both kinds of polishing techniques to prepare the desired GaP substrates.

For mechanical polishing, the GaP wafer was scribed into pieces, $1 \times 1$ cm size. Each time, one piece of substrate was mounted on a polishing holder using wax. The polishing process was carried out on a Buehler polishing machine, which is consisted of a spinning plate with a polishing cloth glued to it. Fine Al$_2$O$_3$ powder was used as the
polishing abrasive, which was mixed with water. The Al₂O₃ powder and water mixture continued to flow on the polishing cloth during polishing. By keeping the GaP surface in touch with the wet polishing cloth with Al₂O₃ powder on it, the homogeneously distributed fine Al₂O₃ powder gradually polished away the roughness on the GaP surface. Running water plays an important role for cooling the substrate and diluting the powder.

Two steps of polishing was used to achieve better polished surfaces. The substrate was first polished using 0.3 μm Al₂O₃ powder until a shiny mirror like surface without scratches was achieved. This process usually took 2-3 hours for a 1 × 1 cm size GaP substrate. For bigger substrates, it took a longer time to achieve satisfactory results, and small amount of uneven mounting may cause non-uniform polishing. During polishing, the substrate should be rotated frequently to realize uniform polishing. Care must be exercised on how much pressure is applied to substrate holder. Too much pressure may cause deep scratches which need a long time to remove. After finishing the first step polishing, the polishing cloth was changed and a finer Al₂O₃ powder with size of 0.05 μm was used to achieve better surfaces. The second step usually took 0.5-1 hour.

After polishing, the substrate was removed from the holder by melting the wax onto a hot plate. The wax was then dissolved away in toluene or trichlorethylene, and the substrate was cleaned subsequently using acetone and methanol in an ultrasonic cleaner.

Beside mechanical polishing, we also used chemical polishing, especially for large wafers, such as the ones used for photolithographic masking. The chemical solution was a 5% Br₂ solution diluted in glycol. The polishing was performed by holding the wafer and rubbing it on a paper cloth that was put on a flat glass plate and wetted by the
Br₂ polishing solution. This chemical polishing process took a relatively short time compared with mechanical polishing. However Br₂ is a very toxic chemical, so we only used this chemical polishing process for big wafers which were too difficult to be polished using mechanical polishing.

4.2 Preparation of pyramidal textured surfaces on GaP (111) B substrates

4.2.1 Photolithography masking

To realize PTJ structures for increasing the current collection efficiency of GaP ARVCs as designed in chapter 3, the GaP substrates for LPE growth should have pyramidal textured surfaces. Photolithographic masking followed by wet chemical etching is a convenient process to realize the pyramidal textured surface structures as illustrated in Fig.15.

GaP (111) has two different faces usually termed A and B, which correspond to that Ga and P atoms on the top surface, respectively. It is well known that these two different surfaces have different chemical and physical properties [4-1]. Before photo masking, we should decide which surface should be used, and detect which side of the wafer is A or B.

According to Gatos and Lavine[4-1], the A (Ga) surface has unoccupied dangling bonds at the surface, while B (P) surface is fully occupied by sp³ electrons which can easily participate in chemical reactions. Therefore, it is generally considered that the (111)B surface is more chemically active than the (111) A surface [4-1, 4-2]. There are different chemical solutions that can be used to identify A and B surfaces of GaP(111)
wafers [4-3, 4-4]. We used a hot aqua regia solution: HNO₃:HCl = 1 : 3. A small piece of GaP diced from GaP(111) wafer was etched in aqua regia solution at different temperatures. Figs.17 show the surface morphologies after etching for both surfaces. One side was always polished after etching, as shown in Figs. 17 (a). This side corresponds to the GaP (111)B surface according to the literature [4-5]. On the other surface, (111)A surface, there were different etch pit patterns at different temperatures. At 40°C, small etch pit holes and scratch lines appeared on the surface, as shown in Figs.17 (b). A much rougher surface pattern was developed after etching at 65 °C, as shown in Figs.17 (c).

Because of the roughness developed after etching, the (111)A surface was not selected for patterning. Therefore, the GaP (111)B surface was used for photo masking. In fact, we patterned both sides of two small pieces of the GaP (111) wafers in an early experiment. After etching (the etching process is described in section 4.2.2), good surface profiles were achieved only on the (111)B GaP surface, which is as expected as the above discussions.

For photolithography masking, a Shipley 1400-26 photoresist was first spun on to the GaP surface and then baked at 90°C for 1 hour. It was then exposed to UV light (i.e., wavelength of 365nm) through a patterning mask. The exposed patterns were developed subsequently using a NaOH based Shipley developer. The photo resist was baked again at 120°C to improve adhesion.

The photolithography patterns are shown in Fig.18. Square shape thin layer photoresists were periodically arranged along [ 0 -1 1 ] and [ -2 1 1 ] directions. The
square size is 15μm and spacing between adjacent squares is 3μm. Therefore, each period is 18μm.

Figure 17. Surface morphologies of GaP (111) surfaces after etching in aqua regia solution. (a) corresponds to (111)B surface, (b) and (c) correspond to(111)A surface after etching at 40°C and 65°C, respectively.
4.2.2 Wet chemical etching of GaP

In order to achieve a good surface profile, it is important to find a good etching solution. This solution should result in smooth etching facets, easily controllable etching speed and no damage to the photo resist. There are a few chemical solutions that are frequently used for etching GaP, such as aqua regia (3 HCl : 1 HNO₃), Chlorine-Methanol and Bromine-Methanol, and H₃PO₄ [4-6, 7, 8, 9, 10,11, 12]. However, these etching solutions either have problems associated with too fast etching or they damage the photo resist coating itself.

In our experiments, we selected an etching solution: HCl:CH₃COOH:H₂O₂, which was developed for selective etching of GaAs, GaInP, and InP by adjusting the ratios of
the three components[4-13,14]. For our experiments, we chose the solution ratio of HCl:CH₃COOH:H₂O₂ = 1:1:1, because this composition was expected to result in a medium etching speed for GaP with smooth etching surfaces [4-14].

For optimizing the etching conditions, we did a series of etching experiments for different etching time. The etching samples were scribed from the photo resist patterned wafer. Each sample has a size of about 2-3 mm. Since the etching solution is self reacting and exothermic, each sample was put into a similar amount (~15ml) of solution using the same size glass cups to avoid temperature differences for better comparison. Every sample was put into the solution right after the solution was prepared to avoid solution aging which affects the etching speed and results in poor reproducibility for different etching times. To prepare solution mixture, CH₃COOH should be mixed with HCl (or H₂O₂) first, and then the third component H₂O₂ (or HCl) can be added. HCl and H₂O₂ should not be mixed first because they react very fast, resulting in dissociation of critical etching chemicals.

The etched surface profiles were studied using field emission scanning electron microscopy (FE-SEM). Figs.19 show the SEM surface profiles after different etching times of 2, 5, 7 and 10 minutes in 15 ml HCl:CH₃COOH:H₂O₂ = 1:1:1 solutions. After 2 minutes etching, the patterned top surface remained approximately the square shape, while its size reduced to 10 μm, corresponding to 2.5 μm undercutting from the mask edges. The depth of etching is 4.6 μm. From Figs.19(a), we can see that the two corners of the top surface were obviously curved. After etching for 5 minutes, the two corners were cut more deeply. The top un-etched surface shape was no longer square as shown in Figs.19 (b). One side, which is believed to be the [0 -1 1] direction still remained
Figure 19. Surface morphologies after etching on photo resist mask patterned GaP (111)B surfaces in HCl:CH₃COOH:H₂O₂ = 1:1:1 solution for various etching time, (a) 2 minutes, (b) 5 minutes, (c) 7 minutes and (d) 10 minutes.
straight line, while the other three sides were curved. The slopes of the side walls became smaller than those after 2 minutes etching, and the etching depth in [111] direction increased to 6 \( \mu \text{m} \).

Further increasing the etching time to 7 minutes, the top surface of the patterned area became triangular as shown in Figs.19 (c). This is more clear from the top view image shown in Fig.20. One can see each angle of the top triangle is about 60\(^\circ\). The three sides of the triangle were believed to correspond the directions of \([ 0 \ 0 \ 1 ]\), \([ -1 \ 1 \ 0 ]\) and \([ 1 \ 0 \ -1 ]\) since these three directions can form equilateral triangle, and the \([ 0 \ -1 \ 1 ]\) direction side was always kept as straight line during the development of etching. From Figs.19 (c), we can see that three facets were revealed at the top of the pyramids, while the bottom region still had slightly curved surfaces. The three revealed facets were identified to be \((1 \ 0 \ 0 )\), \((0 \ 1 \ 0 )\) and \((0 \ 0 \ 1 )\) facets according to their angles with the \((1 \ 1 \ 1)\)B surface. The etching depth was increased to only \(6.5 \mu \text{m}\) after 7 minutes of etching, indicating a reduction in the etching rate after 5 minutes.

![Figure 20. Top view image of surface profile after etching for 7 minutes on a patterned GaP (111)B surface.](image)
After etching for 10 minutes, the top un-etched surface had almost disappeared, as shown in Figs 19(d). Typically, pyramids were formed with three revealed (1 0 0), (0 1 0) and (0 0 1) facets. Because (1 0 0), (0 1 0) and (0 0 1) planes are identical for GaP crystals, we use the (1 0 0) to represent all the three planes for simplicity.

It is obvious that the etching process is anisotropic for GaP crystal according to the evolution of the surface profiles shown in Figs.19. This is not surprising since different crystal directions in GaP crystals have different chemical and physical properties. The appearance of (1 0 0) facets was also observed for etching of GaAs (1 1 1) patterned surface[4-15]. However, a satisfactory explanation for the evolution of the (1 0 0) facet was not presented. Qualitatively, we attribute the evolution of the (1 0 0) facets to differences in the etching rate for different crystal planes.

Since the lattice distance for (1 0 0) direction is the largest, the chemical bonding should be the weakest. Therefore, we expect that the etching rate for (1 0 0) planes should be the fastest among different crystal planes. Considering the undercutting of each patterned top surface, we suppose that the etching proceeds down through different planes. The etching speeds are different for different planes according to their lattice distances. Fig.21 shows a qualitatively illustrative diagram of the undercutting etch progress.

During the early etching stages, the fast etching planes, i.e. (1 0 0) planes were not available. The undercutting beneath the photoresist mask was mainly determined by side wall planes, namely (0 -1 1) and (-2 1 1) and their reverse direction planes. Therefore, the
Figure 21  Illustrative diagram of etch undercutting beneath photo resist. The arrows indicate the undercutting progress along (1 0 0) planes.

Patterned areas remained approximately square shape after 2 minutes of etching as shown in Figs. 19(a). However, the lower region of the side wall with intersection line of [0 -1 1] might encountered etching through (1 0 0) plane since this plane can be exposed as the un-patterned region was etched down. This can explain the downward curves on the side walls along the [0 -1 1] direction, as can be seen from Figs. 19(a). At the two corners along [0 1 -1] side, the (1 0 0) planes can cut right through the two corners intersecting (1 1 1) plane, as indicated in Fig. 21. Because the corners have very small area (or volume), the (1 0 0) planes can easily be revealed due to their faster etching speed than other planes. Because of these early revealed small (1 0 0) planes and their fast etching speed, these two corners encountered faster undercutting, as evident from Figs. 19(a) and (b).
As the etching continues, etching through the (1 0 0) plane included a great contribution from the side wall along the [0-1 1] side, as increasingly large areas of the (1 0 0) plane were revealed. The small region of the (-2 1 1) plane was gradually cut away. This is supported by the fact that this side wall plane clearly became flatter after 5 minutes of etching as shown in Figs.19(b). The two corners that have intersections with (1 0 0) planes were cut more and more at evidently faster speeds than that of the undercutting along their adjacent side walls. Thus the square shape surface under photoresist no longer existed after 5 minutes etching as shown in Figs.19 (b). The curved shape for the two corners might be due to the mixed contributions of etching through (1 0 0) planes and their adjacent side wall planes.

Further increasing the etching time, etching of the [ 0 -1 1] side wall was dominant for the (1 0 0) plane. Etching through (1 0 0) planes also dominated the etching of the two curved corners. These (1 0 0 ) planes gradually cut away the adjacent side walls and met the other ( 1 0 0) plane. Therefore, an equilateral triangle formed on the top surface, as shown in Figs. 19(c). The triangle was then cut smaller and smaller, until the triangle finally disappeared, and sharp pyramidal peaks were left as shown in Figs. 19 (d).

The smaller slope near the bottom of the pyramids (compared with the top) may also be explained as due to the etching speed difference between (1 0 0 ) and (1 1 1 ) planes. As indicated in Fig.22, etching near the bottom region of the pyramids can not follow the movement of (1 0 0) planes because the downward etching through (1 1 1) plane is slower than that through the (1 0 0) planes. So the etching of the bottom region
of the pyramids had mixed contributions from (1 0 0) and (1 1 1) planes, resulting in slightly curved facets near the bottom of the pyramids.

![Illustrative diagram for etching through (1 0 0) and (1 1 1) planes.](image)

Fig. 22  Illustrative diagram for etching through (1 0 0) and (1 1 1) planes.

The dependence of etching depth in [111] direction of GaP in a freshly prepared 1HCl: 1CH₃COOH:1H₂O₂ solution with time is shown in Fig.23. The depth increased quickly with etching time at early etching period ( < 3 minutes), and then the etching rate gradually decreased. After 5 minutes, the etching depth was gradually saturated. This

![Graph showing etching depth vs etching time.](image)

Figure 23. The relation of etching depth in (111)B direction of GaP and etching time in 1HCl: 1CH₃COOH:1H₂O₂ solution.
etching depth dependence with time indicates that the etching depth of GaP in 1HCl: 1CH₃COOH:1H₂O₂ solution is self regulating for etching times longer than 5 minutes. This behavior is helpful for controlling the etching depth since one need not worry unduly about over etching.

The self controlled etching behavior of GaP in 1HCl: 1CH₃COOH:1H₂O₂ solution is believed to be due to the dissociation of the etching species in the solution. When the solution was fresh, it was slight yellow in color, and remained still for about 2 minutes. After 2 minutes, some bubbles appeared and the solution temperature increased. The bubbling and temperature rise became more pronounced up until 5 minutes. The temperature usually reached 80°C from room temperature. Afterwards, fewer and fewer bubbles evolved and the temperature decreased. After about 8 minutes, the solution was calm. The temperature decreased back to room temperature after about 20 minutes. The above effects obviously reflect the self reactions of the etching solution. In fact, we observed that the self reactions of the solution were not related to GaP etching.

The self reaction mechanism of HCl:CH₃COOH:H₂O₂ solution is important for understanding the etching process of GaP. It is known that acetic acid is a solvent in a HCl:CH₃COOH:H₂O₂ solution[4-13]. In the solution, Cl⁻ can be oxidized by H₂O₂ in possible reaction forms listed in Table 4-1 with different Gibb's free energy ΔG°[4-14, 16]. The reaction which releases Cl₂ gas is the most favored reaction because it has the lowest Gibb's free energy. This is supported by the fact that yellow color appeared when HCl and H₂O₂ are mixed together. Cl₂ is well known to be an effective etching agent for III-V compounds, including GaP.
Table 4-1  Standard Gibb’s free energy of reactions between H₂O₂ and Cl⁻.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>ΔG° ( KJ/ mol H₂O₂ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂+2HCl(<em>{(aq)}) = Cl₂(</em>{(g)}) +2H₂O</td>
<td>-80.4</td>
</tr>
<tr>
<td>H₂O₂+HCl(<em>{(aq)}) =HClO(</em>{(aq)}) + 2H₂O</td>
<td>-56.7</td>
</tr>
<tr>
<td>H₂O₂+HCl(<em>{(aq)}) =1/2HClO₂(</em>{(aq)}) + H₂O</td>
<td>-39.8</td>
</tr>
<tr>
<td>H₂O₂ + 1/3Cl⁻(<em>{(aq)}) =1/3 ClO₃⁻(</em>{(aq)}) +H₂O</td>
<td>-62.7</td>
</tr>
<tr>
<td>H₂O₂ + 1/4Cl⁻(<em>{(aq)}) =1/4 ClO₃⁻(</em>{(aq)}) +H₂O</td>
<td>-74.7</td>
</tr>
</tbody>
</table>

where \(_{(aq)}\) and \(_{(g)}\) denote aqueous and gaseous, respectively.

In a freshly prepared solution, there is enough dissolved Cl₂ in the solution from the reaction of HCl and H₂O₂ for very effectively etching of GaP, resulting in the fast etching rate at short etching times (see Fig.23). As the self reaction of the solution continues, a large amount of Cl₂ is produced. However, the solubility of Cl₂ in the solution is limited. Excess Cl₂ comes out of the solution. This was evident in our experiment that a lot of bubbles appeared in the solution. The temperature increases as the result of the reaction. The increased temperature might accelerate the bubbling out of the Cl₂. For the times close to 5 minutes, the dissolved Cl₂ may decrease since most of the Cl₂ was evolved and the production of Cl₂ can not compensate for the loss, since most of HCl and H₂O₂ was exhausted. It was evident in our experiment that the yellow color of the solution turned much lighter for times close to 5 minutes, and no color could be seen after 8-10 minutes. It was most probably due to the reduction in the concentration of Cl₂ in the solution, that the etching rate greatly decreased after 5 minutes. The etching was hardly effective after 10 minutes since almost all Cl₂ escaped out from the solution, and HCl and H₂O₂ were dissociated.
We did some experiments using aged solutions. Putting a sample into a solution prepared for 10 minutes, we observed only about 0.2 μm of etching of GaP after 10 more minutes etching. This further confirmed the dissociation of the solution.

4.3 LPE growth of GaP layers

4.3.1 GaP LPE growth mechanism

Epitaxy is defined as "the deposition of a single crystalline layer on a single crystal substrate in such a way that the crystalline structure continues into the layer". Liquid phase epitaxy (LPE) refers the growth of the epitaxial layers is from dilute solutions at elevated temperatures. The LPE technique was first demonstrated by Nelson in 1961[4-17]. Compared with other epitaxy techniques, such as molecular beam epitaxy (MBE) and MOCVD, LPE has the advantages of being relatively simple to establish and maintain, presenting small safety risk and offering fast growth rates and high quality crystal layers. The disadvantages of LPE come from the problems of layer thickness uniformity and difficulties in controlling the growth of very thin layers. For GaP ARVCs, thick epilayers are required. LPE is therefore preferred over MBE and MOCVD for this particular purpose.

LPE growth of GaP can be viewed by reference to the Ga-P binary phase equilibrium. The thermal equilibrium atomic fraction of P in a Ga-P solution with temperature is shown in Fig. 24. The solubility of GaP in Ga increases exponentially with the liquidus temperature. On cooling down a saturated GaP-Ga solution, the solution will become over saturated with GaP. This over saturated GaP can form nuclei
Figure 24. Thermal equilibrium fractions of P in Ga-P system at different liquidus temperatures. After Ilegems et al [4-18]

and precipitate. When there is a GaP substrate in touch with this solution, heterogeneous nucleation of GaP can occur and result in epitaxy. Since GaP layer growth on a GaP substrate is homoepitaxial growth, there is no problem of lattice mismatch.

Theoretical treatments of LPE growth process usually contains mainly three areas:

(a). Diffusion limited growth theory

(b). Theoretical solid-liquid phase diagram calculations

(c ). Impurity incorporation models.

In this section, the theory of diffusion limited growth is briefly introduced. Impurity incorporation is discussed in section 4.3.3.

Diffusion limited growth theory has been widely used to explain the LPE growth kinetics for a wide range of growth temperatures and different growth techniques, e.g., step cooling, ramp-cooling and supercooling [4-18, 19, 20, 21]. For isothermal
growth from solution, the one-dimensional diffusion equation for a binary compound, e. g., GaP, is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + v \frac{\partial C}{\partial x} \quad (4-1)$$

where $C$ is the solute concentration, $D$ the diffusion coefficient of rate determining species in solution and $v$ the growth velocity. Assuming the growth rate is low enough that the term $v \frac{\partial C}{\partial x}$ in Eq. (4-1) is negligible, which has proved to be a very good assumption for growth rates of $10^{-6}$-$10^{-5}$ cm/s by the early workers [4-22,23], the diffusion equation can be simplified to:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4-2)$$

The analysis of the growth process relies on solving Eq.(4-2) under relevant boundary conditions. The thickness of layer at time $t$ is given by:

$$d(t) = \left( \frac{1}{C_S} \right)_0 D \left( \frac{\partial C}{\partial x} \right) dt \quad (4-3)$$

There are three major techniques for LPE growth, i.e. ramp-cooled growth, step-cooled growth and super-cooled growth. For different growth techniques, the boundary conditions are different, resulting in different relationships between layer thickness and growth time. Several early workers solved the diffusion equation for the three growth techniques[4-21, 24, 25]. Here we simply introduce the results derived by Hsieh[4-24], who assumed that the solutions had a semi-infinite thickness.

For ramp-cooled growth, the solution is initially at thermal equilibrium condition with liquidus temperature $T_0$ and a uniform solute concentration $C_0$. Therefore,

$$C(x, t = 0) = C_0 \quad \text{for all } x. \quad (4-4)$$
The temperature is reduced at a constant rate $\alpha$, resulting in a temperature-time relation of:

$$ T(t) = T_0 - \alpha t. $$  \hspace{1cm} (4-5)

If small temperature cooling intervals ($<10^\circ$ C) are assumed, the liquidus composition can be considered to be a linear function of temperature with $dT_E/dC_E = m$, then:

$$ C(x=0, t) = C_0 - \alpha t/m. $$  \hspace{1cm} (4-6)

Hsieh [4-24] obtained the result of:

$$ d(t) = (4/3)(D /\pi)^{1/2} (\alpha/C_0 m) t^{3/2} $$  \hspace{1cm} (4-7)

The layer thickness increases with growth time with the relation of $d(t) \propto t^{3/2}$. This relationship provided an excellent fit to experimental results on ramp-cooled growth of GaAs layer[4-24].

For the step cooled growth, the solution initially has a uniform concentration $C_0$ and corresponding liquidus temperature of $T_0$. Before contacting the substrate, the solution was cooled down a temperature of $\Delta T_S$.

$$ C(x=0, t) = C_0 - \Delta T_S /m \quad \text{for all } t $$  \hspace{1cm} (4-8)

where $\Delta T_S$ is small enough that the liquidus concentration can be considered to have a linear dependence on temperature. Hsieh [4-24] derived the relation of

$$ d(t) = 2 \Delta T_S (D /\pi)^{1/2} (\alpha/C_3 m) t^{1/2}. $$  \hspace{1cm} (4-9)

The layer thickness has square root dependence on growth time. This relationship was in good agreement with Cook et al.'s experimental results for growth times of less than 30 minutes[4-26], while deviations occurred for $t > 30$ minutes, indicating that the assumption of a semi-infinite solution for long growth times is poor.
For super-cooled LPE growth, the solution is super-cooled by a temperature interval of $\Delta T_S$, similar to step cooled growth. However, the solution encountered a ramp cooling rate of $\alpha$, starting when the solution is placed in contact with the substrate. The concentration at the solution and substrate interface is:

$$C(x=0, t) = C_0 - \frac{\Delta T_S}{m} t - \frac{\alpha t}{m}. \quad (4-10)$$

After solving the diffusion equation using this condition, Hsieh[4-24] derived the layer thickness relation with growth time of:

$$d(t) = \left(\frac{1}{C_S m}\right) \left(\frac{D}{\pi}\right)^{1/2} \left(2 \Delta T_S t^{1/2} + 4R t^{3/2}/3\right). \quad (4-11)$$

Not surprisingly, the dependence of layer thickness with time for the super-cooled growth is a combination of that for 'step-cooled' and 'ramp-cooled' growths. Hsieh demonstrated his experimental results in comparison with theoretically calculated results for super-cooled growth of GaAs, as shown in Fig. 25. At short growth time $t$, the

Figure 25  Layer thickness against growth time for supercooled LPE growth of GaAs at 800°C (after Hsieh[4-24]).
results fall close to theoretical line for step-cooled growth, while for long growth time, the results are close to the ramp-cooled theoretical line. In between, Eq.(4-11) can well explain the growth rate behavior.

In our experiments, we mainly used supercooled LPE growth technique to grow GaP layers on both flat and textured substrates. The characterization of LPE growth of GaP layers are presented in chapter 5.

4.3.2 Doping in GaP LPE layers

Beside thickness control, doping control in the LPE layer is also very important to realize optimal device performance, and the latter is usually more difficult. The substrates for our experiments were commercial S-doped n-type GaP with doping concentration of $\sim 5 \times 10^{17}$ cm$^{-3}$. In order to obtain p-n junction structure for ARVCs, we needed to grow p-type epi-layers on the substrates.

For GaP, there are two frequently used p-type dopants, one is zinc (Zn) and the other is magnesium (Mg). Both dopants have low activation energy, less than 0.1 eV. However, Zn has much higher diffusion coefficient than Mg, and was not considered as a high diffusion coefficient is detrimental for forming abrupt p-n junctions. LPE growth of GaP layers needs relatively high temperature, normally 850°C to 1000°C, which is much higher than that for GaAs growth. This is because the solubility of GaP in Ga is much lower than that of GaAs. Therefore, Mg was chosen for p-type doping of the GaP LPE layers.

The concentration of an impurity element in an LPE layer is determined by the so-called segregation coefficient, $K_i$, which is defined as:
\[ K_i = \frac{\text{concentration of species in the solid}}{\text{concentration of species in the solution}} \]  \hspace{1cm} (4-12)

When the concentrations are expressed using atomic fractions, the segregation coefficient can be expressed as

\[ K_i^* = \frac{(N_d-N_a)}{2N} \cdot \frac{\text{MW_s}}{\rho_s X_i^L} \]  \hspace{1cm} (4-13)

where \((N_d-N_a)\) or \((Na-Nd)\) is the net donor or acceptor concentration in the LPE layer, \(N\) is the Avogadro’s number. \(\text{MW_s}\) is the molecular weight of the solid, \(\rho_s\) is the density of the solid and \(X_i^L\) is the atom fraction of the impurity in the growth solution. Different impurity species in different LPE layer materials have different segregation coefficients. \(K_i^*\) also depends on growth temperature and the orientations of the substrates[4-28].

The mechanism of impurity incorporation is a highly complex subject. There are two models which have been widely used to describe impurity incorporation in LPE layers. One is the equilibrium theory and the other is the surface-controlled incorporation [4-27]. The former explains the linear relationship of doping concentration with impurity concentration in the solution for low level doping, and transition from linear to square root relationship for high level doping, while the latter only provides a linear dependence of the doping concentration on impurity concentration in the solution. The experimental results of doping concentration of Mg in GaP LPE layers are presented in chapter 5.

4.3.3 LPE system and growth procedures for GaP layers

Several kinds of LPE systems have been used so far addressing different concerns on LPE growth. The major differences between different systems are in the boat designs,
since the boat is the most critical component of a LPE system. The boat controls how to put the solution into contact with the substrate, and how to remove the solution away. According to different boat designs, LPE systems mainly have four different types[4-27], i.e. tipping systems, dipping systems, horizontal sliding boat systems and rotary slider systems. Amongst them, the horizontal sliding boat system is the most popular since it has the advantages of convenience of operation, ability to achieve good solution removal after growth and suitability for multi-layer growth.

Our LPE system is a conventional horizontal sliding boat system. It is shown schematically in Fig.26. The system is composed of five major parts, which are: (a) a growth boat, (b) a vacuum system, including quartz tube, (c) a high temperature furnace, (d) a temperature control system and (e) a gas supply and flow control system.

Since the growth boat is the critical component of a LPE system, we discuss the boat design in detail. Our LPE boat contains three parts as shown in Figs.27, i.e. a base bar with substrate holding wells, a sliding bar with solution holding bins and a cover plate, which are all made of graphite. There are six solution bins on the sliding solution holding bar, which allow maximum of six different compositions of multi-layers to be grown in one run. The movement of the sliding solution holding bar on the graphite base is controlled from outside of the vacuum tube using a quartz rod, as indicated in Fig.26. The graphite cover is important to prevent evaporation of the group V element from the substrate and the solution. It is especially important for GaP growth since phosphorus is quite volatile.

The quartz vacuum tube is positioned in a high temperature furnace and connected to mechanical and turbo pumps. The vacuum pressure is usually pumped down to
Figure 26 A schematic diagram of the LPE system

(a) Top cover plate

(b) Sliding solution holding bar
Figure 27  Diagrams of different parts of the graphite sliding boat.
5\times10^{-5} \text{ torr} \text{ before flowing H}_2 \text{ gas through the system. The furnace is a three zone temperature controlled electrical resistance furnace. The temperature is controlled by an Omega 818 programmable temperature controller, which provides automatic temperature rise, dwell and cooling control. The growth temperature is detected by a thermocouple situated directly beneath the graphite boat.}

Ultra high purity H\(_2\) gas was used as an ambient gas to prevent oxidation of substrates and solution. Moreover, H\(_2\) is able to reduce metal oxides which may be present on the surface of the solutions\textsuperscript{[4-27]}. H\(_2\) gas inserted in the quartz tube is commercial ultra high purity H\(_2\) and further purified using a palladium diffused H\(_2\) purifier. H\(_2\) gas flow is controlled using a flow meter and a needle valve.

The LPE growth procedures for GaP are illustrated in the processing diagram shown in Fig.28. The preparation procedures for GaP substrates were discussed in sections 4.1 and 4.2. Before growth, the polished substrates were usually cleaned using hot H\textsubscript{2}O\textsubscript{3} (~20\%) followed by ultrasonic cleaning in deionized water, acetone and methanol. The solution components of Ga, GaP and Mg (for p-type doping) were measured using an electronic balance which has a sensitivity of 0.1 mg. Special care should be exercised for measuring the weight of magnesium since the quantities required for doping are close to the balance sensitivity limit.

When the substrate and solution components were ready, they were loaded into the graphite boat at the designed positions. The boat was then covered by the graphite cover and loaded into the quartz tube. The quartz tube was subsequently closed and pumped down using the mechanical and turbo pumps to a vacuum of \(~5 \times10^{-5}\) torr. When the desired vacuum was achieved, the pumping valve was closed and H\(_2\) gas was
introduced. When the pressure in the tube is close to the desired pressure (~ 150 KPa), the needle valve was slowly opened to control the H₂ gas flow. Before opening the needle valve, one must ensure that pressure in the tube is higher than atmospheric pressure, otherwise air may flow into the system.

Figure 28  The processing diagram for GaP LPE growth.

The temperature was raised by turning on the temperature controller after a stable H₂ flow rate of ~ 20 SCCM was achieved. The temperature control program was set to control the solution baking time and cooling rate. The Ga was baked for 5 hours at 1050°C before use to reduce background impurities. The solution was normally baked for 2 hours before starting the growth to further reduce un-intentional impurities. When the desired temperature was reached, the solution was moved onto the substrate using the quartz push rod. After growing for desired time, the solution was removed off the
substrate and the power to the furnace was turned off to cool down the furnace. The H₂ gas flow was stopped when furnace temperature was cooled down below 80°C, and the boat was unloaded out to remove the substrates and solution. After removal, samples were usually etched in HNO₃ (20%) to remove any Ga droplets and residue.

4.4 Metal contacts

In order to achieve good p-n junction ARVCs, it is important to fabricate good ohmic contacts on both sides of the junction. Non-ohmic contact may introduce a Schottky barrier between the contact metal and the semiconductor. This Schottky barrier can increase the contact resistance significantly. When a Schottky barrier is irradiated by alpha particles, it may generate a reverse current which will compensate the p-n junction generated current.

The ohmic contact characterization for p- and n-type GaP are discussed in chapter 5. In this section, we simply introduce the techniques for Ohmic contacts, including metal evaporation and rapid thermal annealing.

4.4.1 Evaporation

Gold-zinc (Au-Zn) is commonly used for ohmic contacts to p-type III-V semiconductors, including GaP, while for n-type, gold-germanium (Au-Ge) is widely used. In our experiments, vacuum evaporation was used to deposit both Au-Zn and Au-Ge on p- and n-type GaP, respectively.

The vacuum evaporation system is shown schematically in Fig.29. A mechanical pump combined with a diffusion pump were used for pumping down the system. Before starting evaporation, the vacuum pressure was usually 2 ×10⁻⁵ torr. A tungsten
wire basket was used as the heating element by introducing high current (~15A) through it. The evaporation was terminated when all the Au in the basket was observed to have evaporated.

For Au-Zn deposition, pure Au and Zn were used, where the amount of Zn was about 5% of that of Au. Since Zn evaporates at a much lower temperature than Au, a very thin Zn layer was first deposited on the GaP p-type surface, which played the role of ohmic contact, while the Au layer on it served to reduce the sheet resistance of the conducting layer. For Au-Ge deposition, commercial Au-Ge alloy was used for the first contact layer, and a pure Au layer was deposited on top of the Au-Ge layer to further reduce the contact layer sheet resistance.

The deposited Au film thickness can be calculated from the distance between the Au source and sample holder, and the amount of Au evaporated. Since the tungsten basket was open in all directions, the source can be considered to act as a point source. The Au layer thickness ($d_{Au}$) can be determined from:

$$d_{Au} = \frac{W_{Au}}{4\pi L^2 \rho_{Au}}$$

(4-14)
where $W_{\text{Au}}$ is the weight of Au, $\rho_{\text{Au}}$ is the density of Au and $L$ is the distance between Au source and sample. In our case, $L$ is 6 cm. To deposit a 100 nm film of Au, it requires about 80mg of Au.

4.4.2 Rapid thermal annealing

After evaporation of metals on both sides of GaP p-n junction, the samples need to be thermally annealed. The thermal annealing serves two basic purposes, one is to increase bonding strength between the metal and the semiconductor, while the other is to reduce the contact resistance.

Thermal annealing for our samples was carried out in a computer controlled rapid thermal annealing system. Normally the annealing was performed at 550°C for 5 minutes in H$_2$ gas ambient, and satisfactory ohmic contacts were achieved. For a few cases, samples were annealed at 650°C for 2-4 minutes in order to reduce series resistance of p-n junction. However, most of samples could not sustain this high temperature annealing before the p-n junctions were damaged. Only those p-n junction samples with very low leakage current were able to be annealed at 650°C.

Chapter 5 Characterization of GaP LPE layers

5.1 Surface morphology of GaP LPE layers

The surface morphology is an important characteristic used to verify the quality of LPE layers. The surface morphologies of our LPE grown layers were analyzed using FE-SEM. It is not surprising to realize a good smooth mirror-like LPE layer on a well
polished flat substrate. However, in order to achieve the textured p-n junctions as designed in chapter 3, we need to obtain good quality LPE layers with flat smooth surface morphology on non-flat substrates. In this section, we mainly discuss the morphologies of LPE layers on non-flat substrates, (i.e., randomly roughened substrates and periodically patterned pyramidal substrates).

5.1.1 Surface morphology of LPE layers on randomly roughened substrates

Usually LPE growth is made on well polished flat substrates in order to obtain better surface morphologies and to reduce dislocations. However, in some special cases, a smooth surface morphology of an LPE layer can be realized on a rough substrate. There were several reports that described the LPE growth of GaAlAs layers on roughened GaP substrates [5-1, 2]. The LPE layers were reported to have much smoother surfaces than the substrates. The authors believed the improvements of surface morphologies were due to remarkable increase of nucleation density on the roughened surfaces. However, this approach was reported to lead to increased defect states at the interface and in the LPE layer [5-2], and hence has not been used for device fabrications.

We made LPE growths of GaP layers on un-polished (111) and (1 0 0) S-doped n-type GaP substrates. The SEM image of a typical un-polished (111) surface is shown in Fig. 30. The un-polished (1 0 0) surface has the similar morphology. After LPE growth using the growth conditions shown in Table 5-1, the GaP layers on (1 1 1) substrate became smooth and shiny, while the layers on (1 0 0) substrates were still rough. The typical surface SEM images for LPE layers on (1 1 1) and (1 0 0) substrates
are shown in Figs. 31 (a) and (b), respectively. It can be clearly seen that GaP LPE layer on the (1 1 1)GaP roughened substrate completely smoothed away the surface roughness, and achieved flat and smooth surface as shown in Figs. 31 (a). On the other hand, GaP LPE layer on a (1 0 0) GaP rough substrate became rougher than the substrates as shown in Figs. 31 (b).

![Image](image.png)

**Figure 30** Surface morphology of an un-polished GaP (111) substrate

<table>
<thead>
<tr>
<th>Table 5-1 LPE growth conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$</td>
</tr>
<tr>
<td>850 °C</td>
</tr>
</tbody>
</table>
The totally different morphologies of GaP LPE layers on (1 1 1) and (1 0 0) GaP roughened substrates indicate that the smoothing effects of LPE layers on roughened substrates are not simply due to increased nucleation density. The surface orientation obviously played an important role in the smoothing effects. For III-V zinc-blende LPE layers, Sangster [5-3] suggested that the orientation effects on the growth behavior was attributable to the differences of surface atomic structure. He proposed that if the number of the dangling bonds of a surface is unchanged or decreased when a group III or group V atom bonds to the surface, there is no barrier to nucleation, whereas, if the number of the dangling bonds increases, then the nucleation is likely to be difficult on that surface.

For a (1 0 0) surface, each atom has two dangling bonds. When a group III (or group V) atom bonds to this surface, it costs two bonds to bond with two surface atoms. Two extra bonds are left as dangling bonds. Therefore, the number of dangling bonds are not changed on incorporation of new atoms during the LPE growth. However, for a (1 1 1) surface, each atom has only one dangling bound. When a single A atom (e.g. Ga) is added on a (111) B surface, only one bond is used to bond with a B surface atom (e.g. P), leaving three un-bonded dangling bonds. This cause a net increase of two dangling bonds. This situation is the same for a B atom (e.g. P) bonding to (1 1 1)A surface. Therefore, the nucleation and growth rates on (1 1 1) surfaces are generally lower than for (1 0 0) surfaces, which was indeed proved experimentally [4-27].

Sangster’s model might be useful to explain the growth behavior of GaP layers on roughened (1 1 1) and (1 0 0) substrates shown in Figs. 31. Since (1 1 1) surface is not favored for nucleation compared to other facets, the nucleation is most likely to initiate on the side wall facets of the micro-features shown in Fig. 30. There might be no nucleation
Figure 3.1 Surface morphologies of GaP LPE layers on roughened GaP (1 1 1), (a), and (1 0 0), (b), substrates.
on the tops of these micro-features. Therefore, the early stages of LPE growth can involve filling those micro-valleys first, and then the epilayer can grow uniformly. Thus smooth and flat surfaces can be realized, which is supported by the fact shown in Figs.31 (a).

For (100) substrates on the other hand, the top facets of the micro-features indicated in Fig. 30 are (100) surfaces. Because the (100) surface is the most favored plane for nucleation, the nucleation for LPE growth most probably started on the top facets of these micro-features. Moreover, the [100] direction has a high growth velocity, so that the early protrusions can rapidly develop in the direction normal to the substrate surface. These fast developing nuclei may prevent GaP nuclei developing in the valleys of those micro-features. Fast vertical growth velocity probably also prevented lateral coalescence of nuclei from forming continuous layer. These might be the reasons for the island mode morphology shown in Figs.31 (b).

5.1.2 Surface morphology evolution of GaP LPE layers on pyramidal surfaces

Since LPE growth on GaP (111) substrates can smooth away the roughness of the substrate surfaces, we proposed the idea of developing a new device structure—the PTJ structure for ARVCs to increase current collection efficiency. We designed the p-n junction interface structure as discussed in Chapter 3, and we realized pyramidal surfaces using photolithography masking followed by wet chemical etching as discussed in Chapter 4. LPE growth of high quality GaP layers on the pyramidal surfaces is the critical step to realize PTJ structure ARVC devices as expected.
In order to understand the growth behavior of LPE layers on the pyramidal surfaces, it is important to understand the evolution of the surface morphology during growth. For this purpose, we did a series of LPE growths for different growth times. The pyramidal surface substrates were prepared using the procedures described in section 4.2. The photoresist mask patterned GaP (111)B substrates were etched for 6 minutes in 1HCl: 1CH₃COOH: 1H₂O₂ solution to prepare substrates for the LPE growth.

The surface morphology before growth is shown in Fig.32, which was taken from the un-grown region of the substrate after one growth run in the LPE system. One can see that the surface exhibited signs of erosion due to evaporation of the surface atoms during

Figure 32. SEM image of the pyramidal surface of GaP substrate after etching for 6 minutes and baking for 2 hours at 860°C.
the baking and growth period in the LPE system. This sample was baked at 860°C for 2 hours. The growth period is about 40 minutes corresponding temperature change from 860°C to 800°C.

A series of LPE growths were made with growth times of 1, 3, 10 and 25 minutes on pyramidal substrates similar to those shown in Fig.32. The other growth conditions were the same as those listed in Table 5-1 except for the growth time. The corresponding SEM images of their surface morphologies are shown in Figs. 33 (a), (b), (c) and (d).

Initially, growth started mainly on the side walls of the pyramids and on the base floor of the substrate. There was hardly any growth on the top surfaces of the pyramids as can be seen from the surface image after 1 minute of growth [Figs.33(a)]. After 3 minutes of growth, the surfaces of the pyramids became circular-conical in shape, as shown in Figs.33(b), and the side wall facets of pyramids revealed originally using wet chemical etching no longer exist. The elliptical shapes of side walls of pyramids shown in Figs.33(b) were due to the tilting of the sample surface from horizontal. The top view SEM image in Figs. 34 (a) shows clearly the exactly circular shape of the side walls of the pyramids. From Figs.33(b) one can also see the base floor was raised, while little growth is evident on the tops of the pyramids. The height of pyramids was hence reduced. This can be seen more clearly from Fig.35, which shows the SEM image of a transition area separating a region grown using 1 minute from the one for 3 minutes growth. Compared to 1 minute growth, the slope of side wall of each pyramid after 3 minutes growth was obviously smaller. This indicates that the bottom region of the pyramids encountered faster growth than the top region.
After 10 minutes growth, the base floor was further raised, which further reduced the height of pyramids since no obvious growth on the top surfaces of the pyramids was observed. The dimensions of the cones and their side wall slopes were also reduced, which can be seen from Figs. 33(c) and Figs. 34(b). However, the size of the pyramidal tops had no obvious increase between 3 minutes and 10 minutes growth. The different top shapes shown in Figs. 33(b) and Figs. 34(a) were probably due to non-uniformity of the wet chemical etching for different regions. The top triangular shapes show further evidence that no growth occurred on the pyramidal tops since the top triangles were formed due to wet chemical etching as discussed in chapter 4.

The surface image of a GaP LPE layer after 25 minutes of growth is shown in Figs. 33(d) together with a transition to 10 minutes growth. The pyramids were completely buried under the LPE layer after 25 minutes growth, and the surface became flat and smooth without any sign of the pyramids underneath. This growth behavior can be seen more clearly in Fig. 36, which shows the SEM image of a LPE layer after 30 minutes growth at a growth temperature of 850°C, super-cooling of 10°C and cooling ramp rate of 2°C/minute on a pyramidal surface. Fig. 36 also shows the pyramids that were not touched by the solution. The LPE layer surface is very smooth and flat, which totally covered the pyramids. The un-grown pyramidal surface again shows obvious signs of surface decay due to preferential phosphorus loss during the baking and growth period.

LPE growth on non-planar substrates with preferentially etched channels was studied to develop laterally confined laser structures[5-4, 5, 6, 7]. There are two kinds of growth behavior for LPE growth of different materials on preferentially etched channels of different substrates. One type of growth behavior is strongly direction dependent, and
Figure 33. Surface morphologies of GaP LPE growth on pyramidal textured substrates for various growth times, (a) 1 minute, (b) 3 minutes, (c) 10 minutes and (d) 25 minutes (including a region having only 10 minutes of growth).
Figure 34  Top view SEM image of GaP surface after LPE growths for 3 minutes (a) and 10 minutes (b) on a pyramidal textured substrate at a growth temperature 850°C.
Figure 35  Surface morphology of GaP layer showing a transition region separating from 1 minute from 3 minutes of growth, on a pyramidal textured substrate.

Figure 36  GaP LPE layer on a pyramidal surface grown at 850°C for 30 minutes.
was demonstrated in the LPE growth of GaInAsP layers on preferentially etched channels of InP substrates having different side-wall facet orientations [5-8]. The LPE growth behavior is different on different side-wall facets of the preferentially etched channels. The other type of growth behavior shows independent of facet orientation, which was found in LPE growth of AlGaAs or GaAs layers on preferentially etched channels on GaAs substrates [5-4, 5]. In this case, the etched channels were filled using LPE growth regardless of the side-wall facet orientation, and flat layer surface were achieved once the channels were filled. The LPE growth behavior of GaP layers on pyramidal surfaces (shown in Figs. 33-36) follows this latter type of behavior. We refer to this growth mode as “smoothing”.

Smoothing for the growth of AlGaAs or GaAs on preferentially etched GaAs substrates was proposed as due to the surface tension caused by the excess chemical potential of a curved solid-liquid interface. The excess chemical potential can be minimized by a return to planarity [5-4]. This suggestion is supported by the fact that the LPE layers (AlGaAs or GaAs) always grow in so as to minimize the solution-crystal interfacial area. The layers grow most rapidly on concave surfaces, and most slowly on convex surfaces.

We believe that the smoothing of GaP LPE growth on pyramidal substrates is also due to the excess chemical potential of the curved solution-crystal interfaces. The LPE growth always tends to reach the lowest energy state, which can be satisfied by minimizing the solution-crystal interface area. This is strongly supported by the fact that the pyramids became conical after short growth time (~3 minutes). The top surfaces of the pyramids, which are approximately convex, experienced the slowest growth velocity,
while the bottom regions (including base floor surface), which are approximately concave, had the fastest growth velocity. This model is fully supported by our experimental findings (Fig. 33).

5.1.2 Interface morphology of GaP LPE layers

From the surface morphology evolution of GaP LPE layers on pyramidal substrates we observed that LPE growth can overcome the surface unevenness to achieve a flat and smooth epilayer surface. Thus a textured interface with a flat surface can be successfully realized, which is what we had anticipated from the design in chapter 3. However, two critical issues have to be investigated in order to make this kind of textured p-n junction devices applicable. The first issue is impurity diffusion. We used Mg for p-type doping in the LPE layers to make p-n junctions on n-type substrates. Since LPE growth is conducted at elevated temperatures, e.g. 850°C and 950°C for our experiments, the n-type pyramids might be compensated by p-type impurities due to diffusion. The second issue is the quality of the interface. If the growth over textured surfaces introduce significant dislocations, this kind of p-n structure device may not be applicable because dislocations act as recombination centers which can cause significant leakage current on p-n junctions. In order to study these two issues, we analyzed the interface structures of the Mg doped LPE layers on n-type pyramidal substrates as compared with growth on flat substrates.

An Hitachi S4500 FE-SEM was used to analyze the p-n junction interfaces from the cleaved cross sectional surfaces. An ordinary SEM machine can barely distinguish homo-material p-n junctions. However, the S4500 FE-SEM machine can provide
excellent doping contrast. This doping contrast results from electron energy variations of the secondary electrons from p- and n-type regions, because p- and n-type semiconductors have different work functions. However, this energy difference is very small compared to the incident electron's energy. The lower detector in the SEM normally cannot distinguish homo p-n junctions, except using very low acceleration voltages, such as 2 KeV. However, the upper detector of the FE-SEM mainly picks up the lower energy electrons, and thus has very good doping contrast for homo p-n junctions.

Fig. 37 shows a cleaved cross-sectional FE-SEM image of a typical p-type layer over an n-type pyramidal substrate (sample No.0105), which was grown for 50 minutes with other growth conditions listed in Table 5-1. It is clearly shown that the p-type layer covered the n-type pyramidal surface with a sharp n-to p-type transition interface. The

Figure 37  FE-SEM image on the cross-sectional surface of a PTJ structure grown at 850°C for 50 min.
p-n junction interface followed the pyramidal interface as expected. The cleaved surface in the layer is as perfect as in the substrate. No structure defects, such as grain boundary lines and pin holes etc. were observable in the layer and at interface.

The surface of the layer is very flat and smooth, in agreement with surface morphologies shown in Figs. 33(d) and Fig.36. From Fig.37 one can also see the periodically arranged pyramidal structures. However, the period length is about double of that of the photo resist mask array. This is because the cleavage line is along a direction illustrated in the diagram beside the image in Fig.37. Actually, one can see the small angle of the pyramid between the two adjacent pyramids cut by the cleaved edge.

In order to compare the growth behavior and the device properties on pyramidal textured and flat surfaces, we prepared PTJ and flat junction (FJ) structures using LPE by putting one piece of a flat polished substrate and one pyramidal textured substrate together in the same holding well and using the same solution. In this case, the growth conditions should be exactly the same for two types of substrates except the unavoidable non-uniformity. The cleaved cross-sectional FE-SEM images of one pair of these samples (sample No.0705) are shown in Figs. 38 (a) and (b). The growth conditions were the same as for the sample shown in Fig.37. The layer on the pyramidal textured substrate has a sharp p-n junction interface following the pyramidal textured surface as shown in Figs. 38 (a), which is similar to that shown in Fig.37; while the layer on the flat surface has a flat sharp p-n junction interface, as shown in Fig.38 (b).

Surprisingly, the total thickness of the layer on pyramidal textured surface from the base floor to the layer surface is almost the same with the layer thickness on the flat substrate. This result shows further evidence that the top surface of the pyramids did not
Figure 38  FE-SEM images on the cross sectional surfaces of the LPE layers on pyramidal textured (a) and flat polished (b) substrates under the same growth conditions.
grow before the valleys were filled. However, it is surprising that the side wall growth of
the pyramids did not accelerate the layer thickness growth. Probably the gap between
pyramids are too wide for the side wall layers to overlap before being engulfed by
the base floor layer. Figs.33 suggests some explanations. One can see the gaps between
pyramids were obviously increased from 3 minutes growth to 10 minutes growth, and the
base floor layer surface after 10 minutes growth was much flatter than that after 3
minutes growth. Regardless of the mechanisms, the results shown in Figs.38 are very
satisfactory since they provide a convenient way to compare the alpha irradiation
response of the PTJ and FJ structure devices since they have similar layer thickness.

We also made LPE growth of Mg doped GaP layers on pyramidal substrates at
growth temperature of 950°C, since we found that the p-n junction devices grown at
850°C had a high leakage current due to the high level of unintentional impurity
incorporation in the epilayer. A detailed discussion on this issue is presented in
chapter 6. Fig.39 shows the cross-sectional FE-SEM image of sample No.1807, which
was grown for 9 minutes with a growth temperature of 950°C, cooling ramp rate of
2°C/minute, and a super-cooling interval of 10°C. It also clearly shows a sharp textured
p-n junction interface with periodically arranged pyramids. The cleaved surface of the
epilayer is also as perfect as that of the substrate without any sign of structural defects.
The period length of pyramids on the cleaved edge is also doubled to that of the photo
resist masks. This is because the cleaved edge is along a similar direction of the
periodical pyramid array with that shown in Fig. 37.

Fig.40 shows the cross-sectional FE-SEM image of sample No.2507, which had
the same growth conditions as sample No.1807 except that its growth time was 6
Figure 39  FE-SEM image of GaP LPE layer grown on pyramidal textured substrate with a growth temperature of 950°C, cooling rate of 2°C/min, supercooling of 10°C and growth time of 9 minutes.

Figure 40  FE-SEM image of GaP LPE layer grown on pyramidal textured substrate with a growth temperature of 950°C and a growth time of 6 minutes.
minutes. The p-type layer had the similar features as sample No.1807, but the layer thickness was thinner. The period length of the pyramids on this cleaved edge is about the same with that for photo resist mask array, which indicates that this sample was cleaved right along one of periodic arrangement directions of the photo resist masks. There was a brighter region in the p-type layer, which can be seen in both Fig. 39 and Fig. 40. This thin region corresponds to the highly doped thin p-type layer, which was introduced to improve ohmic contact.

5.2 GaP LPE layer thickness

For optimizing p-n junction devices, it is necessary to control the LPE layer thickness, or the p-n junction depth from the surface. The dependence of LPE layer thickness on growth time under different growth conditions was discussed in section 4.3. For different LPE growth techniques, i.e. step-cooled, ramp-cooled and super-cooled, the thickness-time relationships are different.

In our experiments, all samples were grown using super-cooled growth since super-cooling proved to be helpful for improving the morphology due to increased nuclei density[5-1, 9, 10]. The solutions were normally super-cooled for 10°C before being brought into contact with the substrates. Our early attempts were to make optimized GaP p-n junction ARVCs using LPE growth at relatively low temperatures, e.g. 850°C. A set of LPE growths with different growth time were made on flat (111)B GaP substrates using a growth temperature of 850°C, supercooling of 10°C and cooling ramp rate of 2°C/minute. The layer thickness was measured using a TENCOR Alpha-Deck step equipment, which has a resolution of 0.01μm, high enough for our samples.
The layer thickness-time relationship was shown in Fig. 4.1. For short growth times \( t < 4 \) minutes, the layer thickness was approximately proportional to square root of growth time, i.e. \( d(t) \propto t^{1/2} \), which is the relationship for step-cooled growth. For longer growth times \( (25-30 \) minutes), the layer thickness closely approximates the dependence for ramp-cooled growth, i.e. \( d(t) \propto t^{3/2} \). In between, the time dependence of thickness is a combination of the step-cooled and ramp-cooled relations as predicated in Eq.(4-11).

![Graph showing layer thickness and growth time relationship](image)

**Figure 4.1** Relationship between layer thickness and growth time for supercooled LPE growth with growth temperature of 850°C, cooling rate of 2°C/min. and supercooling of 10°C.

These results are in good agreement with Heist's theoretical prediction and experimental results for super-cooled growth of GaAs [4-24], as discussed in section 4.3. For short growth times, step-cooled behavior dominates due to the large super-cooling temperature interval. As growth time increased, the nuclei forming from ramp-cooling made a more
significant contribution, and finally dominated when growth time was long enough to make nucleation from step-cooling negligible.

However, we can see that the growth rate did not follow the theoretical ramp-cooled growth after growth times exceeding 30 minutes, as shown in Fig.41. This probably indicates that the semi-infinite solution approximation, which assumes that the supply of GaP is un-limited, is no longer valid. Actually, due to a large temperature drop after a long growth time, the precipitation of GaP in the solution decreases significantly because the solubility of GaP in Ga solution decreases exponentially with decreasing temperature. Therefore, the population of GaP nuclei participating the growth dropped significantly after long growth times, resulting in lower growth rates than predicted theoretically.

The growth rate of GaP LPE layers at growth temperature of 950°C are much faster than for 850°C with the same 10°C super-cooling and 2°C/minute ramp rate. From FE-SEM in Fig.40, we can see the layer thickness is 8 μm for only 6 minutes of growth. It takes more than 30 minutes to grow this thick layer at 850°C. For 9 minutes of growth, the LPE layer thickness reaches about 11.5 μm, as can be measured from the cross-sectional FE-SEM image shown in Fig.39. Although a complete set of experiments on layer thickness versus time were not done as for growth temperature of 850°C, the layer thickness could be well controlled within the alpha particle penetration depth.

5.3 Doping concentration in GaP LPE layers

Doping concentration control in both p- and n-type layers are very important for p-n junction devices, including ARVCs. GaP substrates used in our experiments were
S-doped with a carrier concentration of $5 \times 10^{17} \text{cm}^{-3}$. No efforts were made to optimize n-type doping since photo resist masks were made directly on the substrates. In this section we mainly discuss the Mg doping concentration in p-type LPE layers.

In order to monitor the hole concentration in the Mg doped p-type layers, we made LPE growth of GaP layers on (111)B semi-insulating substrates with different Mg mole fractions in the Ga-GaP solutions. Before investigating the relation of doping concentration in the epilayer to Mg fraction in the solution, we studied the background doping concentration in the unintentionally doped samples.

For the unintentionally doped GaP LPE layers grown start at 850°C, we found layers had background doping concentrations of $\sim 10^{17} \text{cm}^{-3}$, which were estimated from the resistivity of the layers calculated from the I-V curves. Hall measurements for these samples were not successful due to poor Ohmic contacts. The background doping was n-type, which was detected using a simple thermo-electric probe technique. This technique is illustrated in a diagram [5-11] shown in Fig.42. When a hot and a cold probe electrodes contact on a n-type semiconductor, the electrons will diffuse away from the hot side to the cold side since electron is the majority carrier, resulting in an electric field pointing from hot side to cold side. Therefore, a positive voltage can be measured between the hot and cold spots. For the p-type semiconductors, the electric field is reversed because the majority carrier hole is thermally diffused away from the hot spot. For the unintentionally doped LPE layers, we always detected positive voltages for the hot side. Thus it was sure that the background doping was n-type.

Because the background doping is too high (above $10^{17} \text{cm}^{-3}$) for LPE growth at a growth temperature of 850°C, it is difficult to control the p-type doping concentration to
a level of $\sim 10^{17}$ cm$^{-3}$. Normally only when the p-type doping concentration was close to $10^{18}$ cm$^{-3}$ or above could the LPE layer become p-type for growths at 850°C. High background doping is very detrimental to p-n junction performance, which is discussed in more detail in Chapter 6. Actually, no good p-n junction properties were obtained using 850°C LPE growth in this work. For this reason, doping concentrations were not systematically monitored for LPE growth at 850°C.

For LPE growths at 950°C, the background doping in GaP epilayers is still n-type. However, the unintentional background doping concentration was significantly reduced to $\sim 10^{16}$ cm$^{-3}$. Thus the p-type doping could be controlled to levels on the order of $10^{17}$ cm$^{-3}$ without significant compensation. A series of GaP layers were grown at 950°C on semi-insulating GaP (111)B substrates using different mole fractions of Mg in Ga-GaP solutions. The doping concentrations were measured using Hall effect measurement. Each sample was controlled to have thickness of about 10µm.
The metal contact profile used for Hall measurements is as shown in Fig. 43; this was based on the method developed by van der Pauw [5-12, 13]. He showed how the resistivity, carrier concentration, and mobility of a flat sample of arbitrary shape can be determined. The resistivity is given by:

\[ \rho = \frac{\pi d}{\ln(2)} \left( \frac{R_{12,34} + R_{23,41}}{2} \right) F \]  

(5-1)

where \( d \) is the layer thickness and \( R_{12,34} = V_{34} / I_{12} \). The current \( I_{12} \) flows from contact 1 to contact 2 and \( V_{34} = V_4 - V_3 \) is the voltage between contacts 4 and 3. \( R_{23,41} \) is similarly defined. \( F \) is the function of the ratio of \( R_{12,34} / R_{23,41} \), which is 1 for symmetrical samples such as circles or squares.

With the magnetic field perpendicular to the sample surface, the Hall coefficient \( R_H \) can be obtained from:

\[ R_H = t \frac{(\Delta V_{13} + \Delta V_{24})}{2 B I} \]  

(5-2)

where \( \Delta V_{13} \) are the Hall voltage between contacts 1 and 3 with current flow from 2 to 4, and \( \Delta V_{24} \) is similarly defined. \( B \) is the strength of the magnetic field. The Hall mobility is defined as:
\[ \mu_H = \left| R_H \right| / \rho. \]  

(5-3)

The Hall mobility is not identical to the conductivity mobility. There is a Hall factor \( r \) that relates the between Hall mobility to the conductivity mobility, and which is defined as

\[ \mu_H = r \mu_p, \quad \mu_H = r \mu_n. \]

(5-4)

For many semiconductors, \( r \) is usually not unity, but larger than unity. However, \( r \) is frequently taken as unity. The doping concentration can be determined by:

\[ p = 1/q R_H \]

(5-5)

for p-type semiconductors and

\[ n = -1/q R_H \]

(5-6)

for n-type semiconductors.

In case of both electrons and holes are present, the Hall coefficient becomes:

\[ R_H = \frac{[(p-b^2)n + (\mu_n B)^2(p-n)]}{q[ (p + bn)^2 + (\mu_n B)^2(p-n)^2]} \]

(5-7)

where \( b = \mu_p / \mu_n \). In most cases, the magnetic field is small, and \( B \ll 1/\mu_n \) can be satisfied. Therefore Eq. (5-7) can be approximated to:

\[ R_H = \frac{(p-b^2)n}{q(p + bn)^2} \]

(5-8)

Based on Hall measurements of the GaP LPE layers for different Mg doping, we obtained the relationship between the carrier concentration and the Mg mole fraction in the Ga solutions, which is presented in Fig.38. For high level doping, the concentrations were simply calculated from Eqs. (5-2) and (5-5), and the hole mobility were derived from Eqs. (5-1, 2, 3). For doping levels close to \( 10^{17} \text{cm}^{-3} \), the carrier concentration
and hole mobility were derived using Eqs.(5-1, 2, 8) assuming an n-type concentration of $10^{16}$ cm$^{-3}$ and mobility of 150 cm$^2$/V·S [5-9]. This is because the GaP LPE layers grown at 950°C always had a n-type background doping concentration of around $10^{16}$ cm$^{-3}$.

The hole concentration in the GaP LPE layers shows an approximately linear relationship with the mole fraction of Mg in the Ga-solution, as shown in Fig. 44. Using Eq.4-13, we calculated the segregation coefficient of Mg doping in GaP (1 1 1)B LPE layers at 950°C as 0.02, which is in good agreement with previously reported results, which is 0.021[5-15].

![Graph](image)

Figure 44  Relationship of carrier concentration, p, in GaP LPE layer with the mole fraction of Mg in the Ga solution with growth temperature of 950°C.

The room temperature Hall mobility for Mg doped p-type GaP LPE layers is shown in Fig. 45. The mobility decreases with the doping concentration. Especially after
doping concentration is higher than $10^{18}\text{cm}^{-3}$, the mobility decreases much faster than that for lower doping. The room temperature Hall mobility from our Hall measurements shown in Fig.45 is about 2 time less than the generally reported mobility for p-type GaP[5-15]. This is probably due to the non-unity of Hall factor $r$ indicated in Eq. (5-4), or the high total concentration of ionized impurities (i.e., high degree of compensation).

![Graph](image)

Figure 45  Dependence of room temperature Hall mobility with Mg doping concentrations.

5.4 Ohmic contacts

Since Ohmic contacts on both p- and n-type sides of p-n junction devices are very important for device performances, we studied metal contacts on both p- and n-type GaP. I-V measurements on single p- or n-type GaP were used to characterize the contact properties.

For the n-type substrates, Au-Ge was used as contact metal as described in chapter 4. After annealing at 550°C for 5 minutes, good ohmic contacts were realized on
the n-type substrates. A typical I-V curve is shown in Fig. 46, which shows very good linear dependence of current with applied voltage, indicating good ohmic contacts. This is not surprising since the carrier concentration of the n-type substrates is $\sim 5 \times 10^{17} \text{cm}^{-3}$, which is quite high for n-type GaP, and usually good ohmic contacts can be achieved using Au-Ge.

For Mg doped p-type LPE layers, Au-Zn was used as the contact metal. The samples were also annealed usually at 550°C for 5 minutes. Fig. 47 shows the I-V curves of two samples of Mg doped LPE layers with carrier concentrations of about $1 \times 10^{17} \text{cm}^{-3}$ and $2 \times 10^{18} \text{cm}^{-3}$, respectively. The I-V curve of the less doped sample obviously has non-linear dependence on the voltage, indicating non-ohmic contacts. This means there is a Schottky barrier between the metal and the GaP semiconductor. However, this Schottky barrier is very weak compared to typical Schottky diodes because its low voltage bias current is much higher than that for a typical Schottky diode. At this doping level, the low bias current is considered to be dominated by thermionic-field emission [5-16,17], which means the carriers can be thermally excited to an energy level where the barrier width is sufficiently narrow so that the carriers can tunnel through the barrier.

For the highly doped sample, the I-V curve is linear and the resistance for low bias voltage was greatly reduced, which means good ohmic contacts were realized. It is known that the Schottky barrier height does not depend on doping concentration for the same metal and semiconductor. The decrease of the contact resistance is due to the narrowing of the barrier width. The carriers can easily tunnel through the barrier directly, known as field emission [5-16,18].
The contact resistance due to poor metal-semiconductor contacts mainly affect the series resistance of the p-n junction devices. Fig. 48 shows the I-V curves of a GaP p-n junction.

Figure 46 I-V relation of Au-Ge contact on n-type (~5x10^17 cm^-3) GaP substrate after annealed at 550°C for 5 minutes.

Figure 47 I-V curves for Mg doped GaP layers using Au-Zn contacts for two different carrier concentrations of 1x10^17 cm^-3 (dashed line) and 2x10^18 cm^-3 (solid line).
junction device with Au-Zn for p-type contact and Au-Ge for n-type contact after annealing at different temperatures of 550 °C and 650 °C. After annealing at 650°C for 4 minutes, the high forward bias (~2 V) current increased more than an order of magnitude compared to the same device after annealing at 550°C for 5 minutes. However, at the lower voltage bias region (V < 1.2 V), the current almost had no change, as shown in Fig.48. These results indicate that the series resistance reduced significantly after higher temperature annealing. However, very few samples could sustain high temperature 650°C annealing before the p-n junctions were damaged. For most of our devices, a thin highly doped p-type layer is prepared to improve contacts for annealing at 550°C.

Figure 48  I-V characteristics of GaP p-n junction device after annealing at 550°C and 650°C.
Chapter 6  GaP p-n junction device characterization

6.1 Electron beam induced current (EBIC) analysis

EBIC is based on electron-voltaic effect, which has the same mechanism as an ARVC except that an electron beam is used for the excitation source. EBIC is a very powerful technique to analyze barriers in semiconductor devices, including p-n junction barriers and Schottky barriers. It can be used to identify junction profiles[6-1], analyze junction failure[6-2] and estimate minority carrier diffusion lengths[6-3,4].

In our studies, the EBIC analysis was carried out using a Hitachi S4500 FE-SEM system on the cross sectional surfaces of GaP p-n junction devices, as shown in Fig. 49.

![Figure 49 The diagram of EBIC analysis.](image-url)
The electron beam scans the cross-section to create e-h pairs. However, only the e-h pairs near the junction (p-n junction or Schottky barrier) region can be collected to produce a current. This current signal is then amplified and converted to an image to show the current collection distribution as a map analogous to a secondary mode image.

The excited electrons or holes in the p- or n-type regions need to diffuse to the depletion region edge and then be collected by the junction. Only the electrons and holes within about one diffusion length of the junction contribute to the EBIC signal. Therefore, the minority diffusion lengths of electrons and holes can be estimated from the EBIC signal width in p- and n-type regions, respectively. If the surface recombination is neglected, the EBIC signal strength can be expressed as [6-5]:

$$I_E = I_{\text{max}} e^{-X/L}$$  \hspace{1cm} (6-1)

where $X$ is the distance of the beam from the junction and $L$ is the minority diffusion length. $I_{\text{max}}$ corresponds to the maximum current which occurs at the junction place. For the EBIC signal in the p-type region, the minority diffusion length $L$ corresponds to electron diffusion length $L_n$, while in n-type region, $L$ corresponds to hole diffusion length $L_p$.

Figs. 50 shows EBIC measurement results for a typical pair of GaP p-n junction devices of PTJ and FJ structures grown at 950°C for 6 minutes, both grown at the same time for the same growth conditions. Figs.50 (a) and (c) show the SEM mode images with EBIC signals, while Figs.50 (b) and (d) show the EBIC mode images. The total thickness of the layer on the textured substrate is about the same with that on the flat substrate, as shown in Figs.50(a) and (c). The peak positions of the EBIC signals are right at the p-n junction interfaces. For PTJ structure, this position follows the textured
Figure 50  SEM and EBIC mode images of GaP PTJ structure, (a) and (b), and FJ structure, (c) and (d) devices grown at 950°C for 6 minutes.
junction interface. This is evident from Figs. 50 (b), where the current collection region follows right along the textured p-n junction interface. For the FJ structure, the current collection region is just flat as shown in Figs. 50(d). Obviously, the current collection area can be increased using a textured p-n junction interface compared with simply FJ structures.

According to Eq.(6-1), the minority carrier diffusion lengths for electrons and holes can be estimated from the EBIC signal line width at its 1/e position. However, this estimation is not very accurate since the line width changes with the electron beam acceleration voltage[6-3,4]. This is because the radius of electron energy dissipation volume changes with electron beam energy. In our experiments, we also observed that the line width changes with electron beam scanning speed and some other measurement conditions, such as magnification, gain and suppression. Therefore, it is hard to get an accurate minority diffusion length from the EBIC signal width shown in Figs.50. However, the current collection region width is very close for FJ and PTJ structures according to EBIC analysis. $L_n + L_p$ is about 1.5 $\mu$m according to the EBIC signal line width shown in Figs.50, while the estimated value of $L_n + L_p$ is about 2.5 $\mu$m from the measured mobility and reported minority carrier lifetimes [6-6]. This deviation may partially be attributable to surface recombination that was neglected for the derivation of Eq.(6-1).

From Fig.50, we can also see a small signal beside the p-n junction in the n-type region side for both device structures. This signal looks stronger for PTJ structure than for FJ structure. We observed this kind of signal in all of our samples. This signal is most probably due to doping variation in this small region, or a n-n+ barrier. Because of inter
diffusion of n- and p-type dopants near the junction region during the LPE growth, the n-type substrate near the junction might be partially compensated, leading a relatively low doping concentration compared to bulk substrate region. Thus an n-n+ barrier can be formed. The relatively strong intensity of this kind of signal for the PTJ structure can be attributed to the textured features since the generation volume has a specific radius.

From Figs. 50, one can also see there is no EBIC signal at the surface region for both PTJ and FJ structure devices, indicating good Ohmic contacts. We also checked the back contacts for these samples. No EBIC signals were detected. Actually, we detected EBIC signals for Schottky barriers (i.e., poor Ohmic contacts) on some of our early samples. Fig. 51 shows one example, which has an reverse EBIC signal at the surface region compared to the p-n junction signal. This reverse current corresponds to a dark

Figure 51 EBIC mode image and signals of an FJ GaP device with poor Ohmic contact to the GaP layer surface.
current collection region near the surface compared to the neutral region. This indicates that this Schottky barrier will produce a reverse current that will compensate the p-n junction current. Obviously this is detrimental to ARVC devices and explains good Ohmic contacts are essential to good ARVC devices.

6.2 I-V characteristics

I-V characteristics are very important for p-n junction devices. For an ideal p-n junction diode, I-V characteristics are described as:

\[ I = I_s (e^{V/kT} - 1) \]  

(6-1)

where \( I_s \) is the reverse saturation current defined in Eq.(2-2). Under forward bias, the current increases exponentially with the voltage since \( e^{V/kT} \gg 1 \) for \( V > 0.1 \) V. For reverse bias, the \( e^{V/kT} \rightarrow 0 \) when \( V < -0.1 \) V, so the current should quickly saturate to \( I_s \).

However, the I-V characteristics of real p-n junction devices often significantly deviate from the ideal case, especially for large band gap materials. The departures are mainly attributed to the following effects: (a) The generation-recombination of e-h pairs in the depletion region, (b) voltage drops in p- and n-type regions outside the depletion region, (c) current arising from leakage across the surface of the junction, and (d) the onset of high level injection. These effects are all neglected in the derivation of the ideal I-V characteristics. Effects (b) and (d) mainly affect high current level properties under forward bias, which are not critical for ARVCs since they work at low current level. We focus on the generation-recombination current in the depletion region since it is the dominant internal effect that causes deviation of I-V characteristics from ideal diode.
In the depletion region, there are generation-recombination centers like in neutral p- and n-type regions. These centers are formed due to deep level impurities and defect states, which usually have energy levels located in the middle region of the band gap. Under forward bias, some of the injected electrons and holes from n- and p-type region are lost by recombination in the depletion region. This gives rise to a recombination current which is neglected in the ideal diode model. Under reverse bias, carriers in the depletion region are emitted, so the electron and hole concentrations are far below their equilibrium values. Thus there is a net generation of carriers, giving rise to a generation current.

The excess carrier recombination rate \( U \) in the depletion region under a bias voltage \( V \) can be expressed as [6-7]:

\[
U = \frac{n_i^2 (e^{V/kT} - 1)}{\tau_{po}(n+n_1) + \tau_{no}(p+p_1)} \tag{6-2}
\]

where \( n_i \) is the intrinsic carrier concentration, \( n_1 \) and \( p_1 \) are equilibrium concentrations of electrons and holes when the Fermi level lies at the trap energy level \( E_t \). \( \tau_{po} \) and \( \tau_{no} \) are defined as

\[
\tau_{po} = \frac{1}{\sigma_{cp}u_{th}N_t} \quad \text{and} \quad \tau_{no} = \frac{1}{\sigma_{cn}u_{th}N_t} \tag{6-3}
\]

where \( \sigma_{cp} \) and \( \sigma_{cn} \) are the capture cross sections for electrons and holes, \( u_{th} \) is the thermal velocity of carriers and \( N_t \) is the trap state concentrations.

For a reverse bias, \( U \) is negative, representing a net generation of electron-hole pairs. The generation current is:

\[
I_{gen} = -qA\frac{n_i W}{2\tau_o} \tag{6-4}
\]
where \( \tau_{po} = \tau_{no} = \tau_o \) is assumed. For forward bias, the recombination current is:

\[
I_{rec} = (qAn_iW / 2 \tau_o)(e^{V/2kT} - 1)
\]  
(6-5)

Eqs. (6-4) and (6-5) can be combined as:

\[
I_{rg} = I_{RO} (e^{V/2kT} - 1)
\]  
(6-6)

where

\[
I_{RO} = qAn_iW / 2 \tau_o
\]  
(6-6a)

The current \( I_{rg} \) represents the generation current \( I_{gen} = -I_{RO} \) under reverse bias and a recombination current for forward bias.

For a real diode, the total current is obtained by adding the diffusion current for the ideal diode and the generation-recombination current. Thus,

\[
I = I_s(e^{V/kT} - 1) + I_{RO}(e^{V/2kT} - 1).
\]  
(6-7)

Under reverse bias, the two exponential terms in Eq.(6-7) become negligible when \(|V| > 6kT/q\), leading to:

\[
I \approx -(I_s + I_{RO}).
\]  
(6-8)

Under forward bias with voltage excess 0.1 V, the current can be written as

\[
I = I_s e^{V/kT} + I_{RO} e^{V/2kT}
\]  
(6-9)

For convenience, Eq.(6-6) is often expressed as a single equation:

\[
I = I_o (e^{V/nkT} - 1)
\]  
(6-10)

where \( n \) is known as ideality factor, which has a value of 1 for diffusion current and approximately 2 for recombination current. When the two currents are comparable, \( n \) is between 1 and 2. \( I_o \) includes the reverse saturation currents due to diffusion (\( I_s \)) and recombination (\( I_{RO} \)).

The I-V characteristics of GaP p-n junction devices for both FJ and PTJ structures were measured at room temperature. Figs.52 (a) and (b) show the I-V characteristics of
Figure 52. I-V characteristics of GaP p-n junction devices grown at 850°C (a) and 950°C (b). Samples 0705-1 and 2507-1 have PTJ structure, while 0705-2 and 2507-2 have flat junctions.
the FJ and the PTJ devices grown at 850°C and 950°C, respectively. The currents were normalized to unit area for comparison. For devices grown at 850°C, the reverse biased current increased with bias voltage for both FJ and PTJ structures, and the current level is quite high for the GaP p-n junction devices. Because GaP has a large band gap, 2.26eV at room temperature, \( n_i \) is only 2 cm\(^{-3} \), leading to a very low diffusion current \( J_S \) (\( \sim 10^{-30} \text{ cm}^{-3} \)). Therefore, the reverse bias current should be controlled by the generation current in the depletion region expressed in Eq.(6-4). According to Eqs.(6-3) and (6-4), this current is proportional to the trap state density \( N_t \), and increases with depletion width \( W \).

The high level of the reverse current shown in Fig. 52 (a) indicates that there is a high concentration of trap states in both FJ and PTJ structure devices. These trap states are most probably due to high concentrations of deep level impurities incorporated during the relatively low temperature (850°C) LPE growth. As mentioned in Chapter 5, the background doping concentration is quite high (around \( 10^{17} \text{ cm}^{-3} \)) for this growth temperature. However, the FJ device does not have better results than PTJ device for this particular pair of samples, which is encouraging since the PTJ structure does not show any obvious defect-related leakage current compared to FJ device.

The increase in the reverse current with voltage shown in Fig.52 (a) is much faster than that predicted in Eq.(6-4), which should result in \( I_{\text{gen}} \propto (|V|+V_{\text{bi}})^{1/2} \). This is especially evident for the FJ structure devices. The current at -3V is 2 orders higher than that at -1V. This increase is obviously much higher than that due to the depletion width increase, which is less than a factor of two. From the forward bias curves, we can extrapolate \( J_0 \) and \( n \) from Eq.(6-10). For both the FJ and the PTJ structure devices, \( J_0 \) is
close to $10^{-9}$ A/cm² for both structure devices, which is very high for a GaP p-n junction diode. The $n$ factors are 1.4 and 1.6 for FJ and PTJ devices, respectively. Since the recombination current dominates, $n$ should be about 2 according to Eqs.(6-9) and (6-10). The deviations of the I-V characteristics from a generation-recombination mechanism predicted relations for both reverse and forward bias indicate that some other carrier transport mechanisms are responsible for the excess leakage current in these poor performance p-n junction diodes.

The poor I-V characteristics of GaP p-n junction devices grown at 850°C make them to be not suitable for ARVCs. A lot of the generated current will be lost due to the high leakage current, and the open circuit voltage will be very small. Actually, those samples were all from our early attempts. Later we increased the growth temperature to 950°C and achieved much lower background doping concentrations as mentioned in Chapter 5. Figs.52 (b) provides the I-V characteristics of a pair of FJ and PTJ structure devices grown at 950°C at the same time, under the same growth conditions. Under reverse bias, the currents are much lower than those of samples grown at 850°C for FJ and PTJ devices, and the reverse current increases very slowly with bias voltage. This indicates that trap density was greatly reduced.

From the forward bias curves, $J_0$ is extrapolated to be about $2\times10^{15}$ A/cm² for both FJ and PTJ devices, which is very good for GaP p-n junction devices compared to reported results[6-8]. $J_0$ was reduced by more than 5 orders of magnitude compared to those devices grown at 850°C. The $n$ factors are close to 2 for both types of devices, indicating that the recombination current dominates the carrier transport. This is not surprising since the diffusion current is extremely low compared with the recombination
current for $V< 1.6V$. For higher voltages, series resistance and high level injection effects become important, which further decreases the slope of the I-V curves.

For a forward bias of less than 0.8V, one can see an almost invariant current region for both structure devices. This is most likely due to current leakage from the surface of the junctions. Hughes et al. [6-8] also observed this phenomena. This leakage current can be reduced using a mesa structure or surface passivation.

From Figs. 52(b) one can see FJ and PTJ structure devices have very similar I-V characteristics. These results show that PTJ structure did not introduce obvious defect states that may degrade the device performance[4-27]. The excellent performance of the PTJ device indicates that PTJ structure is very promising not only for improving the efficiency of GaP ARVCs, but also for the devices that require large junction interface area.

### 6.3 C-V characteristics

C-V characteristics are also an important property of p-n junction diodes. It provides information on the capacitance dependence on bias voltage. From C-V characteristics, one can derive information on the doping concentration and built-in voltage of the junction barrier.

In an abrupt, uniformly doped p-n junction, the depletion width $W$ changes with bias voltage $V$ as[6-9]:

$$W = \sqrt{\frac{2\varepsilon(N_A + N_D)(V_{bi} - V)/qN_A N_D}{\varepsilon}}$$  \hspace{1cm} (6-11)
where $\varepsilon$ is the dielectric constant of the diode semiconductor material. Under reverse bias, $V < 0$, the depletion width increases with increasing reverse bias voltage. Since almost all of the bias voltage is dropped in the depletion region, the capacitance per unit area of the p-n junction diode can be expressed as:

$$C = \varepsilon / W = \frac{q \varepsilon N_A N_D}{2 (N_A + N_D)(V_{bi}-V)}^{1/2} \quad (6-12)$$

Eq.(6-12) can be converted to:

$$\frac{1}{C^2} = \frac{2(N_A + N_D)}{q \varepsilon N_A N_D} (V_{bi}-V) \quad (6-13)$$

From Eq.(6-13) one can see that $1/C^2$ should change linearly with bias voltage, and the built-in potential $V_{bi}$ can be extrapolated from the $1/C^2 - V$ relationship.

The $1/C^2 - V$ curves for GaP p-n junction diodes with the FJ and the PTJ structures are plotted in Fig.53. These two samples are the same as those whose $1 - V$ characteristics are shown in Figs.52(b). In the reverse bias region, $1/C^2 - V$ lines are slightly curved, indicating slight non-uniform doping concentration in the LPE layers. Extrapolating from the reverse bias region, $V_{bi}$ would be about 3 V for both FJ and PTJ structure diodes. This value is obviously not reasonable for GaP diodes since the band gap of GaP is only 2.26eV. This departure might be due to a high-low n$^+$-n junction near the p-n junction, which is observable from the EBIC images shown in Figs.50. This n$^+$-n junction can also contribute a capacitance which is in series with the p-n junction capacitance. Therefore, the actual voltage drop across the p-n junction is less than the applied voltage, leading to a smaller slope of $1/C^2 - V$ curves. However, relatively reasonable values of $V_{bi}$ were obtained by extrapolating the forward bias part of the $1/C^2 - V$ curves. Under forward bias, the small potential barrier of the n$^+$-n high-low
junctions can easily be overcome by the applied voltage. Therefore, the barrier no longer exists to affect the total capacitance of the device. The FJ and the PTJ diodes have about the same $V_{bi}$ of 2.2eV.

From Fig. 53, one can see that the capacitance per unit area of the PTJ structure is obviously larger than that of the FJ structure due to the increased p-n junction interface area. Because the two kinds of samples were grown at the same time and the substrates were from the same wafer, the doping concentrations in both p-type layers and the n-type substrates should be about the same. Therefore, the depletion width can be assumed to

Figure 53 $1/C^2$--$V$ curves for GaP p-n junction diodes with FJ (dashed line) and PTJ (solid line) structures grown at 950°C for 6 min.

be the same for both kinds of devices, resulting in a same capacitance per unit p-n junction interface area, $C_0$. One can estimate the increase of p-n junction interface area for the PTJ structure according to the increase of its capacitance compared to FJ counterpart. For the FJ structure, capacitance per unit area is
while the capacitance per unit area for PTJ is

\[ C_{PTJ} = A' C_0 \]  \hspace{1cm} (6-15)

where \( A' \) corresponds to the real p-n junction interface area for unit area of sample surface. According to Eqs.(6-14) and (6-15), one can get:

\[ C_{PTJ} = A' C_{FJ} \]  \hspace{1cm} (6-16)

From our experimental results shown in Fig.53, \( C_{PTJ} = 1.25 C_{FJ} \) at 0 bias voltage, leading to \( A' = 1.25 \). This means the textured p-n junction interface area is 25% larger than the flat p-n junction area. This result is pretty close to estimated surface area increase after 6 minutes etching, which is about 30% according to the dimensions of the pyramids.

Chapter 7  Performance of GaP ARVCs under alpha particle irradiation

7.1  Alpha irradiation test set up

Our GaP ARVC devices were tested under alpha irradiation using an \(^{241}\)Am alpha source. The dose of the alpha source is 1mCi, and the particle energy is about 4.6 MeV. The source has a circular emission window with a diameter of 12.7mm. The corresponding alpha irradiation power flux is about 20 \( \mu W/cm^2 \).

The alpha irradiation test set up is illustrated in Fig.54. The distance between alpha particle emission surface and the sample surface is about 1 mm. The
measurements were made under dark condition to eliminate light influence. I-V characteristics of the devices before and under alpha irradiation were measured using a computer controlled I-V measurement system.

![Diagram of alpha irradiation test set up.](image)

**Figure 54** Diagram of alpha irradiation test set up.

### 7.2 Alpha irradiation response of GaP ARVCs

Under the alpha irradiation test conditions mentioned in session 7.1, the current-voltage response of a typical pair of GaP ARVCs of PTJ and FJ structures are shown in Fig.55. These samples were grown at 950°C for 6 minutes, and their p-n junction profiles are shown in Figs. 50 (a) and (c).

From Fig. 55 one can see that the value of the short circuit current of PTJ device is significantly higher than that of the FJ counterpart. $I_{SC}$ is $0.62 \mu A/cm^2$ for PTJ ARVC,
but only 0.33μA/cm² for FJ device. The open circuit voltage $V_{OC}$ of PTJ device is also a little higher than that of FJ structure, the former is 0.82V, while the later is 0.78V. The improvement of $V_{OC}$ might be due to the increase of $I_{SC}$ according the $V_{OC}$ to $I_{SC}$ relation expressed in Eq.(2-3). The ARVC parameters for both PTJ and FJ devices extrapolated from Fig.55 are listed in Table 7-1. The conversion efficiency of PTJ ARVC is double that of the FJ ARVC. The $J_{SC}$ increase of the PTJ device compared to the FJ counterpart is about 88%, while the improvements in $V_{OC}$ and fill factor FF made up for the rest of the contribution. These results are repeatable within 15% deviation in our experiments for different samples prepared under similar conditions. The deviation might be mainly resulted from the uncertainty of background doping and non-uniformity of Mg doping.
The current increase for the PTJ structure device compared to the FJ counterpart is higher than the p-n junction interface area increase. The former is 88%, while the later is just about 30%. This indicates that there are some other factors which contribute to the increase in the current collection. One possible factor is the lateral trajectories of the alpha particles. According to the Monte carlo simulations discussed in Chapter 3, the alpha particles do not penetrate into GaP material in a straight path. Their trajectories are laterally broadened because of lateral movements of the particles caused by scattering. For the FJ device structure, it has a very limited chance to capture the lateral traces of alpha particles, whereas the PTJ structure device has much more chance since it has p-n junction area almost perpendicular to the device surface. However, quantitative estimation of this increase is quite difficult.

According to the results shown in Table 7-1, one sees that the increase in the performance of the GaP PTJ structure ARVC is significant compared to the FJ structure counterpart. This is very encouraging for PTJ structure devices. Actually, our

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ (μA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$P_m$ (μW/cm$^2$)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTJ</td>
<td>0.62</td>
<td>0.82</td>
<td>0.60</td>
<td>0.30</td>
<td>1.50</td>
</tr>
<tr>
<td>FJ</td>
<td>0.33</td>
<td>0.78</td>
<td>0.55</td>
<td>0.15</td>
<td>0.075</td>
</tr>
</tbody>
</table>
investigation for this PTJ structure ARVCs has only been to assess feasibility. The geometrical structures for GaP PTJ ARVCs were not optimized to get maximum increase of p-n junction interface area within the alpha generation range. Therefore, further improvements on the performances of PTJ structure GaP ARVCs are expected. By optimizing the geometric structure of PTJ devices, conversion efficiency of the GaP PTJ ARVC listed in Table 7-1 can possibly be further increased to 5-6 times, since the effective current collection volume in this PTJ sample is still less than 1/6 of the total e-h pair generation volume of alpha particles. Therefore, GaP ARVCs can possibly achieve an efficiency of 7-9%, close to or even higher than that of GaP β-cells from the report of R. J. Walko et al.. Since Alpha sources can have much higher power flux than tritium β-sources, GaP ARVCs can realize much higher output power density than GaP β-cells. Moreover, the PTJ device structure can also be used to improve the solar cell efficiency whenever the minority diffusion lengths are much shorter than the photo absorption depth. Polycrystalline Silicon solar cells are typical example where the PTJ structure can also significantly increase the efficiency.

Chapter 8 Suggestions for future work

We realized good performance GaP PTJ structure ARVCs using LPE growth on pyramidal textured substrates prepared using photolithographic masking followed by wet chemical etching. Although the GaP PTJ structure ARVCs demonstrated significant increase in conversion efficiency compared to their FJ structured counterparts, our work has only been on a preliminary level. We expect that further improvements in the
performances of GaP PTJ structure ARVCs can be realized through optimizing: (a) the geometric structure of the textured p-n junctions, (b) the doping concentration in the n-type region and (c) the Mg doping in the p-type region.

Using the photoresist masks shown in Fig. 18, the surface area was increased only by about 30% after 5-6 minutes etching. Not too much improvements can be made by adjusting etching time due to undercutting etch. To optimize the PTJ structure, it is desirable to realize a textured structure as illustrated in Fig. 16. This requires large depth to width ratio. According to the surface profile evolution with etching time discussed in Chapter 4, the undercutting etch speed is similar with that of etching depth for wet chemical etching. Due to the undercutting problem, it is not feasible to realize high depth to width ratio for the textured surface as desired.

To realize the desired textured structure, it is better to use plasma dry etching, also known as reactive ion etching (RIE). This technique is widely used in semiconductor integrated circuit industry since it can avoid undercutting problems associated with wet chemical etching. Fig. 56 shows an example of an extremely anisotropic etching of InP in a 10H2/10H2/5Ar2 plasma at -150V bias[8-1]. One can see that a vertical trench structure with very large depth to width ratio was realized. Using the plasma dry etching technology, it is feasible to realize the ideal textured surface structure as designed in chapter 3. However, one should consider the damages caused by the plasma dry etching, and proper annealing process should be considered to eliminate the damages before LPE growth in order to obtain high quality textured p-n junctions.

Once the desired trench like textured surface structure is realized, LPE growth should be able to realize flat surface with the trench like p-n junction structure. In fact, we
did some experiments on textured surfaces with nearly vertical wall as shown in Figs. 57 (a). The surface morphologies after 1 and 4 minutes growth with 850°C growth temperature were shown in Figs. 57 (b) and (c). One can see the LPE growth can also fill the gaps and finally realize flat surface after certain growth time, in a similar behavior discussed in chapter 5.

Figure 56 SEM micrographs of deep features etched into InP using 10HI/10H₂/5Ar, 10 mtorr, -150V, 200W (ECR) discharge.
Figure 57 Surface SEM images of trench textured structures before growth (a), after 1 minute growth (b) and 4 minute growth (c) at 850°C.

Beside increasing the current collection area, another route to increase current collection is to optimize the doping concentration in both n- and p-type regions to reach as longer minority diffusion lengths as possible. The minority carrier diffusion lengths increase with the decrease of the doping concentrations. However, one should consider the tradeoff between this positive effect and the series resistance. Moreover, the background impurity concentration will limit the lowest achievable carrier concentrations in both n- and p-type regions.
In our studies, n-type substrates with S doping concentration of \( \sim 5 \times 10^{17} \text{cm}^{-3} \) were used as n-type region for the p-n junctions. This doping level is too high for good minority diffusion length \( L_p \). We expect that some improvements should be achieved by growing a lower doped n-type LPE layer before photolithographic masking. In the p-type region, the Mg doping was also at \( \sim 10^{17} \text{cm}^{-3} \). If the doping concentration can be controlled to \( \sim 10^{16} \text{cm}^{-3} \), the minority carrier diffusion length \( L_n \) should be improved without causing any significant series resistance problems. This requires us to further reduce the background doping level to \( \sim 10^{15} \text{cm}^{-3} \). In our experiments, the background doping was \( \sim 10^{16} \text{cm}^{-3} \) level for the 950°C growths. Further increasing the growth temperature to 1000°C or 1050 °C might be helpful to reduce the background doping because more impurities can react with H2 at higher temperatures. However, inter-diffusion between p- and n-type region will be more serious at higher temperatures. One should consider the tradeoff between these factors to optimize the doping in the p-type LPE layer.

Although GaP has good radiation hardness, the radiation damage might still be a major problem for GaP ARVCs because the energy of alpha particles are too high. The long term stability and possible degradation mechanisms should be studied in order to make the ARVCs devices viable.
Chapter 9 Summary

We demonstrated the first GaP based ARVC, and developed a new device structure to improve the efficiency of GaP ARVCs. The PTJ structures were successfully realized through two major fabrication processes. One is the preparation of pyramidal textured substrates on n-type (111)B GaP surfaces using photolithographic masking followed by wet chemical etching. The other is LPE growth of Mg-doped p-type layer on the pyramidal textured substrates.

Photoresist square masks with a size of 15 μm were periodically arranged on the (111)B GaP surface along [0 -1 1] and [-2 1 1] directions with 3 μm spacing. Wet chemical etching was carried out in 1HNO₃: 1 HCl : 1 H₂O₂ solution. As the etching continued down into the GaP at the open regions, the etching also undercut the patterned regions. The undercutting is anisotropic. The features under the patterned regions gradually evolved to form typical pyramidal structures with three (1 0 0) facets after about 10 minutes etching. The etching depth was self-controlled due to dissociation of etching chemical species. A 30% increase in surface area was achieved after etching for 5-6 minutes.

LPE growth of Mg doped p-type GaP layers on the pyramidal textured GaP substrates were carried out to realize the GaP PTJ structure devices. At the early stages of LPE growth, the deposition was mainly on the side walls of the pyramids and the base floor surface. There was hardly any growth observable on the top surfaces of the pyramids before the valleys were filled. The base floor layer growth gradually covered the pyramids and finally resulted in a flat smooth layer surface. The layer thickness on the pyramidal
substrate measured from the base floor was about the same as that on a flat polished substrate under the same growth conditions.

Cross-sectional FE-SEM micrographs showed that sharp p-n junction interfaces with PTJ structures were realized, and no obvious structure defects were observed. EBIC analysis proved that the current collection was right along the textured p-n junction interfaces for the PTJ structure devices, while the current collection region was simply flat for the FJ structure devices. The current collection region thickness was about the same for both the PTJ and FJ structure devices under the same growth conditions.

I-V characteristics revealed that GaP p-n junction diodes grown at 850°C showed very high leakage currents for both PTJ and FJ structures due to high impurity incorporation during the LPE growth. Using a growth temperature of 950°C, the leakage current was remarkably reduced for the GaP diodes using both structures. A reverse saturation current $J_0$ as low as $\sim 10^{-15}$ A/cm$^2$ was realized, which is more than 5 orders lower than that for the devices prepared at 850°C. I-V characteristics of PTJ structure devices is very close to their FJ counterparts under the same growth conditions, indicating that the PTJ structures did not introduce any obvious defect states which may degrade the device performance.

Alpha irradiation test results proved that the GaP PTJ structure ARVCs exhibited a significant increase in current collection compared with the FJ structure counterparts. For a typical pair of samples grown at 950°C, an increase of about 88% in short circuit current was realized for the PTJ ARVC compared to the FJ counterpart, and the increase in conversion efficiency reached 100%. The current increase was higher than the estimated interface area increase according to the geometric dimensions of pyramidal
surfaces and C-V measurement results. The extra increase in current might be due to lateral scattering of alpha particles and other factors.

Our work has been focused on examining the feasibility of the PTJ structure for developing high efficiency ARVCs. The geometric structure of the textured p-n junction was not optimized. We expect that a much more significant increase in conversion efficiency of GaP PTJ structure ARVCs can be achieved by optimizing the geometric structure of the textured p-n junction interfaces and the doping concentrations in both p- and n-type regions.

References:


[4-22] H. T. Minden, J. Crystal Growth, 6, 228(1970)


